16TH EUROPEAN CONFERENCE ON ORGANIZED FILMS

PARIS
8 - 12 JULY 2019
UNIVERSITÉ PARIS DESCARTES
CENTRE UNIVERSITAIRE
DES SAINTS-PÈRES

TOPICS

Langmuir and Langmuir-Blodgett Films
Self-assembly and Nanoscale Organization
Biological and Bioinspired Systems
Membrane and Polymer Films, Multilayers
Inorganic Thin Films and Multilayers
Organic Devices, Graphene and Carbon Materials
Nano-objects, Nano-materials
Thin Films Applications

ABSTRACT BOOK

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ACCURION
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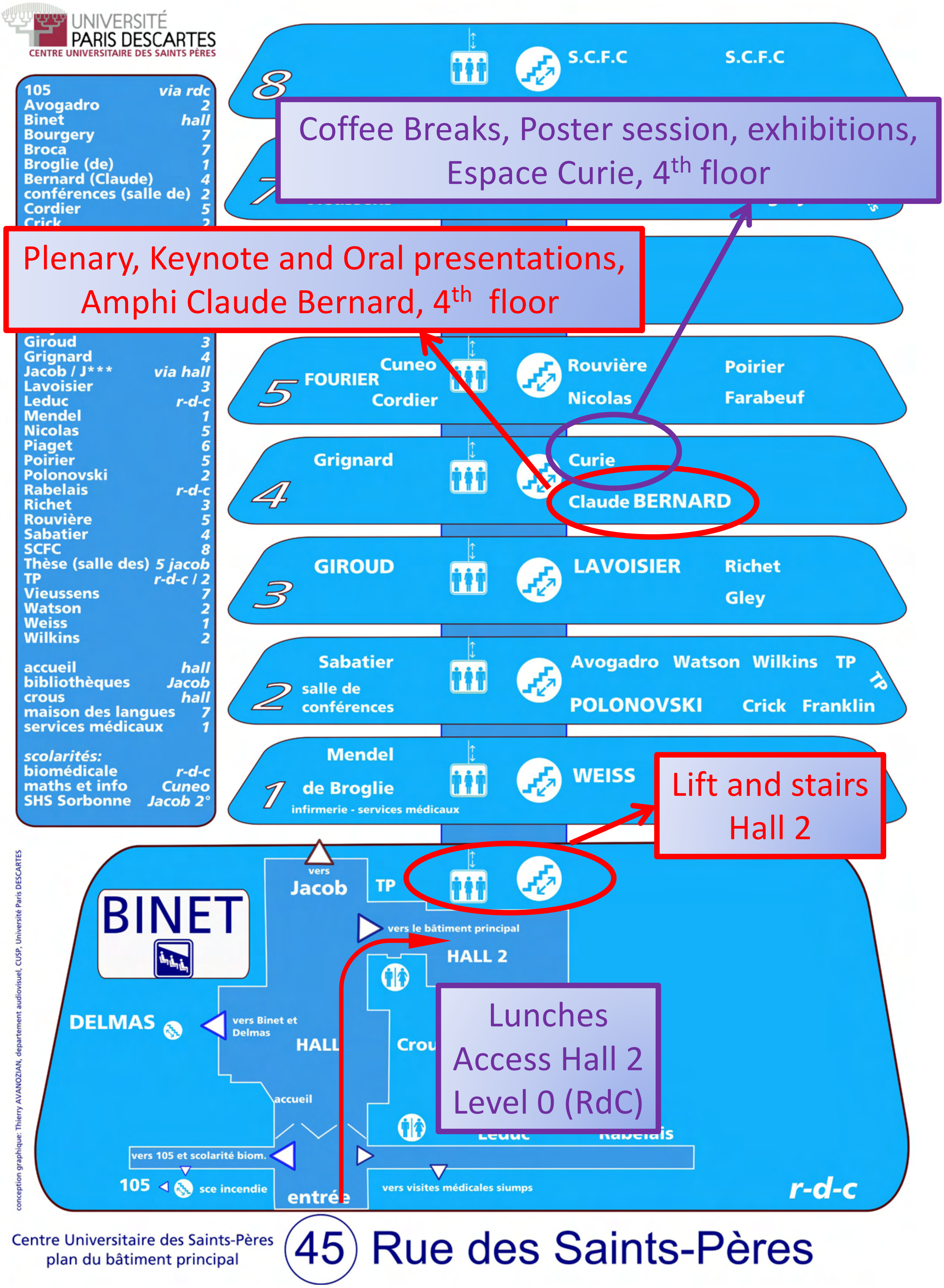
LANGMUIR

Conference location

Amphi Claude Bernard and espace Curie

Centre Universitaire des Saints-Pères (CUSP)
45 Rue des Saints-Pères, Paris 6ème Arrt



Coffee Breaks, Poster session, exhibitions,
Espace Curie, 4th floor

Plenary, Keynote and Oral presentations,
Amphi Claude Bernard, 4th floor

Lift and stairs
Hall 2

Lunches
Access Hall 2
Level 0 (RdC)

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	Monday July 8th	Tuesday July 9th	Wednesday July 10th	Thursday July 11th	Friday July 12th	
9h-9H45		Plenary-1 Andreas Terfort	Plenary-2 John M. Seddon	Plenary-3 Juan J. Giner-Casares	Plenary-4 Fabrice Cousin	9h-9H45
9h45-10h05		Thin Films and Aplications O-1 Faouzi Kezzoula	Biological and Bioinspired Systems O-9 Alexei Nabok	Thin Films and Aplications O-21 Maria-Luz Rodriguez-Mendez	Biological and Bioinspired O-36 Claudia Nunes	9h45-10h05
10h05-10H25		O-2 Lefteris Danos	O-10 Islam Zmerli	O-22 Stephan Eickelmann	O-37 Luciano Caseli	10h05-10H25
10H25-10H45		O-3 Mustapha Boutamart	O-11 Christine Grauby-Heywang	O-23 Thomas Guillemot	Coffee Break	10H25-10H45
10H45-10H55		Coffee Break	Coffee Break	Coffee Break		10H45-10H55
10H55-11H15					K-6 Svetlana Santer	10H55-11H15
11H15-11H25		K-1 José Nuno Canongia Lopes	Poster Session	K-4 Grazia Gonella		11H15-11H25
11H25-11H45					Membrane and Polymer Films, Multilayers O-38 Martin Kind	11H25-11H45
11H-45-12H05		Student Presentations		Biological and Bioinspired Systems O-24 Nikola Bugárová	O-39 Vladimir V. Tsukruk	11H-45-12H05
11H05-12h25				O-25 Dorota Matyszewska	O-40 Anne-Sophie Vaillard	12H05-12h25
12H25-12h45				O-26 Joanna Juhaniewicz-Debinska	Lunch Bag	12H25-12h45
12h45-13h05		Lunch	Lunch	Lunch		12h45-13h05
13h05-14h00						13h05-14h00
14H00-14H20		Langmuir and Langmuir Blodett Films O-4 Matthew Paige	Self-assembly and Nanoscale Organization O-12 Marie-Pier Côté	Langmuir and Langmuir Blodett Films O-27 Christine DeWolf		14H00-14H20
14H20-14H40		O-5 Michal Bodik	O-13 Kuniharu Ijiro	O-28 Sofiya Selektor		14H20-14H40
14H40-15H00		O-6 Epameinondas Leontidis	O-14 Livia Salvati Manni	O-29 Georges R. Ivanov		14H40-15H00
15H00-15h20		O-7 Alexander Shokurov	O-15 Giovanni LiDestri	O-30 Rainhard Machatschek		15H00-15h20
15H20-15H40		O-8 Atsushi Hozumi	O-16 Sousa Javan Nikkhah	O-31 Eduardo J. M. Filipe		15H20-15H40
15H40-16H10		Coffee Break	Coffee Break	Coffee Break		15H40-16H10
16H10-16H40		K-2 Abdou Rachid Thiam	K-3 Virginie Ponsinet	K-5 Grégory Schneider		16H10-16H40
16H40-17h00		Student Presentations	Nano-objects, Nano-material O-17 Takeshi Kawai	Self-assembly and Nanoscale Organization O-32 Antonella Badia		16H40-17h00
17H00-17H20	Check-in, Registration and Welcome Reception: Wine and Cheese		O-18 Ana Luisa Simões Gamboa	O-33 Linda J. W. Shimon		17H00-17H20
17H20-17h40			O-19 Patrick Guenoun	O-34 Andreas Riedinger		17H20-17h40
17H40-18H00			O-20 Patrick Probst	O-35 Ornella Cavalleri		17H40-18H00
18h00-18H20						18h00-18H20
20h				Conference Dinner - Boarding 20H Departure 20H30		

Monday 8th July

17H00– 20H00	**Check-in, Registration and Welcome Reception: Wine and Cheese**

Tuesday 9th July

8H50 – 9H00		**Conference Opening**
9H00 – 9H45	P-1	**Andreas Terfort,** Goethe-University, Frankfurt am Main, Germany *Self-Assembled Monolayers: Alive and Kicking!* Chair: Michel Goldmann Sorbonne Université, Paris, France

Thin Films and Applications

Chair: Alexei Nabok, Sheffield Hallam University, Sheffield, United Kingdom

9H45-10H05	O-1	**Faouzi Kezzoula**, CRTSE- Division, Algiers, Algeria *Effect of a-Si: H layer thickness on the passivation of the c-Si wafers in the Heterojunction solar cells*
10H05-10H25	O-2	**Lefteris Danos**, Lancaster University, Lancaster, United Kingdom *Silicon photosensitisation using organic layers*
10H25-10H45	O-3	**Mustapha Boutamart,** Moroccan Foundation for Advanced Science, Rabat, Morocco *Nano-composite coating for self-cleaning applications*
10H45-11H15		**Coffee Break**
11H15-11H45	K-1	**José Nuno Canongia Lopes**, Instituto Superior Técnico, Lisbon, Portugal *Structure-Property relationships in task-specific ionic liquids* Chair: Fabienne Testard, CEA, Saclay, France

Student Poster Short Presentations

Chair: Jean-Philippe Michel, Université Paris-Sud, Chatenay-Malabry, France

11H45-11H55	P+O-1	**Ons Hmam,** Université de Montréal, Montréal, Canada *Redox-induced ion pairing association of anionic amphiphiles to ferrocene terminated Self-Assembled Monolayers*
11H55-12H05	P+O-2	**Felix Klockmann,** Goethe-University, Frankfurt, Germany *New photo-controllable SAM building blocks for switching of bacterial adhesion*
12H05-12H15	P+O-3	**Cansu Ozkaya,** Balikesir University, Balikesir, Turkey *Metal sulphide sub-nanometre clusters formed within calix[8]arene LB films*

12H15-12H25	P+O-4	**Tomas Rego,** Sorbonne Université, Pari, France *Unexpected order-disorder phase transition in diacetylene alcohol Langmuir monolayer*
12H25-12H35	P+O-5	**Jannis Schlicke**, University of Münster, Münster 48149, Germany *Ionic Conductivity of Polyelectrolyte Multilayers: Influence of pH and Ionic Strength*
12H35-12H45	P+O-6	**Pablo Gomez Argudo**, University of Córdoba, Córdoba, Spain *Promoting the interaction of Fmoc-dipeptides with lipid membranes by the adjustment of the hydrophobicity sequence*
12H45 – 14H00		**Lunch**

Langmuir and Langmuir Blodgett Films

Chair: Maria Teresa Martin Romero, University of Córdoba, Spain

14H00 – 14H20	O-4	**Matthew Paige,** University of Saskatchewan, Saskatoon, Canada *Miscibility and iron-binding in anionic gemini surfactant monolayers*
14H20 – 14H40	O-5	**Michal Bodik,** Slovak Academy of Sciences, Bratislava, Slovakia *Alignment of single-walled carbon nanotubes*
14H40 – 14H50	O-6	**Epameinondas Leontidis,** University of Cyprus, Aglantzia, Cyprus *Lanthanide interactions with zwitterionic lipid monolayers: Remarkable effects revealed by Grazing-Incidence X-ray Diffraction*
15H00 – 15H20	O-7	**Alexander Shokurov** IPCE RAS, Moscow, Russian Federation *Supramolecular preorganization at air/water interface for enhancement of receptor properties of hemicyanine chromoionophore LB films*
15H20 – 15H40	O-8	**Atsushi Hozumi,** National Institute of Advanced Industrial Science and Technology, Nagoya, Japan *Open-air preparation of polymer blushes at large-scale*
15H40 – 16H10		**Coffee Break**
16H10 – 16H40	K-2	**Abdou Rachid Thiam,** Ecole Normale Supérieure de Paris, Paris, France *A dewetting mechanism at the origin of lipid storage organelle biogenesis* Chair: Alae El Haitami, Université Paris Seine, Cergy-Pontoise, France

Student Posters Short Presentations

Chair: Michel Goldmann, Sorbonne Université, Paris, France

16H40 – 16H50	P+O-7	**Henry Banks**, Lancaster University, Lancaster, United Kingdom *Light harvesting using Langmuir Blodgett films of carbocyanine dyes*
16H50 – 17H00	P+O-8	**Helen Ibrahim**, Sorbonne Université, Paris, France *X-Ray surface radiolysis of silver and gold solutions using ionic liquid Langmuir films as a template*
17H00 – 17H10	P+O-9	**Oliver Pemble,** Tyndall National Institute, Cork, Ireland *Design, synthesis and characterization of chitosan-based interpenetrating polymer network membranes produced using a slot-dye technique*

17H10 – 17H20	P+O-10	**Jacob Zessin**, Technische Universität Dresden, Dresden, Germany *Threshold Voltage control of organic field-effect transistors by using fluorinated alkylsilanes*
17H20 – 17H30	P+O-11	**Cecilia Teixeira da Rocha,** Technische Universität Dresden, Dresden, Germany *Coating of smooth polymeric films through high frequency vibration*
17H30 – 17H40	P+O-12	**Katherina Haase,** Center for Advancing Electronics, Dresden, Germany *Exploitation of solution-processed, high-mobility semiconductors for high-frequency organic transistors*
17H40 – 17H50	P+O-13	**Deniz Vurmaz,** NYU Tandon School of Engineering, New York, USA *Agarose Beads with Controlled Pore Structures for High Precision Clinical Biosensing Diagnostics*

Wednesday 10th July

9H00 – 9H45	P-2	**John M. Seddon,** Imperial College London, London, United Kingdom *Complex Lyotropic Liquid-Crystalline Phase Behaviour of Lipid Membranes* Chair: Véronique Rosilio, Université Paris-Sud, Chatenay-Malabry, France

Biological and BioInspired Systems

Chair: Juan Jiner-Casares, University of Córdoba, Córdoba, Spain

9H45-10H05	O-9	**Alexei Nabok,** Sheffield Hallam University, Sheffield, United Kingdom *The use of aptamers immobilized on the surface of transducers for detection of low molecular weight analytes*
10H05-10H25	O-10	**Islam Zmerli,** Institut Galien Paris Sud, Châtenay-Malabry, France *Conception and characterization of new bioinspired nanoparticles with dual activity for esophageal cancer therapy: Preparation and PEGylation strategy*
10H25-10H45	O-11	**Christine Grauby-Heywang**, Université de Bordeaux, Talence, France *Degradation of cellular membrane in photodynamic therapy: contribution of lipid monolayers and Langmuir-Blodgett films to mechanism elucidation*
10H45-11H15		**Coffee Break**
11H45-12H45		**Poster Session**
12H45 – 14H00		**Lunch**

Self-Assembly and Nanoscale Organization

Chair: Virginie Ponsinet, Centre de Recherche Paul Pascal, Pessac, France

14H00 – 14H20	O-12	**Marie-Pier Côté**, Université Laval, Québec, Canada *Development of core-satellite nanostructures via the Langmuir-Blodgett technique: self-assembly and characterization*
14H20 – 14H40	O-13	**Kuniharu Ijiro**, Hokkaido University, Sapporo, Japan *DNA Brush-Directed Aligning Self-Assembly of Gold Nanorods as Photonic Nanomaterials*
14H40 – 14H50	O-14	**Livia Salvati Manni***, ETH Zürich, Zürich,Switzerland* *Beyond freezing: low temperature lipidic cubic phase as biomimetic, nanoconfining matrix*
15H00 – 15H20	O-15	**Giovanni LiDestri,** University of Catania, Catania, Italy *Probing interfacial inter-particle interactions at the air/water interface*
15H20 – 15H40	O-16	**Sousa Javan Nikkhah,** Aalto University School of Chemical Engineering, Finland *Tuning amphiphilic block copolymer assemblies and aggregate structures: a simulation study*
15H40 – 16H10		**Coffee Break**

16H10 – 16H40	K-3	**Virginie Ponsinet,** Centre de Recherche Paul Pascal, Pessac, France *Self-assembled optically resonant nanostructured surfaces* Chair: François Muller, ECE Paris, Paris, France

Nano-Objects, Nano-Materials

Chair: José Nuno Canongia Lopes, Instituto Superior Técnico, Lisbon, Portugal

16H40 – 17H00	O-17	**Takeshi Kawai**, Tokyo University of Science, Tokyo, JAPAN *Snowman-like anisotropic polystyrene particles prepared by combining UV light and solvent treatments.*
17H00 – 17H20	O-18	**Ana Luisa Simões Gamboa,** ITMO University, St. Petersburg, Russia *Kinetics of Photoluminescence Decay of Colloidal Quantum Dots: the Role of the Surface.*
17H20 – 17H40	O-19	**Patrick Guenoun,** CEA, Saclay, France *Ligand-free synthesis of gold nanoparticles incorporated within oriented cylindrical block copolymer film*
17H40 – 18H00	O-20	**Patrick Probst,** Leibniz-Institut für Polymerforschung, Dresden, Germany *Active chiral plasmonics based on strain-induced geometrical reconfiguration*

Thursday 11th July

9H00 – 9H45	P-3	**Juan J. Giner-Casares,** University of Córdoba, Córdoba, Spain *Langmuir monolayers for assembling nanostructured films* Chair: Philippe Fontaine, Synchrotron SOLEIL, Gif sur Yvette, France
		Thin Films and Applications Chair: Svetlana Santer, Potsdam University, Potsdam, Germany
9H45-10H05	O-21	**Maria-Luz Rodriguez-Mendez,** University of Valladolid, Valladolid, Spain *Biosensors fabricated by layer by layer for the electrochemical detection of catechol*
10H05-10H25	O-22	**Stephan Eickelmann,** Max Planck Institute of Colloids and Interfaces, Potsdam, Germany *A low-cost laser-based nano-3D-printer for rapid surface patterning, microarray fabrication and high-throughput chemical synthesis in polymer*
10H25-10H45	O-23	**Thomas Guillemot,** ECE Paris, Paris, France *Elaboration of nanostructured solar cells based on hybrid perovskite: Influence of deposition process and composition*
10H45-11H15		**Coffee Break**
11H15 – 11H45	K-4	**Grazia Gonella**, Max Planck Institute for Polymer Research, Mainz, Germany *How polymers affect protein adsorption* Chair: Sophie Cantin, Université Paris-Seine, Cergy-Pontoise, France
		Biological and BioInspired Systems Chair: John M. Seddon, Imperial College London, London, United Kingdom
11H45- 12H05	O-24	**Nikola Bugárová,** Polymer Institute, Bratislava, Slovakia *Biomodified nanoplatforms for cancer targeting*
12H05 – 12H25	O-25	**Dorota Matyszewska**, University of Warsaw, Warsaw, Poland *Phospholipid layers as simple models of cell membranes to study the interactions with anticancer and cholesterol-lowering drugs*
12H25 – 12H45	O-26	**Joanna Juhaniewicz-Debinska**, University of Warsaw, Warsaw, Poland *Effect of perifosine on model lipid rafts with different cholesterol content*
12H45 – 14H00		**Lunch**
		Langmuir and Langmuir Blodgett Films Chair: Maria Bardosova, Tyndall Micronano Electronics, Cork, Ireland
14H00 – 14H20	O-27	**Christine DeWolf,** Concordia University, Montreal, Quebec, Canada *Reversible Langmuir monolayer-to-crystalline multilayer transition at the air-water interface*

14H20 – 14H40	O-28	**Sofiya Selektor,** A.N. Frumkin Institute of physical chemistry and electrochemistry RAS, Moscow, Russia *Unusual redox isomerism of bis-phthalocyaninates of lanthanides in monolayers at air/water and air/solid interfaces*
14H40 – 15H00	O-29	**Georges R. Ivanov,** University of Architecture, Civil Engineering and Geodesy, Sofia, Bulgaria *Possible biosensor applications. Validity of Gibbs' phase coexistence rule at nanoscale*
15H00 – 15H20	O-30	**Rainhard Machatschek**, Institute for Biomaterial Science, Teltow, Germany *Langmuir monolayers as tool to predict the degradation of architectured macromolecules*
15H20 – 15H40	O-31	**Eduardo J.M. Filipe**, Instituto Superior Técnico, Lisboa, Portugal *Nano-structured films of semifluorinated alkanes "primitive surfactants": formation and size of hemi-micelles by Molecular Dynamics*
15H40 – 16H10		**Coffee Break**
16H10 – 16H40	K-5	**Grégory Schneider**, Leiden University, Leiden, The Netherlands *Nanopores and nanogaps in graphene with chemical approaches: From biomolecular detection to water filtration* Chair: Andreas Fery, Leibniz-Institut für Polymerforschung, Dresden, Germany

Self-Assembly and Nanoscale Organization

Chair: Andreas Terfort, Goethe-University, Frankfurt am Main, Germany

16H40 – 17H00	O-32	**Antonella Badia**, Université de Montréal, Montréal, Canada *Redox-Induced Association of Ionic Amphiphiles to Ferrocene-Terminated Self-Assembled Monolayers*
17H00 – 17H20	O-33	**Linda J.W. Shimon,** Weizmann Institute of Science, Rehovot, Israel *Highly Versatile Metal-Organic Frameworks*
17H20 – 17H40	O-34	**Andreas Riedinger,** Max-Planck-Institute for Polymer Research, Mainz, Germany *Kinetically driven self-assembly of semiconductor nanoplatelets*
17H40 – 18H00	O-35	**Ornella Cavalleri,** University of Genoa, Genoa, Italy *DNA SAMs on flat gold: a combined Atomic Force Microscopy and Spectroscopic Ellipsometry approach*
20H00		**Conference Dinner** **Boarding 20H00** Port de la Conférence, Pont de l'Alma rive droite, Paris 8th Arr. Métro stations : Alma - Marceau (ligne9) Franklin D. Roosevelt (lignes 1, 9)

Friday 12th July

9H00 – 9H45	P-4	**Fabrice Cousin,** CEA Saclay, Gif-sur-Yvette, France *Neutron reflectivity: a unique tool for probing polymer thin films* Chair: Jean-Philippe Michel, Université Paris Sud, Chatenay Malabry, France

Biological and BioInspired Systems

Chair: Grazia Gonella, Max Planck Institute for Polymer Research, Mainz, Germany

9H45-10H05	O-36	**Claudia Nunes,** Universidade do Porto, Porto, Portugal *Siramesine-membrane related anticancer mechanism: mitochondria or lysosomal destabilization?*
10H05-10H25	O-37	**Luciano Caseli,** Federal University of Sao Paulo, Sao Paulo, Brazil *Graphene oxide incorporated in Langmuir-Blodgett films of penicillinase and phospholipids to enhance penicillin detection*
10H25-10H55		**Coffee Break**
10H55 – 11H25	K-6	**Svetlana Santer,** Potsdam University, Potsdam, Germany *Light Responsive Soft Nano-Objects* Chair: Marie-Claude Fauré, Université Paris Descartes, Paris, France

Membrane and Polymer Films, Multilayers

Chair: Fabrice Cousin, Laboratoire Léon Brillouin, France

11H25 – 11H45	O-38	**Martin Kind**, University of Frankfurt, Frankfurt, Germany *Growth Mechanism, Morphology and Coverage: a Concentration-dependent Study of Layer-by-layer SURMOF Formation*
11H45- 12H05	O-39	**Vladimir V. Tsukruk,** Georgia Institute of Technology, Atlanta, USA *Mono and Multimolecular Micellar Films from Branched Poly(ionic liquid)s and Polyelectrolytes*
12H05 – 12H25	O-40	**Anne-Sophie Vaillard**, Université de Cergy-Pontoise, France *Photo-oxidation and cross-linking of a polybutadiene monolayer at the air-water interface*
12H25 – 12H35		**Concluding Remarks**
12H35 – 13H05		**Lunch Bag**

Poster Presentation List

P-1 **Sebastian Balser,** Goethe-University, Frankfurt, Germany
Functionalized Nanomembranes for Structural Analysis of Proteins by Electron Cryo-Microscopy

P-2 **Avia Leader,** The Hebrew University of Jerusalem, Jerusalem, Israel
Langmuir films for biosensing applications

P-3 **Aurélie Berhault,** Université Laval, Québec, Canada
Thermo-responsive microgels as transducers applied to ion-detection: synthesis, characterization and functionalization

P-4 **Philipp Werner,** Goethe University Frankfurt, Frankfurt am Main, Germany
Fluorinated Benzene Derivatives with Dipolar Headgroups for the Fabrication of Electron Injection Layers

P-5 **Cansu Ozkaya,** Balikesir University, Balikesir, Turkey
A study of host-guest interaction between organic vapors and a novel calix[4]arene Langmuir-Blodgett thin film

P-6 **Ferhat Haroun,** Université de Cergy-Pontoise, Neuville sur Oise, France
2D Polymer Networks at the water-air interface based on Nitrile Butadiene Rubber and Polyethylene Glycol-based copolymer

P-7 **Mathias Rößling,** Goethe-University Frankfurt, Frankfurt am Main, Germany
Lifetime of disinfection agents: active chlorine content and surfactant degradation

P-8 **Shoma Arai,** Osaka Electro-Communication University, Osaka, Japan
Continuous fabrication of luminescent organic nanoparticles by visible laser processing of dye solution microdroplets

P-9 **Yusuke Nishijima,** Osaka Electro-Communication University, Osaka, Japan
Silver Nanowire Forest Grown from Gold Nanoparticle Seeds Chemically Bound on SiO2 Layer

P-10 **Ryo Fushii,** Osaka Electro-Communication University, Osaka, Japan
Fabrication of Nanopillar Arrays on Si Wafer Surface: Selective Si Etching Assisted by Au Nanoparticles Deposited Through Arrayed Nanoholes in Anodized Aluminum Ultrathin Film

P-11 **Pablo Gomez Argudo,** University of Córdoba, Córdoba, Spain
Increase of the internationalization rate of Quantum Dots by fluorinated organic ligand

P-12 **Joshua Gies,** Goethe-University Frankfurt, Frankfurt am Main, Germany
Influence of the Anion on the Deposition of Cu-containing Surface Mounted Metal-Organic Frameworks (SURMOF)

P-13 **Sonja Katzbach,** Goethe-University Frankfurt, Frankfurt am Main, Germany
Surface mounted metal-organic frameworks with dipolar N-heterocyclic ligand precursors

P-14 **Ioanna Chazapi,** University of Cyprus, Nicosia, Cyprus
Antibiotic release from well-ordered mesoporous titania films produced via evaporation induced self-assembly

P-15 **Grigory Paris,** Max Planck Institute of Colloids and Interfaces, Potsdam, Germany
Investigation of the polymer thin film behaviour within the combinatorial laser-induced forward transfer

P-16 **Ben Wood,** Lancaster University, Lancaster, LA1 4YB, United Kingdom
Surface passivation of silicon with covalently bound organic monolayers

P-17 **Luis F. C. Morato,** Universidade Estadual Paulista (UNESP), Presidente Prudente, Brazil
Effect of the pesticide acephate on Langmuir monolayers: A PM-IRRAS study

P-18 **Rosanna Pagano,** University of Salento, Lecce, Italy
Conformational changes induced by histidine aqueous solutions on LS films of ethane-bridged bis-porphyrins

P-19 **Ana Carolina Alves,** Sorbonne Université, Paris, France
Simulation of Langmuir Monolayers of Fluorinated Surfactants

P-20 **Svetlana Goloudina,** St. Petersburg State Electrotechnical University, St. Petersburg, Russia
Formation of multilayer graphene films by carbonization of polyimide Langmuir-Blodgett films

P-21 **Arnaud Hemmerle,** Synchrotron SOLEIL, Gif-sur-Yvette, France
SIRIUS: a Multipurpose Scattering and Spectroscopy Beamline devoted to the Study of Solid and Liquid Surfaces at the SOLEIL Synchrotron

P-22 **Antonio Gonzalez,** Accurion GmbH, Goettingen, Germany
Imaging Ellipsometry in the field of Graphene and 2D-materials: From Flakesearch to Fast Full Wafer Characterization

P-23 **Akihiro Tomioka,** Osaka Electro-Communication University, Osaka, Japan
Disentangled Deposition of Luminescent Electrospun Nanofibers Doped with Organic Dyes

P-24 **Serena Gallenti,** ECE-Paris Lyon, Paris, France
Graphene oxide sheets on flexible insulating polymeric folds

P-25 **Patricia Moraille,** Université de Montréal, Montréal, Canada
Nanoscale Spatially Resolved Chemical Analysis of Phase Separation in Pulmonary Surfactant (PS) Monolayers by Resonance-Enhanced AFM-IR Spectroscopy

P-26 **Sousa Javan Nikkhah,** Aalto University School of Chemical Engineering, Finland
Multi-scale molecular modelling of silk-like proteins

P-27 **Ornella Cavalleri,** University of Genoa, Genoa, Italy
Organophosphonate self-assembly on titanium dioxide

P-28 **Ornella Cavalleri,** University of Genoa, Genoa, Italy
Biomolecular nanopatterns through peptide self-assembly

P-29 **Carlos J.L. Constantino,** Universidade Estadual Paulitsa (UNESP), Presidente Prudente-SP, Brazil
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P-30 **Tonya Andreeva,** Bulgarian Academy of Sciences, Sofia, Bulgaria
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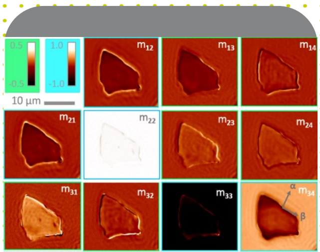
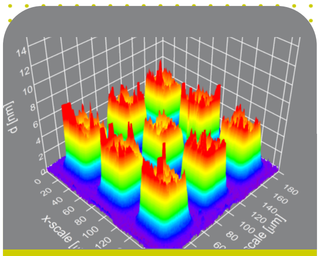


Black-P|SiO$_2$|Si



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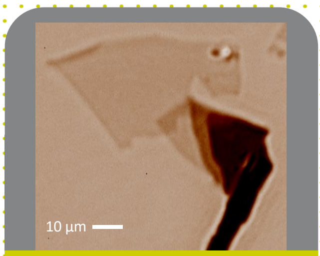
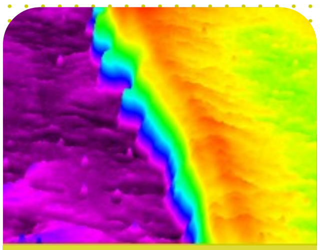


MoS$_2$|WSe$_2$|Glass



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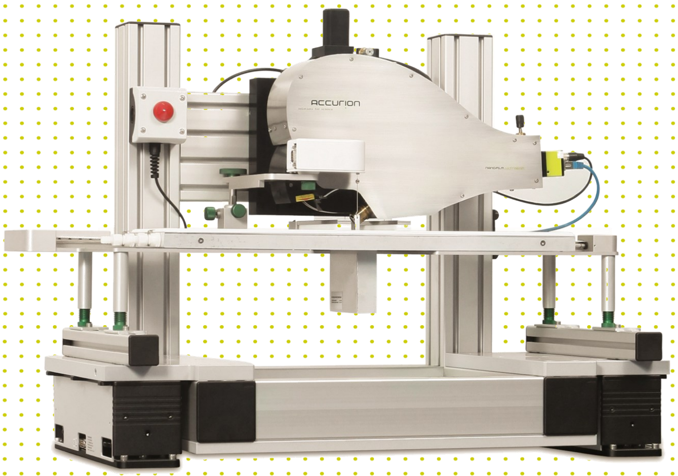

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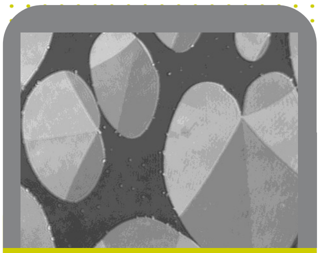

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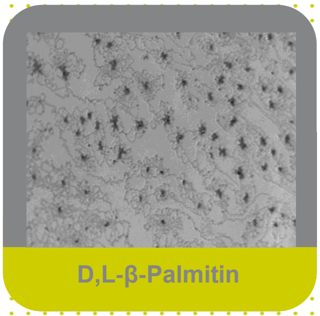
DMPE



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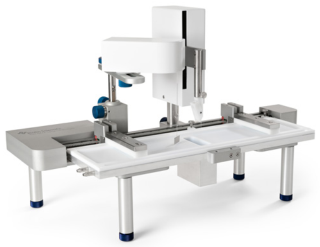

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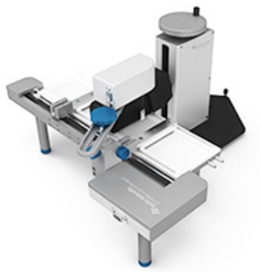

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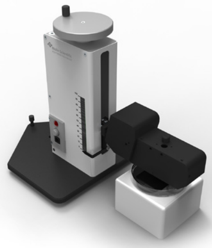
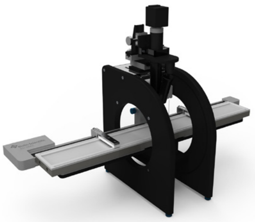


KSV NIMA Brewster Angle Microscope



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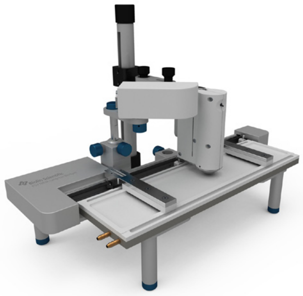

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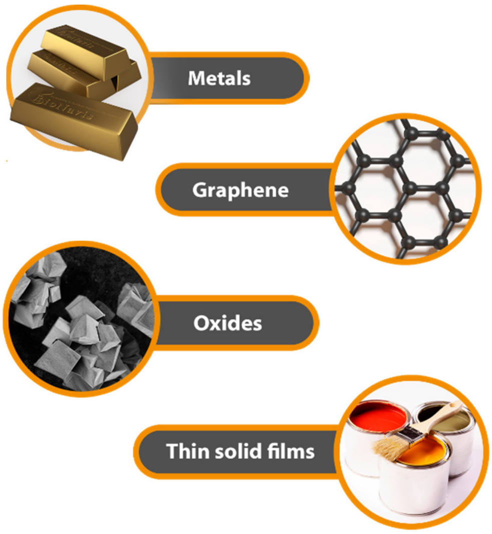

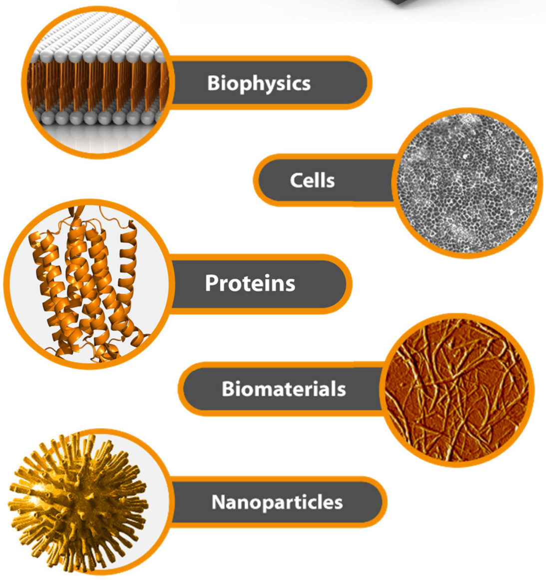

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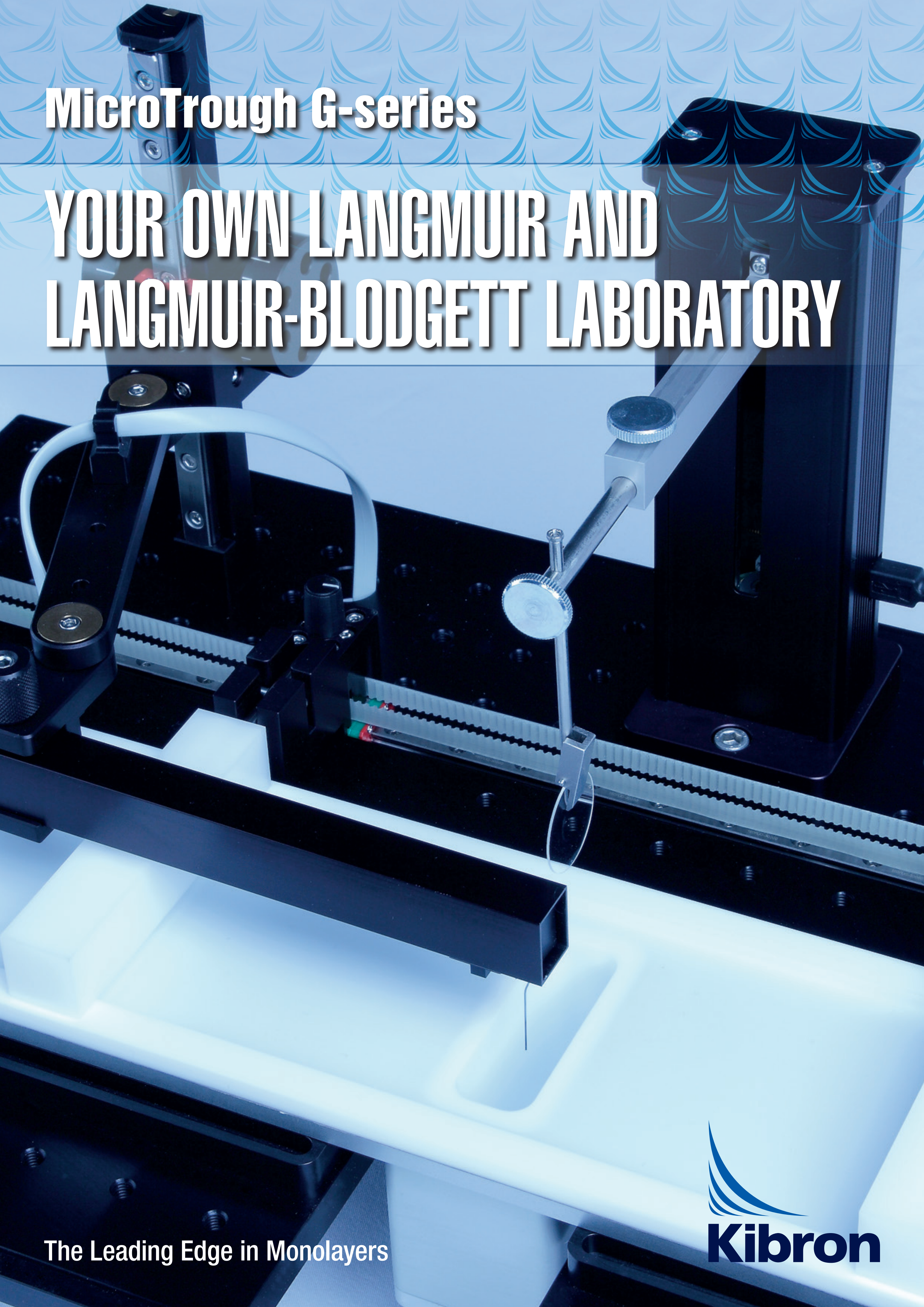

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Plenary lectures

Self-Assembled Monolayers: Alive and Kicking!

Andreas Terfort[1*]

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After the concept of self-assembled monolayers (SAMs) has been established 30 years ago, a gold rush in this area happened for more than a decade. While the first excitement has faded meanwhile, these systems are now considered to be mature tools in chemistry and biochemistry.

In this talk, I hope to show that the area still bears many surprises, room for improvement and – in conjunction with new problems – very innovative approaches for solutions. In this context, a major field of technological progress, (opto)electronics based on organic molecules, strongly benefits from the use of SAMs, as the devices contain many different interfaces, the properties of which have to be carefully adjusted. Starting form approaches to obtain extraordinarily highly ordered systems, we will discuss the problems of semiconductor growth on surfaces and on how to optimize charge carrier injection in such devices, even leading to complex logic circuitry.

In the second part of my talk, I want to introduce SAMs as templates for growth of metal-organic frameworks (MOFs), which due to their defined crystal structure formed from a diversity of organic ligands and metal ions gain a lot of interest. SAMs help to control the growth of these materials not only in two dimensions, but also regarding the orientation of these often highly anisotropic materials, which themselves also show an interesting surface chemistry.

Finally, new uses of SAMs shall be discussed, in which the monolayers become altered in a way that they can be lifted off their substrates. The resulting nanometer thick membranes can be used as supports e.g. in transmission electron microscopy or can be further converted into graphene derivatives with interesting properties.

Complex Lyotropic Liquid-Crystalline Phase Behaviour of Lipid Membranes

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Lyotropic liquid crystals of 1-, 2-, or 3-dimensional periodicity spontaneously assemble when lipids are mixed with solvent under various conditions of temperature, pressure and hydration. There are two quite distinct types of inverse cubic phases: *bicontinuous* ones based on underlying periodic minimal surfaces, and *discontinuous* ones based on simple or more complex packings of inverse micelles.

By incorporation of charged phospholipids, we have been able to swell inverse bicontinuous cubic phases to approx. 500 Å, with water channels of approx. 220 Å diameter, potentially expanding the range of usefulness of such phases for applications [1, 2]. We have studied [3] the effect of chain branching on the phase behaviour of a series of synthetic β-D-glucosides derived from Guerbet alcohols, whose total hydrocarbon chain length ranged from C_8 to C_{24}. A wide range of liquid-crystalline phases was observed, with the C_{16} Guerbet glucoside forming an Ia3d bicontinuous cubic phase of space group in excess aqueous solution, which is very unusual – and potentially useful - behaviour.

We have previously shown that by addition of weakly-polar amphiphiles such as diacylglycerols to phospholipids, we can tune the interfacial curvature to be strongly inverse, leading to the formation of a discontinuous cubic phase of spacegroup Fd3m, with a structure based upon a complex close packing of two types of quasi-spherical inverse micelles. We have investigated the effect of hydrostatic pressure on the structure and stability of this phase, and have discovered a number of novel effects [4]. We have also studied the structure of this phase by contrast variation neutron scattering, and have been able to demonstrate that the more weakly amphiphilic diacylglycerol component is preferentially located in the smaller, more highly curved inverse micelles (A.I.I. Tyler, unpublished data).

We have dispersed this bulk Fd3m phase into 'micellosomes' by sonication in the presence of the amphiphilic block copolymer F127, and have used x-ray diffraction to compare their structure to that of the bulk Fd3m cubic phase (A.M. Sartor et al., unpublished data).

Some time ago [5] we discovered a lyotropic phase of space group $P6_3/mmc$, whose structure is based upon a 3-D hexagonal packing of quasi-spherical inverse micelles, in a hydrated mixture of dioleoyl phosphatidylcholine, dioleoyl glycerol, and cholesterol. This phase is expected to have a greater chain packing frustration than the Fd3m cubic phase, and it appears that the cholesterol is able to relieve the chain packing frustration within this phase, allowing the $P6_3/mmc$ phase to form.

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Langmuir monolayers for assembling nanostructured films

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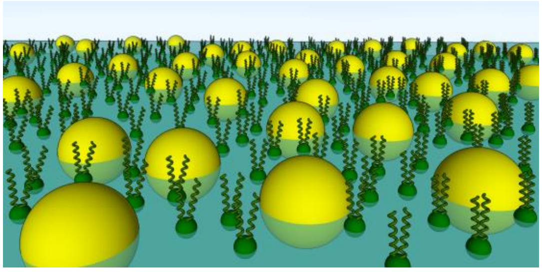
The Langmuir monolayer technique is a well-established experimental methodology for conducting basic studies at the air/liquid interface.[1] With the advent of new in situ probing techniques, the scope and applications of the Langmuir technique have been greatly increased, reaching organic/inorganic hybrid composites, complex biomolecules and functional nanoparticles, among others.[2] The possibility of finely tuning the available surface area per molecule combined with the detailed experimental information that can be attained makes the Langmuir technique a relevant platform to obtain unique insights in Colloid and Interface Science.

Mechanosensation, *i. e.*, conversion of applied pressure to defined modification in molecular arrangements was explored. Gold nanoparticles were hybridized with a purposefully designed self-assembling molecule based on non-covalent intermolecular interactions. The air/liquid interface served in this case for assembling supramolecular structures that mimic biological behaviour.[3]

With the viewpoint on nanoscience, the self-assembly of a set of Fmoc-dipeptides at fluid interfaces was assessed. The impact of the amino acid sequence on the resulting supramolecular structures were evaluated in detail by the Langmuir technique. The partition coefficient appears as a relevant and easily calculated molecular parameter providing an immediate guide for predicting the self-assembly behaviour. This idea was extrapolated to the interaction of the Fmoc-dipeptide derivatives with a model cell membrane.[4] Langmuir monolayers for mimicking biological surfaces are highly versatile and offered stimulating insights on the internalization mechanism of fluorinated quantum dots that could be related with in vitro experiments.[5]

In summary, despite been established on the classical Colloid and Interface Science, Langmuir technique is still contributing with remarkable ideas, techniques and results. Much more fascinating research is certainly yet to come.



Langmuir monolayers might include different nano-entities beyond classical surfactants.

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Neutron reflectivity: a unique tool for probing polymer thin films

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In this lecture, I will show that neutron reflectivity is a unique tool to determine the structure of thin films of polymeric systems in the 1–100 nm range, which are the relevant scales to probe their conformation and gyration radius, whether polymers are in melts or in solution. This comes from the fact that a deuterated polymer has a different scattering length density, that characterizes the probability of a given species to scatter neutrons, that its hydrogenated counterpart, offering the possibility to play with contrast by a clever choice of the Scattering Length Densities (SLD) of components. Such "contrast variations" methods are usually declined with two philosophies: (i) to create some contrasts in binary systems where it does not exist, e g in polymer melts; (ii) or to adjust the contrast of a component of a ternary system to those of another in order to "match" it, simplifying the system to a two-components one from neutron point of view.

First, I will start the lecture by a short overview of recent examples to show the different kinds of scientific issues that can be solved by neutron reflectivity [1]. Second, I will show how the kinetics of interdiffusion between a polymer brush and a melt of the same polymer can be followed [2.a] and, on the same system, how neutron reflectivity can highlight a partial disentanglement of the brush from the melt if this latter is strechted [2.b] ([Fig. 1]) or how the kinetics is changed upon confinement [2.c]. Third, I will show how contrast variation can probe selectively the behavior of each block of a copolymer block adsorbed at the air/water interface as function of physico-chemical conditions. When neutron reflectivity measurements are combined with GISAXS, the full picture of the structure of the system can be detemined, both perpendicular to the interface and within the interface [3.a and 3.b].

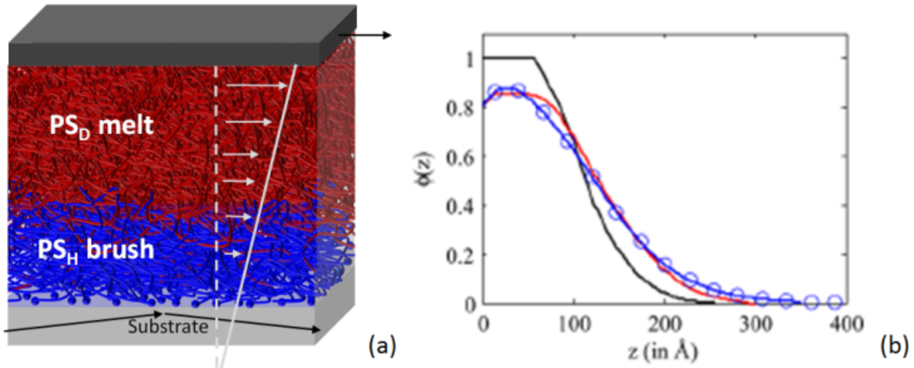

Fig. 1: (a) Stretching of a hydrogenated polystyrene melt (in blue) interdigitated with a polystyrene brush (in red). (b) Profiles obtained from reflectivity curves: at rest (red) and after shear (black)

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Keynotes and Oral Contributions

Effect of a-Si: H layer thickness on the passivation of the c-Si wafers in the Heterojunction solar cells

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Abstract

Passivation of the crystalline silicon (c-Si) wafer surfaces is achieved with very thin intrinsic hydrogenated amorphous silicon (a-Si: H) layers, deposited by plasma enhanced chemical vapor deposition (PECVD) or similar methods. An amorphous silicon (a-Si: H) layer passivates a c-Si surface mainly by hydrogenation of the silicon dangling bonds, leading to a reduction of the interface defect density.

N-type CZ (100) mono-crystalline silicon wafers were used for this study. All samples were RCA cleaned before loading into a DC sputtering system. For amorphous silicon (a-Si: H) deposition, a 99.999% pure silicon target was installed. By using 10% hydrogen and 90% argon gas mixture as the plasma source, 1.5 Ω cm n-type FZ silicon wafers coated with sputtered a-Si: H films. Layer thickness was varied by adjusting deposition time. In addition, we have varied polarization of substrate support between 20V and 40V. After each deposition the layers of a-Si: H were annealed at variable temperatures under nitrogen flow (N2). The effective lifetime τeff was measured with a Sinton WCT120 photoconductance instrument, both as-deposited and after a low temperature gas anneal.

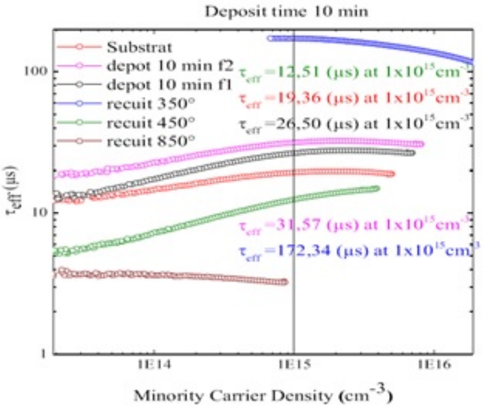

Fig.1 Effective life as a function of injection Δn for different deposition times

Firstly, we notice a significant increase in the lifetime of the deposits from 10 to 30 min and a good passivation for the deposit of 15 min (Fig. 1). On the other hand, the annealing effect is very clear, for temperature of annealing at 850 °C, we notice a significant drop in the lifetime for all samples ~ 2-3 µs, the same behavior was observed for an annealing at 450 °C.

The degradation of the hydrogenated amorphous silicon layer is explained by the fact that an exo-diffusion of hydrogen, during the penetration into the substrate through the amorphous layer (a-Si: H) to passivate the surface, starts from annealing at 400 ° C (thus creating defects).

In conclusion, thanks to the measurement of the lifetime of the minority carriers, we have optimized the deposition time (thickness) which is 20 min and which corresponds to a lifetime of 273 µs after annealing at 350 ° C. Beyond this temperature there has been a degradation of the service life due to the exo-diffusion of hydrogen.

O-2

Silicon photosensitisation using organic layers

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Photosensitisation of silicon occurs via resonance energy transfer from molecules on the surface and could potentially introduce new solar cell paradigms [1,2]. The proposed scheme separates the photovoltaic process into two separate steps; An absorption and a charge generation step which can be treated like two independent processes [3].

Previous experimental studies have demonstrated quenching of molecular fluorescence near the surface of silicon from Langmuir-Blodgett (LB) monolayers [4,5] and dye loaded zeolite structures [6]. All these cases of observed fluorescence quenching could be attributed to photon tunnelling [7] a form of energy transfer via coupling of the evanescence field for distances up to 30 nm and not a Förster type energy transfer which occurs via a near field interaction in the sub-nanometer scale. A recent study demonstrated a Förster type energy transfer with protoporphyrin IX molecules directly attached on the surface of silicon for distances to the surface of silicon of less than 2 nm [8].

In this presentation, we will show phosphorescence quenching observed from Langmuir-Blodgett monolayers of metal complexes (Re, Ru, Os) deposited on the surface of silicon as a function of distance. We have used time resolved emission measurements of the excited state lifetime and have observed a significant quenching over 90% from the free unquenched phosphorescence lifetime. Fluorescence Lifetime Imaging (FLIM) reveals the structure of the deposited organometallic complex monolayers on the surface of silicon, which is the result of hydrophobic forces acting on the monolayer.

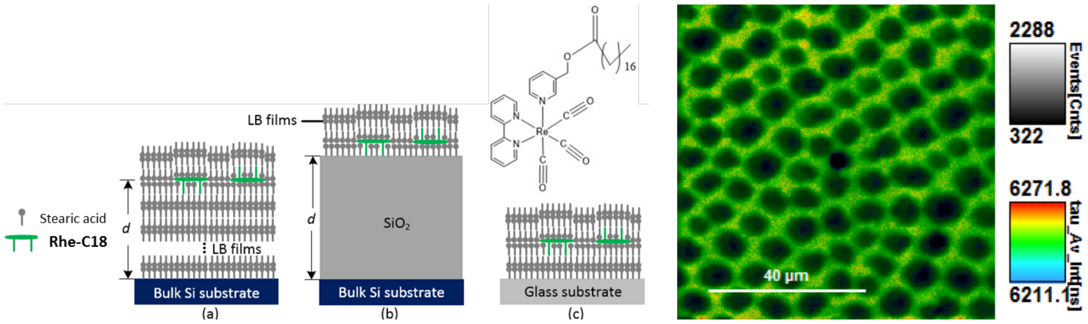

Fig. 1: Example structure of the deposited monolayer(Rhe-C18) with spacers (Stearic acid or SiO_2) and measured FLIM image.

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Nano-composite coating for self-cleaning applications

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Self-cleaning surfaces are obtained by depositing super-hydrophilic and photocatalytic films that impact diverse applications such as lenses for optical devices, automobile windshields, windows, mirrors and building sector[1], [2]. Several colloidal solutions for the fabrication of self-cleaning coatings are already commercially available[3], [4]. However, some practical limitations still restrict their widespread use in the glass sector for the building (the nature of the substrates that affects the photocatalytic activity, efficiency of the coating through the life cycle in outdoor conditions).

This work reports a facile method for preparing nano-composite materials and developing self-cleaning transparent coatings with both photocatalytic and superhydrophilic properties through the sol-gel process, by using spin coating and spray gun techniques to coat small and large glass surfaces. SiO_2 and TiO_2 were prepared by using tetraethyl orthosilicate (TEOS) and Titanium (IV) isopropoxide (TIPT) respectively as precursors. Structural and morphological properties of these coatings were studied. Optical properties as the transmittance of coatings that shows an average transmittance in the visible region that exceeds 80%, gap energy and refractive index were also studied. The self-cleaning properties of the coatings were evaluated by the degradation of Orange G under sunlight irradiation. The evolution of the contact angle over a long period has been studied in order to characterize the aging of the coatings under outdoor conditions.

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Structure-Property relationships in task-specific ionic liquid

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This presentation focuses on the use of molecular modelling and computer simulation to develop new ionic liquids for applications in the domains of energy harvesting and storage. We will show how the design of ionic liquids with the ionic moieties linked to task-specific organic moieties can be optimized with the aid of Molecular Dynamics simulations, by discovering and quantifying structural features of liquid media at the molecular level that can be potentially very important for the development of more efficient photovoltaic panels and more stable lithium-ion batteries. Two distinct research lines will be addressed: a) Chromophoric ionic liquids as photon up-conversion media for solar energy harvesting and b) Solvate ionic liquids as Li-ion (or Na-ion) battery electrolytes for energy storage and delivery.

These two research lines represent areas at the forefront of current research on ionic liquids and its applications [1-3]. Given the extraordinary number of possible ionic liquids and the relatively recent development of this area of knowledge, a theoretical-led effort that tries to establish links between the nano-*structure* of ionic liquids and the key-*properties* that enable their use as paradigm-shifting media in photon up-conversion and Li-ion batteries is an extraordinarily useful route that can lead to breakthrough discoveries in this area, both at the scientific and technological levels.

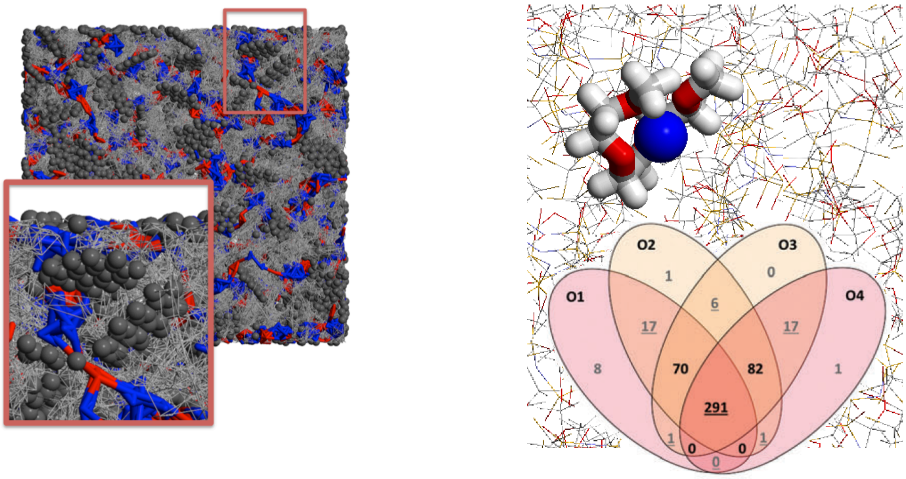

Fig. 1: Two images depicting in a schematic way two relevant structure – property relationships in cromophoric ionic liquids (left) and solvate ionic liquids (right).

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P+O-1

Redox-induced ion pairing association of anionic amphiphiles to ferrocene terminated Self-Assembled Monolayers

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Due to the attractive electrochemical properties of ferrocene (fast electron transfer, low oxidation potential, and two stable redox states), ferrocenylalkanethiolates on gold are the most studied electroactive self-assembled monolayer (SAM) system. Oxidation of the SAM-confined ferrocenes to ferrocenium is accompanied by the formation of ion-pairs with counter-ions in solution. The SAM apparent redox potential has been shown to be sensitive to the aggregation state of anionic amphiphiles in solution and can be used to detect their critical micelle concentration [1-2].

Ferrocene-terminated SAMs exhibit a reversible electrochemistry in the presence of anionic surfactants such as *n*-alkyl sulfates and sulfonates, while the less chaotropic alkyl phosphates and carboxylates lead to irreversible oxidation of the SAM-confined ferrocene [3]. Cyclic voltammetry indicates that these latter surfactants form strong ion-pairs with the oxidized ferrocenium; an oxidation peak is observed for the first anodic potential sweep but no reduction peak is detected during the reverse sweep (Fig. 1). No anodic or cathodic peaks are observed in subsequent sweeps. The anodic peak current densities are greater than that measured in solutions of alkyl sulfates and sulfonates. Also, the SPR signal does not return back to its original value during reduction, indicating an irreversible adsorption of material to the surface which suggests the formation of a stable and insoluble ferrocenium-surfactant anion complex or deposit that blocks the redox process. In this work, atomic force microscopy (AFM) is used to investigate the association of sodium *n*-dodecanoate to the SAM surface.

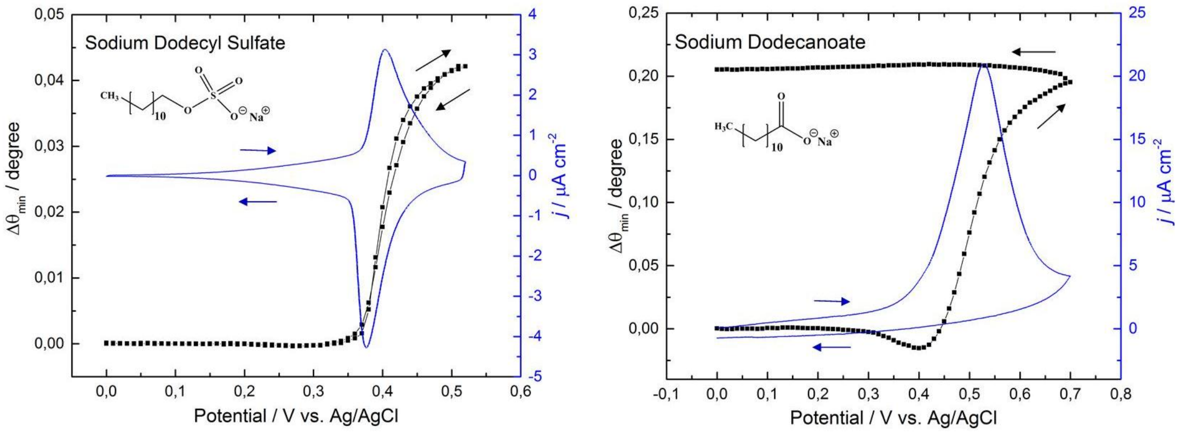

Fig. 1: Current density j and resonance angle change $\Delta\theta_{min}$ versus potential recorded for $FcC_{12}SAu$ SAMs in 30 mM $NaC_{12}SO_4$ (left) and $C_{11}COONa$ (right). Potential scan rate = 10 mVs^{-1}

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P+O-2

New photo-controllable SAM building blocks for switching of bacterial adhesion

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Bacterial infections are initiated by the attachment of the microorganisms to the host cells. Proteins at the membrane of the microbes, so called lectins, are able to adhere to the carbohydrate layer, which decorate most mammalian cells. This interaction can be investigated by glycoarrays, which are conveniently realized e.g. by application of self-assembled monolayers (SAMs).
In previous work,[1] the bacterial adhesion to a mannose-terminated glycoarray could be switched by light: Due to the incorporated azobenzene moiety, the carbohydrate epitope was either accessible or sterically shielded.
In order to further investigate this system, a new SAM building block based on a dibenzodiazocine photo-switch was designed. These cyclic azobenzenes show inverse photochemical behavior compared to the regular azobenzenes since here the Z-isomer represents the ground state.[2] In contrast to the previous works, this enables a complete "switching off" of the recognition, because no photodynamic equilibrium is involved in this state. By irradiation with light of the corresponding wavelength, the adhesion shall be "switched on", for which a non-complete isomerization is fully satisfactory. Here, we present the first synthetic steps towards this new photo-switchable SAM-building block.

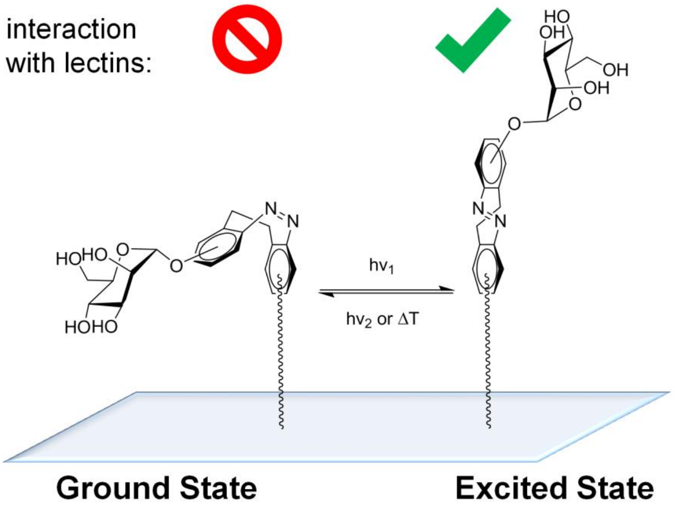

Fig. 1: Left (ground state): the mannosyl moiety is sterically shielded and the interaction with lectins is hindered; right (after photo-switching): the carbohydrate group is exposed and can interact with proteins.

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P+O-3

Metal sulphide sub-nanometre clusters formed within calix[8]arene LB films

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The idea of the formation of metal sulphide semiconductor nano-clusters in Langmuir-Blodgett films of calixarene derivatives [1, 2] was further explored in this work using different bivalent metals, i.e. Cu, Cd, Hg, and Pb. The interest in nano-particulated II-VI semiconductors has been revived recently due to a variety of possible applications in electronics (LEDs) and bio-sensing (luminescent labels).

CuS, CdS, HgS, and PbS nano-clusters were formed within LB films of tetratertbutyl-calix[8]arene carboxylic acid deposited on different substrates (glass, quartz, and silicon) from either the aqueous sub-phases containing respective metal chloride salts (e.g. $CuCl_2$, $CdCl_2$, $HgCl_2$, $PbCl_2$)[1], or by soaking the LB films in the above mentioned salts solutions for 1 hour [3]. The metal ions formed salts with the carboxylic groups in the film. Then the formation of metal-sulphides (MeS) was achieved by treating the samples in H_2S gas for 10-12h in the following reaction: $Me(RCOO-)_2 + H_2S \rightarrow MeS + 2\,RCOOH$. The role of calixarene film matrix was in the restriction of diffusion of metal ions due to the formation of metal-calix[8]arene complexes and the subsequent formation of MeS nano-clusters within calix[8]arene cavities, as has been shown earlier for CdS [1, 2].

The formation of MeS was confirmed by XPS measurements, while UV-vis absorption spectra showed blue spectral shift of MeS characteristic spectral bands due to the effect of quantum confinement of electrons and holes [1, 2]. Moreover, the absorption spectra of all four metal sulphides in Fig. 1 exhibit several spectral bands correspon-ding to the ladder of energy levels appeared as a result of quantum confinement of electrons and holes in a cluster [2]. Simple calculations based on Lifshiz - Slezov model [4] for the spectral shift (*ΔE*) of the main absorption band edge allows the estimation of nano-cluster size as:

$$\Delta E = \frac{\hbar^2 \pi^2}{2Ma^2},$$

where $M = m_e^* + m_h^*$ is the exciton mass, a is a nanoparticle diameter.

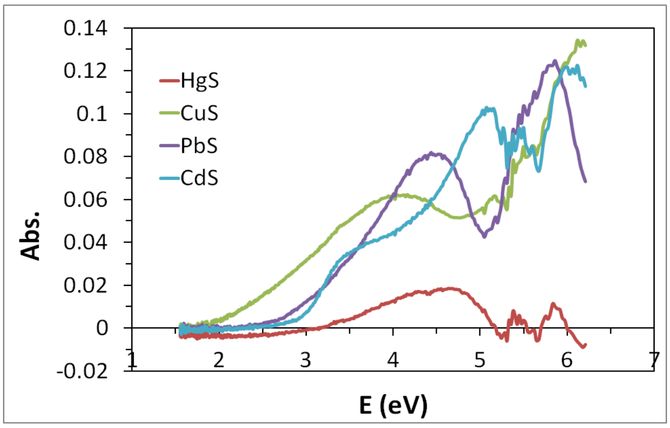

Fig. 1: Absorption spectra of MeS nano-clusters in C[8]A LB film.

The resulting average diameters of MeS clusters ranged from 0.6 to 1 nm, depending on the metal used, correspond well to the size of calix[8]arene cavity, which confirms the hypothesis of MeS clusters embedded in calixanere cavities.

Acknowledgement: Ms Ozkaya would like to thank Erasmus program for sponsoring her research visit to UK.

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P+O-4

Unexpected order-disorder phase transition in diacetylene alcohol Langmuir monolayer

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Diacetylenes are currently targets of extensive research due to their colorimetric properties, when irradiated they polymerize forming, depending on stimuli, a blue or red polymer. 13-4OH ($CH_3(CH_2)_{12}-C\equiv C-C\equiv C-(CH_2)_4-CH_2OH$) is a newly synthesized diacetylenic (DA) alcohol which presents the advantage in forming a stable monolayer at the air/water interface with respect to the well-studied DA acids (such as PCDA), for which the trilayer arrangement is the stable structure at the air/water interface. Both characteristics make DA alcohols the perfect catalyst for the engineering of very sensitive 2D sensors. [1]

While performing Grazing-Incidence X-Ray Diffraction on 13-4OH at Sirius beamline in SOLEIL, one observed an unusual reversible order-disorder phase transition that to our knowledge isn't displayed by any other film. At low surface pressures, diffraction peaks were observed and then disappear if the pressure was increased, meaning the films change from an organized state to a disorganized state with the increase of pressure.

With further study, one noticed a small plateau on the π-A Isotherms, making possible the drawing of the 2D phase diagram (figure 1). Through the analysis of this diagram, another unusual behaviour was discovered, the surface pressure at which this transition occurs decreases with the temperature. This transition has also been identified through Brewster-angle microscopy (BAM) and Atomic Force Microscopy (AFM).

Through Grazing-incidence X-Ray Diffraction and X-Ray Reflectivity, one has characterized structurally these films, however, an explanation has yet to be found. One believes the competition between the alcohol and the diacetylene groups is responsible for this unique behaviour, thus understanding how the distance between groups impacts the structure of the film is the key to explain on explaining this transition.

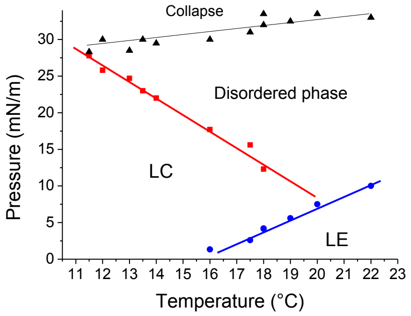

Fig. 1: 2D phase diagram of 13-4OH.

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P+O-5

Ionic Conductivity of Polyelectrolyte Multilayers: Influence of pH and Ionic Strength

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This work illustrates three different approaches of increasing the ionic conductivity of poly(diallyldimethylammonium)/ poly(acrylic acid) (PDADMA/PAA)$_n$ polyelectrolyte multilayers (PEMs). The dc conductivities, which were determined via impedance spectroscopy, are enhanced by orders of magnitude (see figure 1).

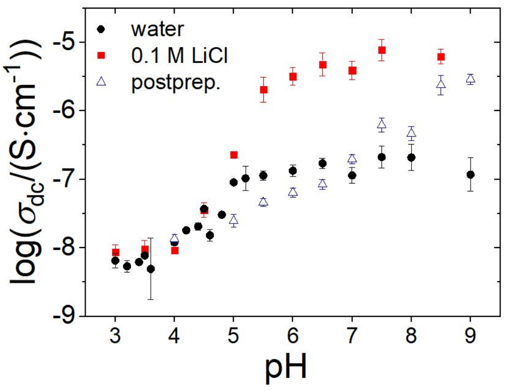

Fig. 1: Different methods of increasing the ionic conductivity of (PDADMA/PAA)$_n$ PEMs. The preparation conditions were varied concerning the pH of the preparation solutions (black: pure water, red: 0.1 M LiCl solutions). Successive postpreparational treatments in 0.1 M LiCl solutions of stepwise increasing pH were also investigated (blue open triangles).

The first two approaches investigate the effect of varied preparation conditions. Two parameters, which are known to significantly influence the composition and conformation of polyelectrolyte multilayers are the charge density of the used polyions and the ionic strength of the deposition solution.[1] First we employed a variation of the pH value of preparation, by which the charge degree of PAA inside the multilayers can be tuned.

The dc conductivities are found to increase with the pH of preparation by more than one order of magnitude (black circles in figure 1) it the case of pure water. This effect of increasing conductivities at higher charge degrees of PAA is further amplified for samples prepared from 0.1 M LiCl solutions. Dc conductivities increase from (8 ± 2) nS·cm^{-1} at pH 3 to (6 ± 2) µS·cm^{-1} for pH 8.5 (red squares in figure 1). Due to their magnitude, these effects are attributed to enhanced ion mobilities, which are most likely caused by increased hydration. The observations are further discussed with regard to film composition and structure.

The third approach to enhance the conductivities involves successive postpreparational treatments of (PDADMA/PAA)$_n$ PEMs prepared at pH 4 which are treated by immersion into 0.1 M LiCl solutions of stepwise increasing pH. A possible pH-driven doping with Li$^+$ ions based on the postpreparational generation of negative excess charges inside the PEMs similar to studies by Parveen et al.[2] and Chung and Rubner[3] was presumed. Exponentially increasing conductivities are observed (open blue triangles figure 1) and the processes caused by the postpreparational treatments are further elucidated by *in-situ* studies utilizing attenuated total reflection infrared spectroscopy and dissipative quartz crystal microbalance.

It is shown that, using different approaches, the conductivity of PEMs from the same polyelectrolyte materials can be tuned in a wide range.

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P+O-6

Promoting the interaction of Fmoc-dipeptides with lipid membranes by the adjustment of the hydrophobicity secuence

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Fmoc-dipeptides appear as a highly relevant building block in smart hydrogels and nanovehicles for biological applications. The interactions of the Fmoc-dipeptides with the cell membrane determine the efficiency of the nanomaterials based on the Fmoc-dipeptides, as the internalization of nanovehicles for drug delivery. Here we aim at the understanding of the interplay of the interactions between the Fmoc-dipeptides and a phospholipid surface as a function of the aminoacid sequence. The DMPA (1,2-dimyristoyl-sn-glycero-3-phosphate) phospholipid in Langmuir monolayers was used as a model cell surface. A set of seven derivatives of Fmoc-dipeptides with a broad range of hydrophobicity were included. Mixed monolayers composed by DMPA:Fmoc-dipeptide in equimolar ratio were built and characterized in situ at the air/water interface. Surface pressure-molecular area isotherms (π–A), Brewster Angle Microscopy (BAM) and UV-vis reflection spectroscopy (ΔR) were combined to provide a holistic picture on the interactions of the Fmoc-dipeptide with the phospholipid molecules. An increase in the hydrophobicity led to an enhanced interaction of the Fmoc-dipeptide and DMPA molecules. The compression of the mixed monolayer could displace a significant fraction of the Fmoc-dipeptide from the monolayer. A high hydrophobicity promoted self-assembly of the Fmoc-dipeptides over interaction with the phospholipid surface. The interplay of these two phenomena was analyzed as a function of the aminoacid sequence of the Fmoc-dipeptides. The results suggest that the adjustment of the hydrophobicity of the Fmoc-dipeptides within a defined range might optimize their efficiency for the interaction with the lipid membranes.

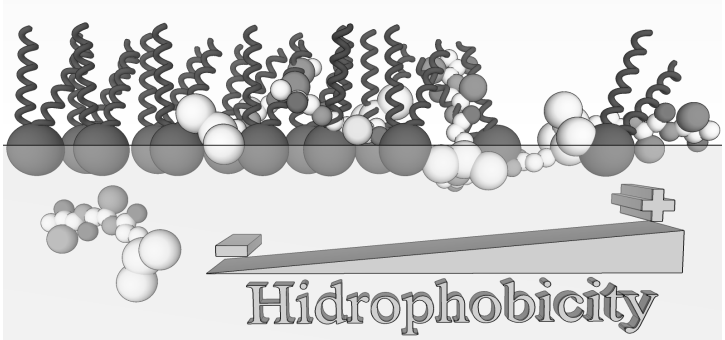

Fig. 1: Interactions Fmoc-dipeptide derivatives with different hydrophobicity and a DMPA phospholipid surface

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O-4

Miscibility and iron-binding in anionic gemini surfactant monolayers

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Anionic gemini surfactants are a minimally explored class of compounds that provide excellent opportunities for exploring the fundamental physical chemistry of monolayer films. My group and others have been investigating film-forming properties of the recently reported N, N, N', N'-dialkyl-N, N'-diacetate ethylenediamine family of anionic gemini surfactants (representative molecule shown in Fig. 1). In this presentation, we discuss recent investigations into three key properties of Langmuir monolayers of these class of compounds: their miscibility with perfluorinated fatty acids; their ability to bind with Fe ions; and their ability to form stabilized catanionic mixtures with quaternary ammonium ion surfactants. Experimental approaches used to assess the systems include classical isotherm measurements, along with surface imaging and synchrotron-based X-ray diffraction and fluorescence techniques. Properties of these systems will be compared with well-studied "monomeric" surfactant monolayers comprised of simple fatty acids and phospholipids.

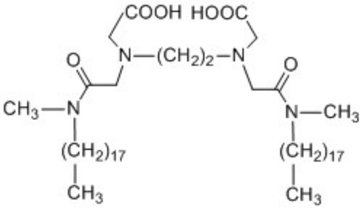

Fig. 1: Chemical structure of a typical N, N, N', N'-dialkyl-N, N'-diacetate ethylenediamine gemini surfactant.

Alignment of single-walled carbon nanotubes

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The alignment of single-walled carbon nanotubes (SWCNTs) in Langmuir films during compression is a well-known phenomenon [1]. Experimentally, the alignment of SWCNTs in a Langmuir trough (Fig. 1) is only possible for polymer terminated SWCNTs. However, the details of the alignment mechanism are still unclear.

In our work we performed a series of numerical simulations with the aim of untangling the origin of SWCNT alignment. To confirm the theoretical calculations, we performed real-time polarized Raman spectroscopic measurements *in-situ* during the compression of Langmuir film.

We introduced an orientation parameter to compare theory with experiment. The temporal evolution of the experimentally obtained orientation parameter and surface pressure validate our numerical model.

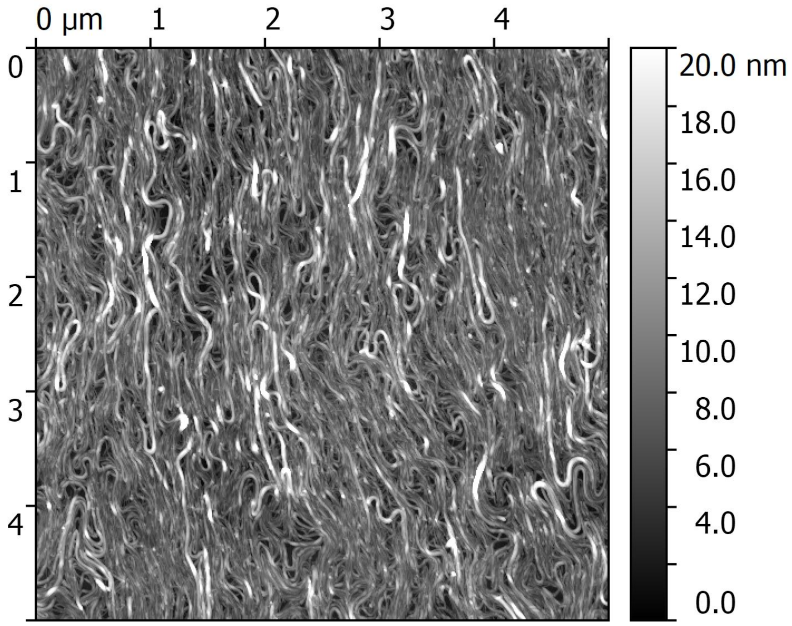

Fig. 1: The AFM image of a Langmuir film of aligned SWCNTs.

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O-6

Lanthanide interactions with zwitterionic lipid monolayers: Remarkable effects revealed by Grazing-Incidence X-ray Diffraction

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Our group has studied the interactions of lanthanides with phospholipid Langmuir monolayers for some time [1]. Recent experiments using grazing incidence X-ray diffraction (GIXD) in the SOLEIL synchrotron have revealed a remarkable range of behaviors related to the nature of the lipid, the lanthanide cation and the anion of its salt. Lanthanide X-ray fluorescence revealed that lanthanides concentrate more strongly at the surface depending on the anion present in the sequence $Cl^- < NO_3^- < SO_4^{2-}$ (Fig. 1a), which reflects the complexation strength of the anion, as seen in Fig. 1a for dipalmitoyl phosphatidylcholine (DPPC) and dimyristoyl phosphatidylethanolamine (DMPE).

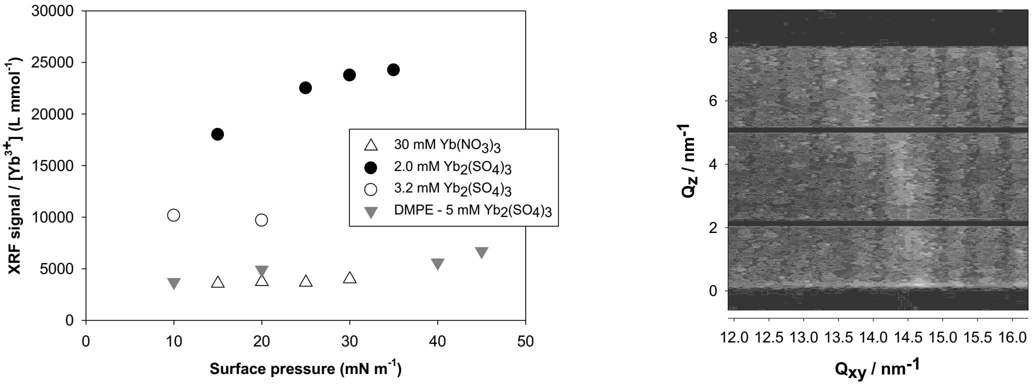

Fig. 1: (a-left) Normalized XRF signal from the adsorption of ytterbium salts on DPPC and DMPE monolayers. (b-right) GIXD contour plot showing superlattice formation by ytterbium sulphate under a DPPC monolayer.

Both the heavier lanthanides and the sulphate salts of essentially all lanthanides were found to form ionic superlattices under the lipid monolayers (Fig. 1b). It is the first time that such superlattices have been observed for zwitterionic monolayers; previous such observations have been made for charged lipids only [2,3]. Interesting modulations of the structures of DMPE and dihexadecyl phosphatidylcholine (DHPC) have also been observed in the presence of lanthanides. Since several of the structures observed are unusual for these phospholipids, we believe that our findings are of considerable interest both in biophysics and in separation technology for lanthanide recovery.

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O-7

Supramolecular preorganization at air/water interface for enhancement of receptor properties of hemicyanine chromoionophore LB films

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Development of novel sensor systems is one of the most promising fields of supramolecular chemistry. In this regard, macroheterocyclic compounds capable of selective binding with various analytes are preeminent. This work is devoted to the study of the mercury receptor properties of the amphiphilic dithia-aza-crown-containing hemicyanine chromoionophore (ChIP – Fig. 1) in monolayers at air/water interfaces and in ultrathin films on solid substrates.

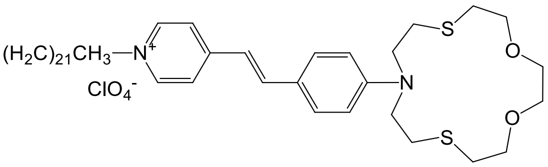

Fig. 1: Chemical structure of the studied amphiphilic hemicyanine chromoionophore.

Investigation of the ChIP monolayers on aqueous subphases with different concentration of mercury ions by means of fiber optic reflection-absorption and fluorescence spectroscopy have shown that the studied chromoionophore interacts with Hg^{2+} at the air/water interface in a way not observed in solution, namely, complexes, in which two ChIP molecules are coordinated by one mercury cation, can form. However, they occur only at high analyte concentrations because of low accessibility of crown-ether moiety due to head-to-tail aggregation. Introduction of "inert" barium cations, which do not bind strongly to crown-ether moieties, inhibits the head-to-tail aggregation of ChIP molecules in the compressed monolayer, promoting such structural preorganization that provides more access to crown-ether fragments of the molecules. This significantly enhances mercury detection threshold of the compressed ChIP monolayers. Such organizational changes induced by a metal cation that does not interact directly with the ionophoric group at the air/water interface were confirmed by X-ray reflectivity, and the nonparticipation of barium ions in compressed monolayer - by X-ray standing waves methods. It was shown that the intensities of the ChIP monolayer fluorescence emission peak observed upon excitation at wavelengths corresponding to both free-form dye and mercury complexes linearly depend on the logarithm of analyte concentration in the aqueous medium. Ratio of these emission intensity values can be used for convenient calibration curve for qualitative determination of Hg^{2+} concentration in the aqueous medium. The advantage of the proposed approach is the presence of internal reference point in the system, analogous to one used in ratiometric sensory devices.

Ultrathin films of ChIP on solid substrates obtained using Langmuir-Blodgett and Langmuir-Schaefer technique retain the receptor properties of the monolayer and show excellent detection threshold and fluorescent response to mercury cations. Langmuir-Schaefer film, in which the ionophoric fragments of the ChIP molecule is oriented in the film towards the aqueous analyte exhibits significant analytic response even at mercury salt concentrations as low as 10^{-10} M. Moreover, almost total regeneration of the described ultrathin film sensor can be performed by simple cleaning with KCl solution. Thus, this compound can be considered promising for development of solid-state sensors for mercury cations using the above described approach.

The study was supported by RFBR grant no. 16-29-05272, and RSF project no. 17-73-20268.

O-8

Open-air preparation of polymer blushes at large-scale

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Polymer brushes (PBs) prepared by surface initiated-atom radical polymerization (SI-ATRP) have been in the focus of significant interest in polymer research due to their unique properties.[1] Although there are many scientists/engineers engaged in research on PBs by SI-ATRP, their primary attention has been paid to the development of new synthetic pathways and the investigation of the properties of the PBs. Improving new synthesis methods for initiator layers, which is the first step of the SI-ATRP process, has been ignored so far, and thus, average preparation size of PBs have been limited to ~10 cm^2.

Here, we applied a sol-gel process for preparing large-scale initiator layer because this method has been widely and practically employed in industrial processes for production of functional films.[2] Initiating functional group-terminated organosilane for ATRP ((*p*-chloromethyl)phenyltrimethoxysilane, CMPTMS) was mixed with tetraethoxysilane (TEOS) in the presence of ethanol and hydrochloric acid (Fig.1a). For example, the sol-gel precursor solution was then coated on PET roll film *via* a roll-to-roll process. The resulting initiator layer was transparent and the size was 40 cm × 100 m (40 m^2, Fig.1b). Our sample may be the largest among the initiator layers so far reported. We also confirmed that at least 34 kinds of PBs could be prepared from our sol-gel initiator layer. For example, the surface wettability can be tuned between 5°-90° by an appropriate selection of monomers. Using the "Paint-on" SI-ATRP technique[3] recently developed by some of the authors, analogues to AGET/ARGET-ATRP, we could successfully prepare large-size PB films (1600 cm^2). We also confirmed that our hydrophilic PB films showed anti-fogging properties, and nitrogen-containing PB films worked as a scaffold for uniform and site-selective electroless copper plating. Our approaches demonstrated here undoubtedly possess great potential and can be being developed to industrial processes for polymer brushes fabrication.

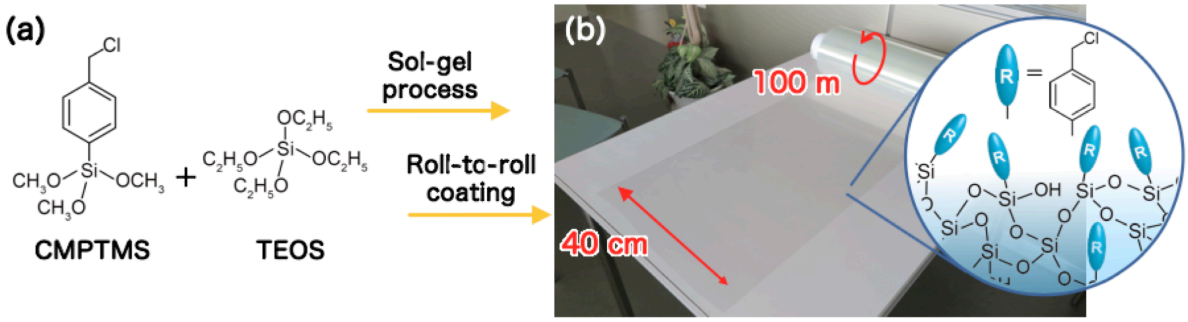

Fig. 1: (a) Sol-gel solution of (*p*-chloromethyl)phenyltrimethoxysilane (CMPTMS) and tetraethoxysilane (TEOS), *and (b) sol-gel derived initiator layer formed on PET roll film via a roll-to-roll process.*

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A dewetting mechanism at the origin of lipid storage organelle biogenesis

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Organisms have the ability to buffer energy fluctuations so as to sustain to environmental nutrient constrains[1,2]. Excess nutrient is stored in cells in organelles called lipid droplets. They are dynamic intracellular oil-in-water droplets, which are covered by a phospholipid monolayer containing proteins. They form in the presence of excess nutrient and are consumed during scarcities so as to provide energy. The biogenesis of these organelles starts from a cellular phospholipid bilayer membrane. Initially, neutral lipid oil molecules are fabricated and embedded in the interstice of the two monolayers forming the bilayer[3–5]. At a critical oil concentration, the molecules spontaneously gather to form an oil lens in the bilayer[4]. By acquiring more oil molecules, the lens grows to become a spherical droplet that protrudes from the bilayer. Mechanisms controlling these steps are currently under investigation by many labs. Our lab is particularly interested in understanding how the transition from a lens to a droplet shape happens. For this purpose, we developed biomimetic systems reproducing a bilayer containing and oil environment. To do this, we take advantage of droplet interface bilayer systems, which are adhering water-in-oil droplets, each covered by a phospholipid monolayer. This system enables indeed to generate a bilayer that opens up into an oil environment, as the previously described lens in the bilayer. With this system we were able to isolate key physical-chemistry parameters modulate the lens-to-droplet budding transition. We identified that the underlying mechanism for this transition follows a dewetting process[6] that has been well studied in interfacial physical chemistry. I will present data showing how cells have been pioneer in controlling interfacial properties to regulate organelle formation.

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Light harvesting using Langmuir Blodgett films of carbocyanine dyes

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Creating a light harvesting surface is an important area of research for improving the efficiency of solar cells. Covering the silicon in an absorbing organic layer may allow for light absorption to occur separately from electron-hole pair generation.[1] One proposed solution is a layer made up of donors and acceptors undergoing resonance energy transfer to absorb sunlight. This concept is analogous to the light harvesting step in photosynthesis, using the transfer of excitation energy from a high number of donor molecules to a small number of acceptor molecules to funnel the energy towards a specific location within a structure.[2] Cyanine dyes have been shown to have film forming properties and can be quenched by silicon, therefore work was continued on these dyes.[3,4]

For this study, two carbocyanine dyes were dissolved in chloroform and mixed in six different molar ratios. These were then spread on the surface of water on a Nima Langmuir Blodgett trough. The films were then repeatedly compressed to give information about the behaviour of the dyes in a thin film. Langmuir Blodgett monolayers could then be prepared and deposited onto glass slides. The films were ordered, six layers of stearic acid, a single monolayer of dyes and two more layers of stearic acid to protect the dyes. (figure 1)

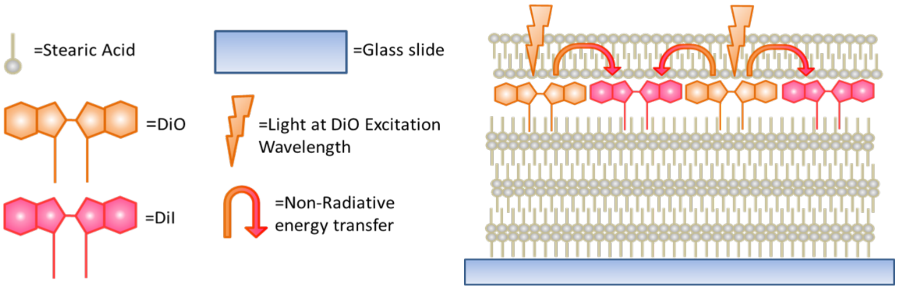

Fig. 1: Side-on diagram of a sample structure. Six layers of stearic acid give a good surface for the dyes to adhere to. The top two layers protect the dyes from the atmosphere.

The dyes used in this study were 3,3'-Dioctadecyloxacarbocyanine Perchlorate (DiO) which acted as the donor and 1,1'-Dioctadecyl-3,3,3',3'-Tetramethylindocarbocyanine Perchlorate (DiI) which acted as the acceptor. The ratios used were 1 (DiI) to 1, 10, 25, 50, 75 and 100 (DiO).

The samples were studied using time resolved fluorescence spectroscopy/microscopy. The results showed quenching of the donor dye, denoted by a decrease in the fluorescence lifetime of the donor. This suggests evidence of energy transfer between this donor-acceptor pair. Quenching was observed in every ratio; indicating excitonic diffusion through the donors terminating at acceptors.

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P+O-8

X-Ray surface radiolysis of silver and gold solutions using ionic liquid Langmuir films as a template

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Combining the properties of organic amphiphilic molecules and inorganic species is of interest to form ultrathin films with adjustable functionalities and tunable properties (optical, electronic, catalytic...) [1]. X-Ray surface radiolysis of Langmuir films deposited onto metallic subphases becomes one of the approaches for such synthesis and leads to metalorganic films with controlled shapes.

We have successfully demonstrated that the X-Ray irradiation of the surface of an acid behenic dense Langmuir film deposited at air-silver (Ag^+) solution interface leads to the formation of a metalorganic nano-layer oriented by the organic film [1]. We have also evidenced the formation of a metalorganic thin film of gold and amphiphilic copolymer (polystyrene 2-dimethylaminoethyl methacrylatePS - PDMAEMA. Indeed, due to the interaction between the charged head groups of the amphiphilic species and metal ions, the radiolysis provided metallic atoms coalescence localized onto the surface of the Langmuir film. We are planning to enlarge this approach to form nano-objects of metallic alloy in interaction with organic molecules. Therefore, we attempted to study Langmuir films of amphiphilic molecules charged by both positive and negative ions, deposited first on single then on mixture of metallic ions solutions subphases. Ionic liquids (IL) or molten salts known for catalysis applications and as liquid electrolyte are composed of cation and anion [2]. We choose to study the IL 1-alkyl 3-methylimidazolium bis (trifluoromethylsulfonyl) imide $[C_{20}mim]^+[N(Tf)_2]^-$ at air-water and air-metallic ions solutions interfaces since it is one of the rare IL capable of forming stable Langmuir film at air-water interface. Due to the electrostatic interactions between the hydrophilic imidazolium ring, carrying the positive charge of the cation, and the anion, both charges are present at the interface. In these systems, two positive ($C_{20}mim^+$ and Ag^+) (or/and negative ($N(Tf)_2^-$ and $AuCl_4^-$)) charges are competing to be in interaction with only one negative($N(Tf)_2^-$) (or/and positive $C_{20}mim^+$) charges. Surface compression isotherms show that the presence of metallic ions (Ag^+ or $AuCl_4^-$) in the subphase facilitate the transition of the film to its dense phase during its compression. Grazing incidence X-Ray diffraction measurements show diffraction peaks associated to the formation of 3D crystals of silver and an organized 2D layer of the IL after 10 hours of irradiation silver solution subphase. However, on gold subphase after 5 hours of irradiation, we did not observe organization structures of the IL but only diffraction peaks associated to 3D crystals and 2D platelets of gold.

Systems with single metallic ions solution subphases show that the shape (platelets or 3D crystals) of the formed inorganic structure is depending of the sign of the charged ion. Therefore, the presence of the mixture of Ag^+ and $AuCl_4^-$ in the subphase may induce the formation of new and innovative shapes of the alloy in interaction with the organic film.

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P+O-9

Design, synthesis and characterization of chitosan-based interpenetrating polymer network membranes produced using a slot-dye technique

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Chitosan is a polymer derived from naturally occurring sources of chitin and can be used in a diverse range of applications. Some of the limitations currently restricting the application of chitosan-based films is their lack of mechanical strength combined with a lack of methods designed to produce thin film materials in high volume. The first of these shortcomings can be surmounted by creating a co-continuous structure such as an interpenetrating polymer network (IPN). An IPN is defined as "a combination of two polymers in network form, at least one of which is synthesised and/or cross-linked in the immediate presence of the other" (L.H. Sperling). [1]

In this present work, several polymeric compounds were chosen to form IPNs with chitosan; tetraethylorthosilicate (TEOS), 3-aminopropyltriethoxysilane (APTES) and polyacrylamide (PAM). TEOS and APTES naturally crosslink after undergoing hydrolysis and condensation reactions to form cross linked siloxane chains.[2] while both chitosan and PAM are cross linked by glutaraldehyde in acidic media.[3]

The IPNs were formulated into hydrogels which were then cast and dried into large area (25 x 5 cm^2) thin flexible films by a novel slot-die casting technique designed to overcome the second limitation noted above, see figure 1.

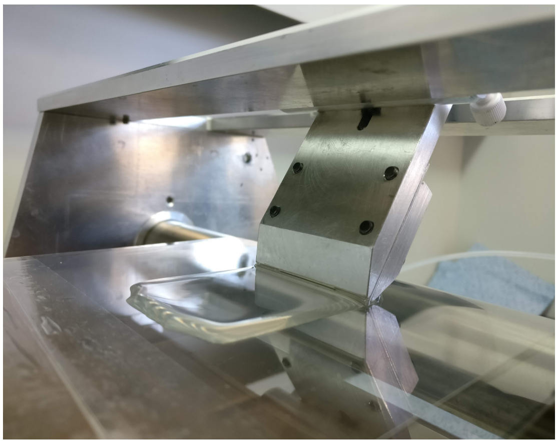

Figure 1: a photograph of the slot dye coating system used to prepare large area (25 x 5 cm^2) chitosan-based IPN membranes

This 'proof-of-concept' method is shown to produce relatively homogeneous films in a short amount of time (45-60 min). The resulting films were analysed as to their uniformity in terms of thickness and their mechanical strength, surface roughness and swelling properties.

The potential applications of such large-area IPNs will be discussed focusing particularly on their possible use in the development of biodegradable packaging and materials which possess a degree of antimicrobial activity.

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P+O-10

Threshold Voltage control of organic field-effect transistors by using fluorinated alkylsilanes

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The doping of the organic semiconductor is an important tool for tuning the properties of organic field-effect transistors (OFETs) such as the turn on and threshold voltages. Fluorinated alkylsilanes are a group of well-studied p-type dopants, which are usually applied by sequential doping at the semiconductor-insulator interface. These silanes are usually either deposited as a self-assembled monolayers (SAMs) on the dielectric oxide[1] or on top of the organic semiconductor.[2]

We show an approach where the fluorinated silane is subsequently deposited on top of the prefabricated OFET in a bottom gate, top contact architecture.[3] As a dopant and semiconductor materials we focused on Trichloro(1H,1H,2H,2H-perfluorooctyl)silane (FTS) and TIPS-pentacene, respectively. While the semiconductor in this work is deposited by vacuum deposition, the dopant is deposited either by vapor phase or solution phase deposition techniques. The solution-based approach relies on the utilization of an orthogonal solvent.

Both approaches (vapor, solution) are leading to comparable results, including voltage-shifted transfer curves, increased conductivity nearly without reduction in mobility. The strength of the doping effect could be controlled by the FTS deposition time or the FTS concentration in solution. Small doping concentrations (short FTS deposition times and small FTS concentrations) were leading to a shift of the threshold voltage up to 28 V with only small degradation of the transistor characteristics. In addition to the electrical measurements, we discuss Kelvin Probe Force Microscopy measurements on these samples in which the doping effect results in a shift in the contact potential difference.

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P+O-11

Coating of smooth polymeric films through high frequency vibration

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In the field of Organic Electronics, the possibility of large-scale fabrication of polymeric semiconducting films is highly desirable and meniscus-guided coating methods are seen as the main enablers for this. An important aspect of high throughput is uniformity.[1] Although Donor-Acceptor copolymers (D-A) are considered to be potential materials for high-performance Organic Field-Effect Transistors (OFETs), the processing of the these can be quite challenging. High viscosity, non-uniform agglomerating of material and appearance of instabilities during the deposition process are a few of the hindrances in the advance of large-scale thin-film deposition.[2]

In this work we present a method for improving the uniformity of shear-coated polymeric thin-films for fabrication of OFETs. Through vibrating our deposition blade with frequencies of a few kHz, we believe to induce Faraday instabilities,[3] mitigating non-uniformities in the semiconductor film. This improvement has been observed for more than one D-A material, and can be adjusted when changing vibration parameters while it does not impair charge-carrier mobility in OFETs. Fig. 1 depicts an example of how adjusting the vibration parameters improves film quality. We believe the vibrating of the blade during the coating process to be extendable to a wide range of materials and an important contribution to the deposition of organized thin films.

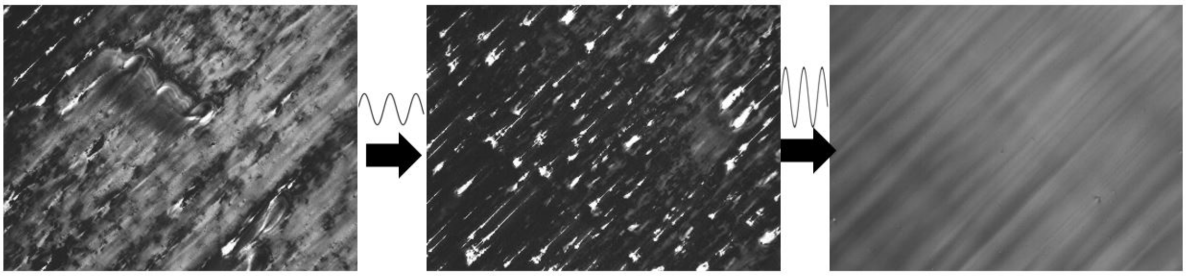

Fig. 1: From the left to right: Meniscus-guided coating of a D-A polymer with several types of non-uniformities; coating of a film with vibration and low acceleration; coating of a film with vibration and high acceleration.

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P+O-12

Exploitation of solution-processed, high-mobility semiconductors for high-frequency organic transistors

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Potential applications, such as flexible and mobile electronics, along with the prospect of large-area and potentially low-cost fabrication have driven the research on the solution-deposition of innovative functional materials, such as small molecule organic semiconductors. Though simple circuits have been already realized[1], the advantages of solution-processing, i.e. the often superior characteristics as compared to vacuum processed films have not been fully exploited and demanding applications like flexible displays or wireless communication devices are still to be shown. Particularly, the exploitation of high-mobility organic semiconductors is usually hampered by different extrinsic factors, i.e. the applied fabrication routines, transistor architecture or combination of materials which can introduce large barriers at the metal-semiconductor interface or undesired effects, such as hysteresis or threshold-voltage shifts.

Here, we study the high-mobility semiconductor 2,7-dioctyl [1]benzothieno[3,2-b]benzothiophene (C8-BTBT) and investigate how the material can be exploited for the use in high-performance organic transistors. Specifically, we are exploring the fabrication of high-mobility films by solution-shearing[2] and investigate the possibility to exploit this property in practical devices. By the optimization of a blended solution with polystyrene (PS), mobility values up to 12 cm^2/vs are obtained within long-channel bottom-gate, top-contact (BGTC) devices. However, while these values reflect on the good film quality and the general potential of the material, the versatility of these thin-films to produce devices operating at high frequency still depends on a range of other factors. Therefore, we are also looking at the interfaces of the organic film and investigate how they can be tuned to improve device performance. Specifically, different contact configurations are explored and compared with respect to the resulting device characteristics and contact resistance. Moreover, the impact of the dielectric-semiconductor interface, which can be tuned by different blending ratios, is explored and the advantageous effect on device stability demonstrated. Finally, short-channel devices are discussed and compared to the non-optimized ones.

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P+O-13

Agarose Beads with Controlled Pore Structures for High Precision Clinical Biosensing Diagnostics

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Increasing the precision and reliability in biosensing is critical for accurate clinical disease diagnosis and rapid implementation of relevant treatment modalities in point-of-care technologies [1]. Polymer-based microbeads have been used to immobilize probes for targeting biomarkers in body fluids, such as serum, saliva and urine, each of which is a complex medium with a large background originating from a wide variety of non-specific biomolecules [2]. Among the key issues associated with the bead-based systems are signal variations due to the non-uniform bead size distribution, surface versus internal structural variations, and the stability of the beads. The limitations also include variability and inefficiency of immobilization approaches as well as the formation and mechanical properties of the beads [3].

We developed a mechanical methodology by which to mass produce agarose gel-based nanoporous and monosize microbeads with controlled surface and internal structures facilitating a close control over functionalization. We used covalent biofunctionalization of disease-specific probes that provide high signal-to-noise ratio biomarker detection. In fig 1, the porous external and internal structure of the agarose beads (a) demonstrate a control in chemi-functionalization by glycidol oxidation (b). We will discuss the use of CRP and CTNI biomarkers for sepsis and AMI, respectively. For this, biofunctionalization of the surface was carried out by capturing antibodies that are specific to disease-specific antigens with significantly enhanced signal-to-noise ratio.

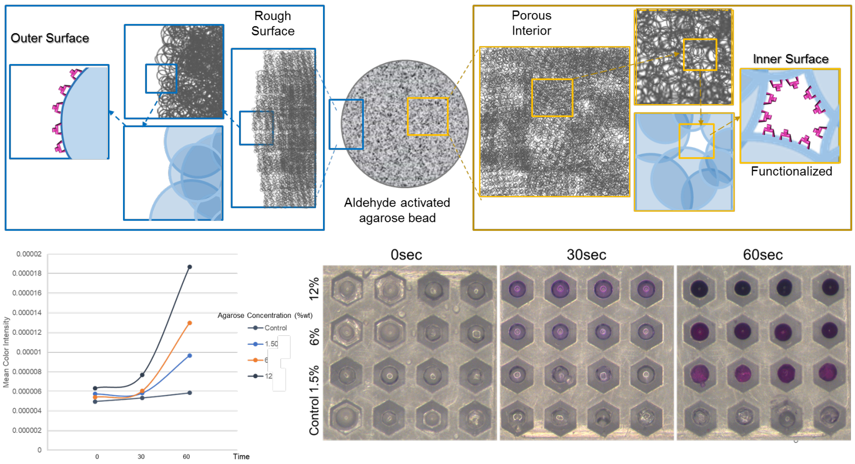

Fig. 1: (a) Schematics of the surface chemi-functionalization of the beads; (b) Quantitative measurement of color intensity of aldehyde groups on agarose fibers with different concentrations before bio-conjugation

The ease of manufacturing and highly efficient performance characteristics of agarose microbeads established here demonstrate a rapid and high precision diagnostic of disease-specific biomarkers paving the way for potential clinical implementations where the rapid and highly efficient detection of the disease-specific antigens is the key.

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O-9

The use of aptamers immobilized on the surface of transducers for detection of low molecular weight analytes

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The detection of low molecular weight molecules of toxins, i.e. mycotoxins , heavy metals, pesticides, organic chemicals, in low concentrations (in ppm level and below) is of paramount importance nowadays, which stimulates the development of chemical- and bio-sensors capable of this task. Antibodies commonly used as natural bio-receptors for different toxins became successfully replaced these days with synthetic receptors, e.g. aptamers or peptides. This work gives several examples of utilization of aptamers for detection of different types of low molecular weight analytes, i.e. mycotoxins (ochratoxin A, aflatoxin B1 and M1), heavy metal ions (Pb^{2+} and Hg^{2+}), and organic molecules (dopamine) using different types of transducers, e.g. optical (total internal reflection ellipsometry (TIRE), localized surface plasmon resonance (LSPR), planar waveguides (PW)) and electrochemical (cyclic voltammograms (CV) and impedance spectroscopy). The aptamers used in this work were immobilized on the surface of gold screen-printed electrodes (for electrochemical measurements) or gold nano-structured layers on glass (for optical LSPR/TIRE measurements) via thiol groups attached at the C5' termini. In case of PW transduces, the same type of aptamers were immobilized on the S_3N_4 surface in the sensing window using intermediate chemicals.

As an example, the electrochemical detection of dopamine using its specific aptamer labelled with ferrocene is shown below. Aptamers change their secondary structure upon biding the dopamine which enhances the charge transfer between the label and the electrode (see the scheme in Fig. 1). Typical CVs and impedance spectra for different concentrations of dopamine are shown in Fig. 1; minimal detected concentration of dopamine was 0.1 nM.

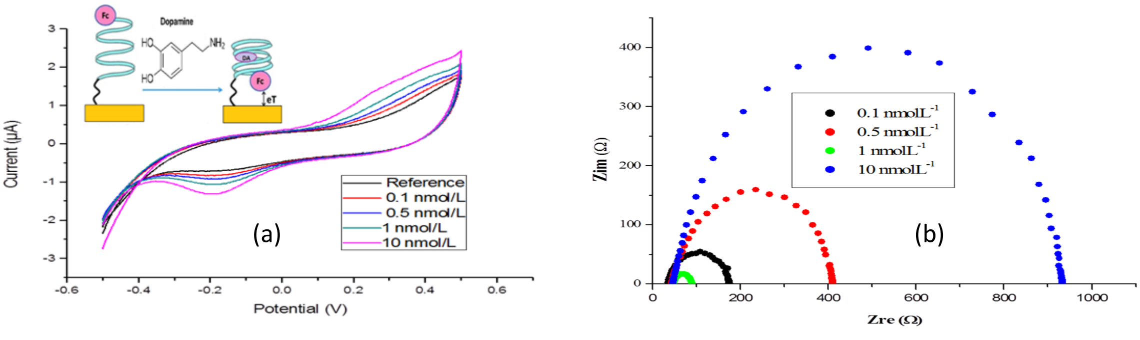

Fig. 1: Detection of dopamine with electrochemical apta-sensor (inset) using CVs (a) and Impedance spectra (b).

Similar results were obtained for electrochemical apta-sensing of Hg^{2+} and Pb^{2+} ions down to 0.1nM in concentrations [1]. Optical detection of mycotoxins (down to 10 ppt in concentration) with specific unlabelled aptamers was achieved using the LSPR/TIRE method [2, 3], while the PW-based apta-sensor allowed the detection of aflatoxin B1 below the 1ppt level [4].

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Conception and characterization of new bioinspired nanoparticles with dual activity for esophageal cancer therapy: Preparation and PEGylation strategy

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In the last decade, polydopamine (PDA) has drawn much attention as a bio-inspired eumelanin-like polymer that can self-assemble into nanoparticles with multiple interesting properties (excellent biocompatibility, biodegradability, further functionalization, and high photothermal conversion ability) [1]. Owing to its unique properties, we decided to establish a new photoactivatable platform with dual activity for efficient and selective cancer therapy. This platform will be composed of pegylated PDA nanoparticles bearing at their extremity a photosensitizer (PS) *via* a linker cleavable under reactive oxygen species, allowing the release of the PS. This nanosystem will take advantage of the photothermal activity of PDA nanoparticles to kill cancer cells by photothermal therapy but also of the photodynamic activity of a photosensitizer that is able to photochemically destroy neovessels.

In this study, spherical monodisperse PDA nanoparticles were synthesized through oxidative polymerization of dopamine under alkaline conditions. Their diameter was found to be easily tunable by varying the base/dopamine molar ratio, dopamine concentration and temperature. The PEGylation of PDA nanoparticles was successfully done and was confirmed using Fourier Transform Infra-Red spectroscopy (FTIR). The photothermal activity of PDA nanoparticles was evaluated in solution after laser illumination at 808 nm and 2 W.cm^{-2}. The impact of nanoparticles size, concentration and PEGylation was also studied.

In order to optimize nanoparticles PEGylation in physiological conditions, we monitored the PEGylation efficiency *in situ* on a PDA film using Quartz Crystal Microbalance (QCM-D) combined to Atomic Force Microscopy (AFM). PEG grafting kinetics, layers densities and thicknesses were thus determined for poly(ethylene glycol) (PEG) chains of different molecular weights under different conditions. The interaction between these grafted chains and fetal calf serum was also studied and compared to bare PDA surface.

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O-11

Degradation of cellular membrane in photodynamic therapy: contribution of lipid monolayers and Langmuir-Blodgett films to mechanism elucidation

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Photodynamic therapy (PDT) is an attractive alternative to chemotherapy in some cases, based on the irradiation of a photosensitizer (PS) after its penetration in cells. This irradiation leads to the formation of reactive oxygen species able to oxidize adjacent biomolecules, causing cell destruction (tumour and vascular system around). Cellular membranes are one of the targets, especially because of lipid oxidation, but a clear understanding of the mechanisms of membrane photodestruction is still missing, whereas this point is crucial in order to optimize for instance the chemical structure of PS. The lipid complexity of membranes is another obstacle, justifying the use of simplified membrane models, such as Langmuir monolayers and Langmuir-Blodgett films. In this context, we studied the interaction of a derivative of bacteriochlorophyll *a* with different lipid planar monolayers and bilayers, made of POPC (phospholipid model of the fluid phase of membranes), DPPC (saturated and more organized phospholipid) and sphingomyelin (SM, sphingolipid typical from raft phase).

Compression isotherms of individual lipid and mixed lipid/PS monolayers were studied. It was shown that the presence of PS impacts mean molecular areas and compressibility as compared to monolayers made of pure lipid. Lipid monolayers were transferred at a surface pressure of 30 mN/m onto planar supports (hydrophilic mica) to be studied by Atomic Force Microscopy (AFM) and contact angle measurements (sessile drop method). Contact angle values give information on the overall state of Langmuir-Blodgett films, whereas AFM gives, among other film characteristics, information in terms of lateral imaging and profile height (with a resolution of 1 nm and 0.1 nm, respectively). Measurements were performed either without any irradiation or after irradiation (in the infrared spectral range during 40 min). Same measurements were performed on pure lipid systems, in order to check their own stability in the absence of PS. In the case of films of pure lipids, contact angles are roughly in a range of 90-100°, confirming that mica surface becomes hydrophobic after the transfer. Moreover, Langmuir-Blodgett films of pure lipids are on the whole resistant to irradiation under our experimental conditions. AFM images of mixed Langmuir-Blodgett films support the idea that PS is not equally distributed. In particular in the case of POPC/PS monolayers, some areas are characterized by a strong sensitivity to IR irradiation, showing an overall reorganization. Such local reorganization leads to significant changes in macro-characteristics of studied model mixed membranes, which were detected particularly by the contact angle measurements. In the case of bilayers, surface plasmon resonance (SPR) and electrochemical impedance confirm the stability of bilayers made of pure POPC or SM under irradiation. In the presence of PS, the photoexcitation leads to significant changes of the surface properties of samples as shown for instance by the decrease of the resonance angle in SPR experiments, which could be due to the degradation of the lipid matrix under the action of active oxygen forms generated by PS. To conclude, we validate here our approach to study the mechanism of photodegradation of lipid membranes and to perform a comparative evaluation of the effectiveness of photosensitizers developed for PDT.

The work was supported by RFBR grants no. 17-53-150013 and French CNRS joint project no.1520 (2017-2019).

Development of core-satellite nanostructures via the Langmuir-Blodgett technique: self-assembly and characterization

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Metal nanoparticles (NPs) possess unique physicochemical and plasmonic properties that make them of great interest for the development of new sensing platforms. Furthermore, core-satellite nanostructures are particularly important because they can exhibit Fano resonances, a phenomenon thatwhich exhibit a greater sensitivity to changes in local the refractive index change than do the spectral features of simply coupled nanostructures [1]. However, the fabrication of an inexpensive device with highly ordered metallic nanostructures at a large scale still remains challenging [2]. In this context, bottom-up approaches based on self-assembly remain attractive, despite their tendency to present a greater heterogeneity than top-down approaches [3].

In the present work, the Langmuir-Blodgett (L-B) technique, a bottom-up approach, is used for the preparation of composite monomolecular films made of metallic NPs and block copolymers (Fig. 1). The main objective of the present study is to correlate the structure of individual nanostructures with their plasmonic properties. First, based on the self-assembly method already developed in our laboratory [4], various generations of core-satellite nanostructures are developed with different population of NPs such as palladium nanocubes and, gold and silver nanospheres. Then, the self-assembly method is optimized to separate nanostructures sufficiently to allow for optical characterization within the diffraction limit. Subsequently, optical properties and structures are analysed by dark field microscopy and scanning electron microscopy, respectively. Through this project, we aim to identify the optimal arrangement of NPs for maximum plasmonic sensitivity to local environment for the eventual production of low-cost chemical sensors.

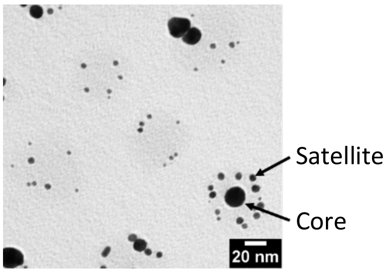

Fig. 1 Transmission electron microscopy image of a composite L-B film illustrating the core-satellite structure.

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DNA Brush-Directed Aligning Self-Assembly of Gold Nanorods as Photonic Nanomaterials

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Self-assembled alignment control of anisotropic nanoparticles such as gold nanorods (GNRs) is an important topic for both fundamental and practical researches. We show that GNRs can be aligned in a single direction by adsorbing positively charged GNRs onto a double-strand DNA-grafted substrate [1] through electrostatic interaction (Fig.1). The ordered structure can be optimized by controlling the density of the positive charges on the surface of the GNRs. We found, in agreement with the results of theoretical simulation, that the resultant structure exhibits plasmonic properties that are dependent on the GNR orientation relative to the direction of an oscillating electric field (Fig.2) [2]. Our approach provides new insights into the polymer-assisted self-assembly of rod-shaped nanoparticles utilizing electrostatic interactions. We will also introduce anisotropic assembly of nanorods focusing on differences in curvature for the fabrication of hierarchical structures [3].

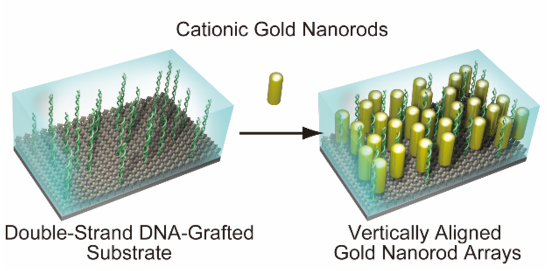

Fig. 1 Scheme of vertical assembly of GNRs using a DNA brush

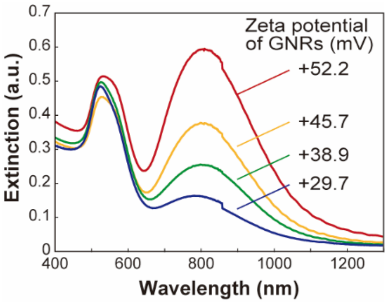

Fig. 2 Extinction spectra of GNRs immobilized on DNA brushes

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O-14

Beyond freezing: low temperature lipidic cubic phase as biomimetic, nanoconfining matrix

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Lipidic cubic phases (LCPs) are used in areas ranging from membrane biology to drug delivery. Because some membrane proteins are notoriously unstable at room temperature, and available LCPs undergo transformation to lamellar phases at low temperatures, the development of stable low-temperature LCPs for biophysical studies of membrane proteins is called for. A family of synthetic lipids with designed cyclopropyl modifications in the hydrophobic chains was synthesised in order to study the relationship between lipid molecular structure and mesophase behaviour. These lipids show a unique liquid-crystalline behaviour at low temperatures, enabling the use of LCP crystallisation in conditions never explored before.[1]

Moreover, the small size of the water channels of one of the LCPs formed by a synthesised lipid can prevent low-temperature crystallization of water, thus creating a state of amorphous water maintenance down to 10 K. The study of water and lipid behaviour unveil a complex lipid/water phase diagram, in which bicontinuous cubic and lamellar liquid crystalline phases containing sub-zero liquid or glassy water, or ice emerge as a competition between the two components, each pushing towards its thermodynamically favoured state.[2]

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O-15

Probing interfacial inter-particle interactions at the air/water interface

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The assembly of nanoparticles (NPs) into monolayers at liquid interfaces has been at the focus of intense experimental and theoretical research in view of potential applications based on the magnetic, electric and optical properties of NPs [1]. However, a full comprehension of the interfacial inter-particle interactions driving the assembly upon NP adsorption is still missing, despite being essential for a fine tailoring of the monolayer structure and properties.

The aim of the present work is to extract quantitative information about interfacial inter-particle interactions by characterizing in-situ NP monolayers at the air/water interface during the application of external mechanical stimuli. In particular, we employed 19 nm negatively charged silica NPs which, when mixed with cetyl trimethylammonium bromide (CTAB), are able to form homogeneous monolayers characterized by a well-defined inter-particle distance depending on the NP/CTAB ratio [2]. After a systematic structural characterization of NP monolayers as a function of the CTAB concentration, carried out via synchrotron radiation grazing incidence small angle x-ray scattering (GISAXS), we will show that inter-particle distance can be significantly reduced by compressing NP monolayers in a Langmuir trough (Figure 1). In particular, both starting and collapse inter-particle distances are significantly influenced by CTAB concentration, suggesting that adsorbed surfactant molecules play a key role in the overall inter-particle interactions. Finally, by dividing the surface work measured during compression in the Langmuir trough by the distance variation determined by GISAXS, we extracted quantitative information on the interfacial inter-particle repulsions, being in the range of 10^2 pN, as well as on their dependence from inter-particle distance.

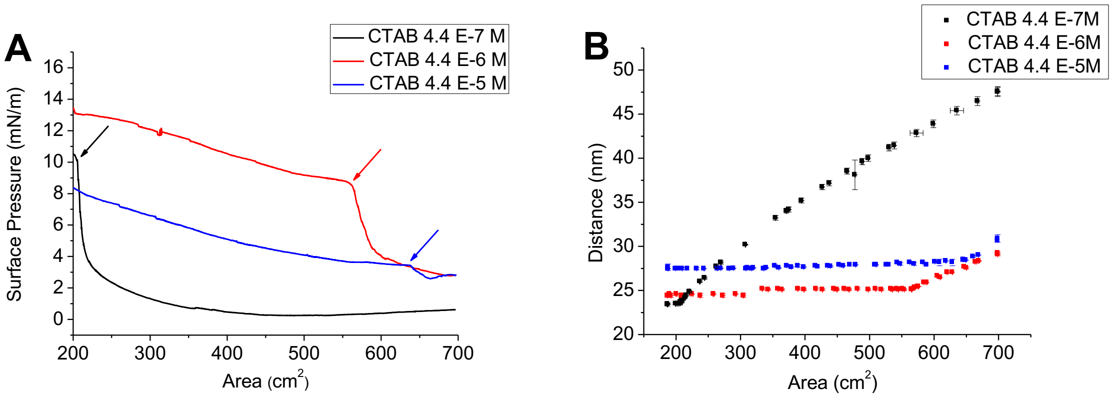

Fig. 1: Surface pressure vs Area compression isotherm of 0.1% wt silica NPs at different CTAB bulk concentration (A), the corresponding monolayer collapse is indicated by arrows. During compression, inter-particle distance determined by GISAXS progressively decreases (B) up to the monolayer collapse, after which inter-particle distance is constant.

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Tuning amphiphilic block copolymer assemblies and aggregate structures: a simulation study

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Amphiphilic block copolymers form in aqueous solution various ordered assemblies and aggregates that can be used in, e.g. drug delivery, solubilization and functional coatings. Block copolymers are particularly interesting due to their high versatility in properties and simple preparation methods which enable large variety in the resulting assemblies, their characteristics, and, consequently, uses and usability. An even wider range of properties for the aggregates is achieved by mixing block copolymers with homopolymers. While general amphiphilic self-assembly in aqueous solutions, in particular polymer micellization, is relatively well-understood, open fundamental questions remain related to interplay of polymer characteristics in polymer mixtures and the usage of the homopolymer additives to tune assembly characteristics.

Here, we use mesoscale molecular modelling, in particular dissipative particle dynamics (DPD) simulations, to examine the assembly of amphiphilic hydrophilic-hydrophobic block copolymers with hydrophobic and hydrophilic homopolymers as solution additives. Prior comparable works have dominantly concentrated on pure block copolymer systems. The amphiphilic block copolymers tend to form polymer micelles: we map the aggregate structure dependency on the relative composition of the block copolymer, concentration and the effect of free hydrophobic and hydrophilic homopolymers. We find that simple changes in the polymer chain length, system composition or concentration can be used to drive the aggregates from multicore micelles formed from monodisperse, highly spherical sub-micelles to fuzzy, interdigitating polydisperse aggregates or to single core, spherical micelles, and finally to phase separation. We generalize the mesoscale modelling findings to realistic polymer systems and connect the findings with experimental data from literature. Finally, we propose guidelines for controlling polymer particle morphology and structure e.g. for drug delivery, tissue engineering, coating and sensor device applications.

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Self-assembled optically resonant nanostructured surfaces

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The control of light propagation and refraction in thin layers of materials is crucial for the development of miniaturized optical and optoelectronic devices for high-resolution imaging and lithography, enhanced photovoltaic and Raman substrates, or optical communication [1,2]. Such control can be obtained by nanostructured metal or dielectric thin films, due to their optical resonances. This has encouraged, in the recent years, active research efforts towards the fabrication of nanostructured materials and surfaces. For such nanostructures, fabrication methodologies based on colloidal chemistry, self- and directed-assembly and soft matter physics are promising [3]. This presentation will show how we use self-assembling block copolymers for the "bottom-up" fabrication of original plasmonic and dielectric nanostructures in bulk and at surfaces [3-5]. The occurrence of specific nanostructure-related optical properties such as high refractive index, hyperbolic propagation or optical magnetism will be discussed.

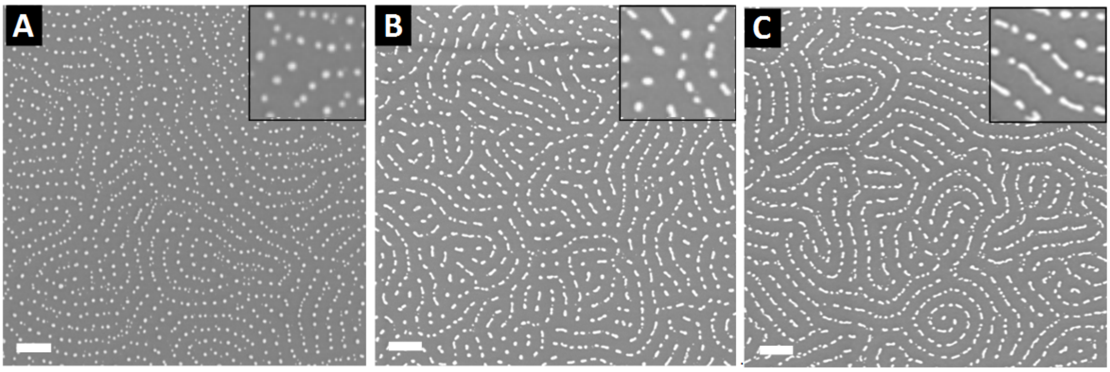

Fig. 1: SEM images of discreet gold nanoparticles arrays formed on a silicon substrate using a PS-b-P2VP block copolymer template by immersion in a 1 wt% aqueous gold precursor solution for different times and a subsequent plasma treatment. (A) 1 h, (B) 48 h and (C) 120 h.

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O-17

Snowman-like anisotropic polystyrene particles prepared by combining UV light and solvent treatments

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Colloidal particles have been extensively used as building blocks for various functional materials such as sensors, photonic crystals, optoelectronic devices, surface enhanced Raman scattering, and microfluidic devices. Recently, anisotropic polymer particles have received much attention because of their unique properties and morphologies. However, only a few ways to prepare anisotropic polymer particles have been reported and most proposed techniques are complicated. In this work, we propose a simple and versatile process for preparing convex domains on spherical polymer particles and show that the combination of UV irradiation and soaking in an organic solvent gives rise to snowman-like particles and a C-shaped convex on the particle surface (Fig. 1).

Spherical polystyrene (PS) particles were spread on water and UV light was irradiated onto the particle monolayer using an optical fiber. After UV irradiation, the particles were transferred on glass substrates and then were soaked with an organic solvent. Here, to prepare C-shaped convex, UV light was irradiated at an inclination angle from the normal under rotating the particle monolayer (Fig.1B). Morphology of the resultant particles was evaluated by scanning electron microscope (SEM).

PS particles held their spherical shape after UV irradiation, but soaking in an organic solvent caused the formation of a hemispherical convex on the top of the particle surface, i.e., snowman-like particles, as shown in SEM images (Fig. 1A). The hemispherical convex increased with increasing the UV irradiation time. The estimated mechanism for producing the hemispherical convex on the top surface is as follows. The solvent causes a swelling of the top region damaged considerably by UV light. The deformed outside is fixed when the solvent evaporates from the convex region, whereas the swollen inside is shrunk due to a slow evaporation, which may cause the formation of a hole inside the particle. The presence of the hole was confirmed by TEM observation.

We also demonstrate that a C-shaped convex on PS particles can be easily prepared by controlling the incident angle of UV light and the rotation speed of PS particle monolayer (Fig. 1B). Interestingly, PS particles with C-shaped convex showed a circular dichroism (CD) property. Further, C-shaped convex samples prepared by changing the rotation direction of the PS particle showed completely opposite CD profiles, and the CD response considerably enhanced by metal deposition (Fig. 1C).

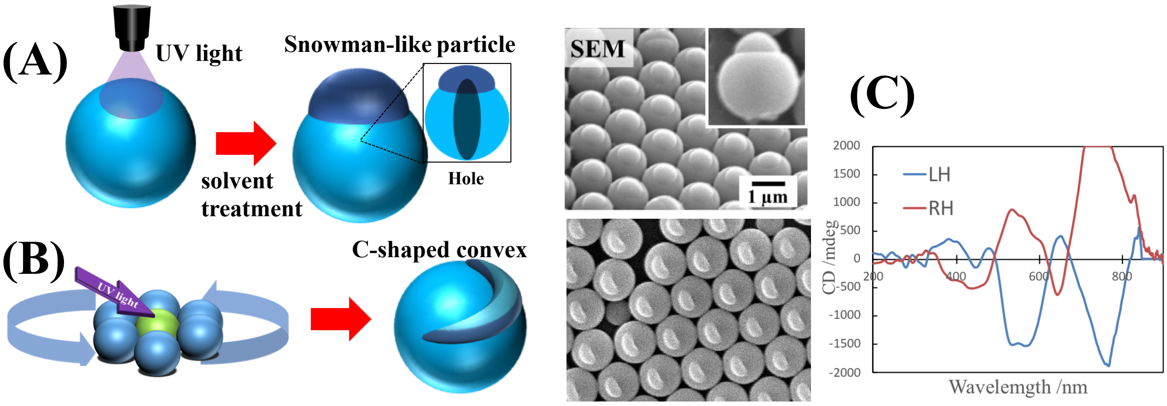

Fig. 1: Schematic illustrations of the preparation method and SEM images of (A) snowman-like particles and (B) C-shaped convex particles. (C) CD spectra of C-shaped convex particles prepared by right- (R) and left-handed (L) rotation directions.

O-18

Kinetics of Photoluminescence Decay of Colloidal Quantum Dots: the Role of the Surface

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Since the first works reporting size-dependent absorption and emission in nanometer sized colloidal semiconductor crystals (colloidal quantum dots, QDs) [1,2], these materials have been intensively investigated theoretical and experimentally due to fundamental scientific interest and potential applications in imaging and sensing, photovoltaics, lasing, photocatalysis, and optoelectronics [3-5]. Interfaces are crucial factors in the majority of these applications, since the chemical and physical properties of QDs, like those of any other colloidal particles, are naturally influenced by the nature of their surface, surrounding environment, and the interactions between the two.

In particular, interfaces condition the size-dependent optical properties of these materials. However, the role played by the interfaces associated with the QD inorganic cores on the kinetics of photoluminescence (PL) decay of these nanocrystals is not fully understood even for the most extensively investigated II-VI QDs. The non-exponential PL decays typically observed are commonly approximated using a sum of exponential functions, but this approach has physical meaning only in some cases [6]. This has led us to search for models that (i) allow to gain insight about the physics of the processes taking place at the interface(s) between the inorganic QD cores and the surrounding materials from the analysis of the PL decays and (ii) are practical to use at the same time [7-9].

It has long been recognized that the surface of QDs is a hotbed of charge carrier traps [5] that affect PL dynamics, because of uncoordinated atoms at the nanocrystal surface, vacancies, adsorbed species, interactions with ligand molecules, etc. In this work, we present a new function for the analysis of the RT PL decay of QDs that accounts for trapping and detrapping of photogenerated charge carriers with physically meaningful parameters (time constant, trapping and detrapping rate constants, and average number of traps per QD) [9] and show how its use for describing the PL decay of CdSe/ZnS QDs in drop-cast films provides valuable information concerning the relevant interfaces, and therefore concerning the nature of the trap states, involved in the recombination of photogenerated charges. This function should be applicable to the analysis of the PL decay of QDs of a variety of compositions, as well as materials beyond inorganic semiconductors.

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ACKNOWLEDGMENTS: This work was partially supported by the Ministry of Education and Science of the Russian Federation (grant no. 14.Y26.31.0028).

Ligand-free synthesis of gold nanoparticles incorporated within oriented cylindrical block copolymer films

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Mixing gold nanoparticles with nanostructured block copolymer films is a self-assembled way of building potential optical metamaterials. We report here the inclusion of gold nanoparticles (AuNPs) without pre-functionalization step in oriented films of block copolymer poly(styrene)-b-poly(vinylpyridine) (PS-b-PVP) on a substrate. After deposition with an appropriate solvent, PS-b-P4VP and PS-b-P2VP are cast as films presenting either perpendicular and parallel cylinders. By including gold salt in these solutions and operating subsequent sonication, AuNPs (with a diameter of 2 nm) are synthetized and found located inside the cylinders of PVP (Fig.1) after deposition of the film by spin-coating.[1] Increasing the initial amount of gold precursors allows the formation of bigger AuPs (d=4 nm). The seeded-growth of the pre-formed AuNPs was also achieved in order to get bigger AuNPs (d=8 nm) with plasmon resonance properties. This method was found more efficient in order to get bigger nanoparticles with a low quantity of gold precursor. The presence of AuNPs in the PVP domains disturbs the organization of the parallel cylinders, while it swells the PVP domains in the case of the perpendicular cylinders without changing their orientation. The formation of AuNPs inside a copolymer was also performed by radiolysis, through the irradiation of the copolymer solution and the copolymer film, both containing the gold salt, and led to similar results. The presence of plasmonic AuNPs of small diameter (~3-4 nm) was evidenced in both cases. GISAXS measurements are presented to characterize and compare the films order before and after gold inclusion, and help proving that cylinder are perpendicular to the substrate through the entire thickness. If time allows, first optical characterizations of the polymer-gold films will be presented.

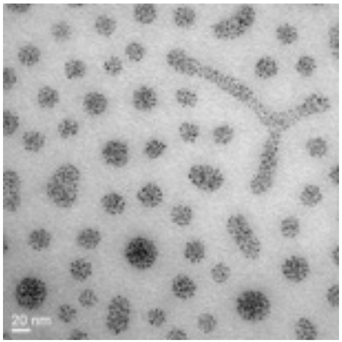

Fig. 1 Top view by TEM of a cylindrical phase of polymer where gold nanoparticles are exclusively included in cylinders

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O-20

Active chiral plasmonics based on strain-induced geometrical reconfiguration

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In contrast to their natural counterpart, chiral plasmonic nanostructures allow for precise tailoring of their outstanding chiroptical response. This opens up applications in sensitive detection of chiral molecules, asymmetric synthesis and polarization engineering.

Despite excellent control over optical properties by design, as demonstrated in literature, in-situ switchable chiral systems remain elusive. In particular, geometrical reconfiguration of nanostructures seemed to be only possible in solution. Based on our experience in directed self-assembly of colloidal building blocks into well-defined plasmonic arrays[1] and mechanical strain-modified inter-particle coupling[2], we present a 3D solid-state system that enables a 100 nm spectral shift of circular dichroism (CD) response upon compression (Fig. 1).

In a scalable, e-beam free approach, gold nanospheres are assembled inside nanochannels. Simple, macroscopic stacking of two substrates produces strongly coupled, crossed particle lines (Fig. 1 A) whose CD of 10 deg can easily compete with structures produced using e-beam lithography. Compression normal to the interface induces nanoscopic rearrangement of particles inside the chains to provide a pronounced blue-shift, while maintaining a CD magnitude of several degrees.

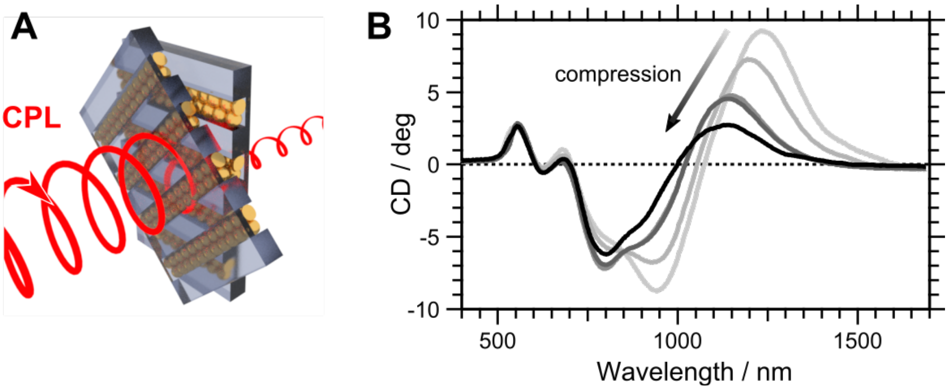

Fig. 1: (A) Schematic representation of crossed particle lines that selectively absorb circularly polarized light (CPL). (B) CD spectra depicting the blue-shift of the near-infrared mode upon normal compression.

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O-21

Biosensors fabricated by layer by layer for the electrochemical detection of catechol

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Layer by layer (LbL) assemblies have received an increasing attention in the field of sensors and biosensors because they give the possibility to fabricate nanostructured layered devices . In addition, this technique is effective to develop sensors containing different sensitive materials using the electrostatic attraction between molecules with opposite charges [1,2].

Herein a biosensor for the detection of catechol has been developed. The LbL technique was used to deposit an underlying electron mediator film layer consisting in a combination of three different materials with complementary activity: a negatively charged sulfonated copper phthalocyanine (CuPc^{SO3}) -a well known electron mediator-, a positively charged ionic liquid(IL) -that increases the conductivity of the films- and a positively charged polysaccharide, the chitosan (CHI) -an effective element to fix enzymes-. Two types of combinations of electroactive materials were tested: The first one (CHI-CuPc^{SO3-}-IL) consisted on trilayers by immersing the ITO in three solutions: 1) 5 min in CHI; 2) 5 min in CuPc^{SO3} and 3) 5 min in IL. The second one (CHI+IL-CuPc^{SO3-}) consisted on bilayers obtained in a two step process: 1) 5 min in CHI+IL 1:1 mixture and 2) 5 min CuPc^{SO3-}. Further, biosensors were fabricated by immobilizing the enzyme Laccase (LAC) on the top of the electron mediator layer. The structure of the sensors characterized by UV-Vis, FTIR and AFM. The responses towards catechol were tested by cyclic voltammetry. Voltammograms exhibited stable redox peaks (anodic wave at ca. 0.95 V and cathodic wave at ca. -0.2 V) with peak currents higher than those obtained when the enzyme was directly deposited on ITO glass, confirming the excellent electrocatalytic activity of the layers. The results were independent of the structure (bilayers or trilayers). The sensitivity and the limits of detection (LOD) were calculated from the calibration curves obtained by chronamperometry at increasing concentration of catechol. The biosensors reached LOD of $10\cdot10^{-12}$M which was several order of magnitude lower than the LOD obtained in the absence of the enzyme ($6\cdot10^{-8}$M) and with excellent reproducibility (CV 4%).

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Financial support of MINECO-FEDER (AGL2015-67482-R) and Junta de Castilla y León FEDER (VA-011U16) are gratefully acknowledged.

O-22

A low-cost laser-based nano-3D-printer for rapid surface patterning, microarray fabrication and high-throughput chemical synthesis in polymer

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We present a laser-based printing setup for less than 200 €, which allows for the defined patterning of planar surfaces with polymer nanolayers [1]. These nanolayer patterns can serve as “solid solvent” spots, which embed different chemicals, chemical building blocks, materials, or precursors. For instance, this enables to quickly pattern a surface with different molecules or materials, mixing them directly on the surfaces for high-throughput chemical synthesis to generate and screen microarray libraries [2, 3]. In contrast to ink-jet or contact printing, this approach does not require pre-mixing of inks, which enables *in-situ* combinatorial mixing and reactions.

Alternatively, the nanolayer patterns can serve as cheap and rapid sacrificial masks for coating or etching techniques [4]. This allows for easy microfabrication of *e.g.* flexible electronics or biological and chemical sensors.

Finally, a very low budget spin coating device is presented, which can be utilized for precise nano- [5] to micrometer [6] thin coatings, required for the presented laser transfer process.

Our system provides sufficient accuracy to generate patterns and arrays down to a spot-to-spot distance of 100 µm and offers a more flexible alternative to expensive spotting robot technology.

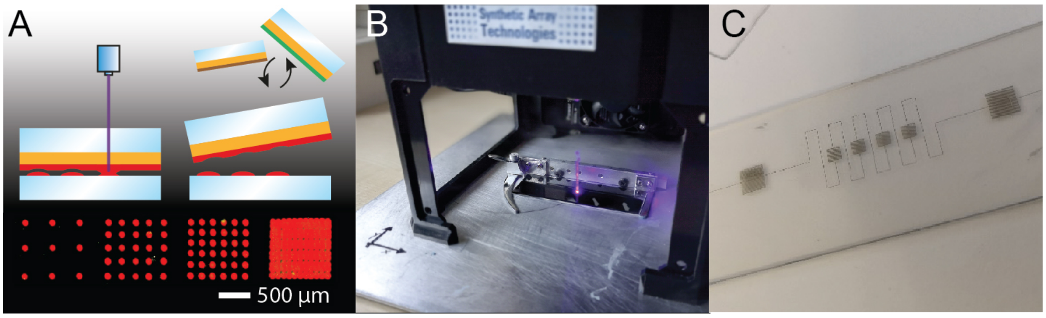

Fig. 1: General procedure of microarray generation with laser-induced forward transfer - LIFT (A), photograph of the low-cost LIFT system during a laser transfer (B), and photograph of a gold pattern after sacrificial mask coating (C).

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O-23

Elaboration of nanostructured solar cells based on hybrid perovskite: Influence of deposition process and composition

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In just a few years, solar cells based on halogenated hybrid perovskite have had a strong impact on photovoltaic research by becoming a credible player against the technologies of the field of first and second generation (mono / polycrystalline, silicone, CIGS, CdTE) with a photoconversion yield of 23.3% single-junction and up to 27.3% in a tandem configuration (Si/Perovskite) [1, 2].
The intrinsic quality of the perovskite thin film and its composition are fundamental criteria for obtaining stable and high performance devices. The study and optimization of the deposition process of the perovskite thin film is therefore a key step in the development of an efficient cell.

Many experimental parameters influence the growth of perovskite. One of the most critical step is the intermediate solvent treatment (anti-solvent) which allows a selective washing of the substrate by removing the main dissolving solvent (DMF) before evaporation [3, 4]. The control of this step substantially increases the reproducibility; this is why we have focused on the temporality of this treatment and the injection rate without the substrate.

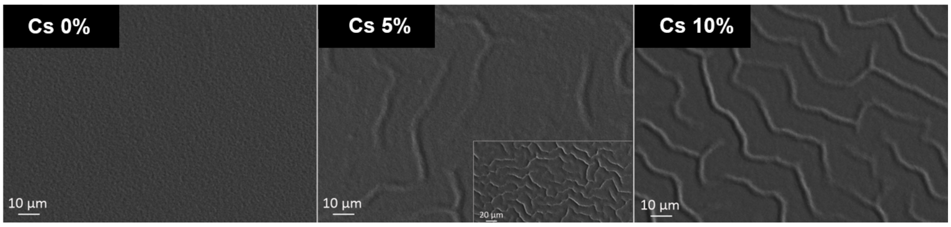
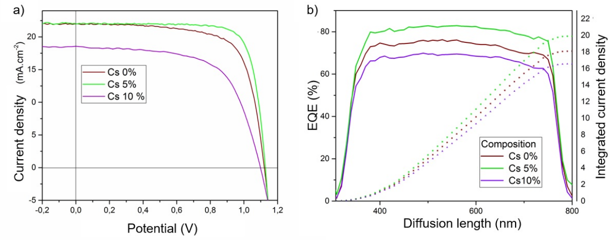


Fig. 1: Influence of the concentration of caesium on the absorber morphology – SEM surface

Subsequently, we have focused on the influence of the chemical composition on the stability, morphology, and photoconversion performance of the perovskite absorber by altering the caesium concentration in a triple cation double anion composition (MA-FA-Cs) Pb (I-Br)$_3$.



[Cs]	Efficiency (%)
0 %	17.58
5 %	19.57
10 %	12.82

Fig. 2: Influence of caesium on device performance: a) I-V curves b) EQE

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K-4

How polymers affect protein adsorption

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Nanoparticles and liposomes are used as versatile drug nanocarriers. Upon injection into the bloodstream a protein layer will immediately coat the nanocarrier surface forming the so-called protein corona. This alteration of the nanocarrier surface chemistry can induce changes of the drug carrier properties and interfere with the carrier's targeting mechanism. In order to prevent this non-specific protein adsorption, drug nanocarriers are often coated with protein repelling polymers. By far the most widely used protein repelling polymer is poly(ethylene glycol) (PEG), but new and more biodegradable non-fouling polymers such as polyphosphoesters (PPEs) have been recently proposed. It has also been shown that the adsorption of certain proteins can be beneficial and promote specific cellular uptake.

A deeper understanding of protein adsorption to surfaces modified with non-fouling polymers is therefore desirable to control and guide protein adsorption and orientation. We use monolayers at the air/water interface as model systems for differently functionalized surfaces. We study polymer/water and the protein/polymer interactions by a combination of complimentary surface science techniques. Our results on PEG and PPEs suggest that, for certain proteins, PEG and members of the PPEs family not only influence the amount of adsorbed protein but also the ordering at the surface [1-3] while for other new non-fouling polymers the interactions seem altogether more complex [2]. These findings will help in designing new polymers for biomedical applications.

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Biomodified nanoplatforms for cancer targeting

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Nowadays, most scientists are looking for early diagnosis and minimization of the side effects of drugs that treat one disease but cause complications or even other diseases. Properties of graphene are extremely sensitive to the environment, which determined using graphene for sensor applications [1]. Biosensors represent promising analytical tools applicable in areas such as clinical diagnosis, food industry, environmental monitoring and in other fields, where rapid and reliable analyses are needed. Recent technological progress and new opportunities in biomedical applications of graphene-based sensors open new possibilities for the invention of new cancer detection tools.

On the base of the previous experience with carbon nanoparticles and their surface modification, graphene oxide (GO) was chosen for the development of a new type of sensor. GO edges and surface are covalently decorated with oxygen-containing functional groups, resulting in sp2/sp3 hybridization and different oxidation degree. GO was prepared by modified Hummer and Offeman reaction from exfoliated graphite. Basic characterization of GO, in terms of the degree of oxidation, exfoliation and nanoparticle size was determined by physical and chemical analyses, as X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and atomic force microscopy (AFM). Diagnostics of oncological diseases stays at the forefront of the current medical research. A large number of oncological markers is available for the early diagnostics. The CA IX (Carbonic Anhydrase IX) is a cell surface, a hypoxia-inducible enzyme that is expressed in aggressive tumours, hence, it can be used as a tumour biomarker [2]. Herein we propose a nanoscale graphene oxide (GO) platform functionalization with the monoclonal antibody specific for the CA IX marker. The CA IX antibody is linked via a biotin-avidin complex to GO nanoplatform. Cytometry and immunofluorescence were done to examine prepared GO-based cancer biosensor with antibodies. The immerse objective was used to confirm the specificity of GO biosensor to cancer cells with CA IX marker by confocal Raman microscopy. In addition, the other 2D materials, as the alternatives, could be used for the creating of nanoplatform sensors.

A single layer of functionalized MoS_2 layer exhibit extraordinary high sensitivity for detection (down to 10 fg/ml) of cancer-related antigens. The benefit of MoS_2 is the strong Raman signal and photoluminescence in red part (above 600 nm) of the visible spectrum. These properties determined MoS_2 as possible biosensors for targeted detection of cancer cells as was proved by our study. Early diagnosis using modified 2D nanoplatforms, coupled with targeted drug delivery, can greatly help to treat the disease without side effects.

Acknowledgements
This work was supported by the Slovak Research and Development Agency under the contracts No. APVV-14-0120 and No. APVV-15-0641.

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Phospholipid layers as simple models of cell membranes to study the interactions with anticancer and cholesterol-lowering drugs.

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Phospholipid monolayers prepared by Langmuir technique can be successfully employed as simple models of one leaflet of cell membranes and are commonly used in the studies of the interactions of drugs, toxins and other biologically important species [1]. Although very simplified, this system has already proved to be useful to investigate the interactions of most commonly used anticancer anthracycline antibiotic: doxorubicin (DOx) and daunorubicin (DNR) [2,3]. However, we also show that other anthracyclines such as idarubicin (IDA) have increased effect on model membranes, which is ascribed to increased lipophilic properties of IDA. It allows the drug to penetrate the model membrane more deeply compared to DNR or DOx due to the increased hydrophobic interactions, which in this case strengthen the electrostatic interactions with negatively charged lipids observed for all anthracyclines. Additionally, the increased interactions of idarubicin with model membranes containing elevated levels of cholesterol has been observed. This conclusion is important for explaining the exact mechanisms of interactions with cell membranes, since some cancerous cell membranes exhibit abnormally high cholesterol levels [4].

We have also used Langmuir monolayers to investigate the influence of selected water-soluble statins (pravastatin, fluvastatin and cerivastatin), which are used as cholesterol-lowering medicines. In this case the model membrane composition (DMPC:DMPS 9:1) was adjusted to mimic the composition of intestinal cell membranes, where the absorption of those drugs takes place. Statins incorporate into the phospholipid monolayers, which is manifested by the shift of the isotherms into higher areas per molecule and decrease in the compression modulus values. Interestingly, the interactions again depend on the lipophilicity of the drugs. Therefore, the strongest effect was observed for cerivastatin, which is the most lipophilic of all the investigated statins. Additionally, the reorientation of the membrane components upon the incorporation of the drugs were followed by surface potential measurements, while changes in the morphology of the layers were visualized by Brewster angle microscopy. In the next step, the phospholipid layers were transferred onto gold electrodes and electrochemical PMIRRAS experiments were performed to obtain additional information on the changes in the orientation and conformation of lipid molecules in the presence of the drug in the supported bilayers. It has been shown that cerivastatin changes the hydration of the carbonyl group in the glycerol ester part of lipid molecules and introduces changes in the tilt angle of the choline moiety of DMPC molecules. The latter effect may be ascribed to the electrostatic interactions between positively charged choline group and negatively charged drug.

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O-26

Effect of perifosine on model lipid rafts with different cholesterol content

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Cancer diseases are one of the main causes of death, right after cardiovascular diseases. Their number is steadily growing despite an extensive development of new drugs and therapies. Synthetic antitumor lipids (ATLs) are a promising group of compounds in cancer chemotherapy.[1] The can divided in two main classes: alkylphospholipids (APLs) and alkylphosphocholines (APCs). They are structurally similar to a naturally occurring lysophosphatidylcholine and possess distinct antiproliferative properties in tumor cells.[2] APLs and APCs do not interfere with the DNA but incorporate directly into cell membranes, where they accumulate and disturb lipid metabolism and lipid-dependent signalling pathways.

Perifosine (octadecyl-(1,1-dimethylpiperidinio-4-yl)-phosphate) is one of alkylphospholipids analog with promising results against a variety of cancers. The studies showed that perifosine accumulates in specific domains in cell membranes called lipid rafts.[3] These membrane micro domains enriched in cholesterol and sphingolipids are the platform of several signalling pathways, including the Akt pathway, one of the most frequently hyperactivated signaling pathways in human cancers and, therefore, a very important target in a global fight against this disease.

The aim of the present study was to assess the effects of perifosine on model lipid membranes reflecting the lipid composition of natural lipid rafts. Model lipid rafts were composed of 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC), sphingomyelin (SM) and cholesterol (Choli). Firstly, the effect of cholesterol on perifosine action on model lipid raft was studied. For this purpose, we prepared model lipid rafts with 0 – 50 % cholesterol content. We have also verified the effect of gangliosides on the perifosine – lipid membrane interactions. Results of Langmuir studies show that perifosine incorporate in model lipid membranes at the air-water interface and the effect of perifosine increases with increasing cholesterol content. The changes in the morphology of the lipid layer in the presence of perifosine were also monitored by Brewster Angle Microscopy. In the next step, solid-supported lipid bilayers were used to obtained more detailed information on the perifosine-lipid interactions. We employed the combination of Langmuir-Blodgett and Langmuir-Schaefer techniques to immobilized model lipid membranes on solid support. Quartz crystal microbalance with dissipation monitoring allowed us to observe the kinetics of the perifosine-membrane interactions and to verify the mechanism of perifosine-induced perturbations within the lipid membrane.

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Reversible Langmuir monolayer-to-crystalline multilayer transition at the air-water interface

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Meta-substituted benzoquinones exhibit an unusual 6π + 6π electron zwitterionic structure [1] with the ability to form strong charge-assisted hydrogen bonding. Their self-assembly on HOPG has been previously shown to be driven by the formation of extended H-bonding networks [2,3]. In this work, we have investigated how such strong intermolecular interactions govern their structural organization and phase behaviour at the air-water interface [4].

Isotherms of Langmuir monolayers of a meta-substituted dioctadecylaminobenzoquinones (see Figure 1) show a first-order phase transition which is determined to correspond to a tilted condensed-to-untilted condensed phase transition. However, a combination of Brewster angle-microscopy, atomic force microscopy and grazing incidence X-ray diffraction (GIXD) reveals multiple co-existing phases over the entire isotherm. Moreover, above the phase transition pressure, a monolayer-to-multilayer transition is observed wherein the multilayer is formation is driven by the formation of crystalline headgroups. Despite the heterogeneity of the films and the crystallinity of the multilayers, all of the phase transitions are highly reversible over multiple cycles. This work will be discussed in the context of interplay between van der Waals (chain length), π-stacking and charge assisted hydrogen bonding (headgroup) interactions in molecular self-assembly and thin film organization.

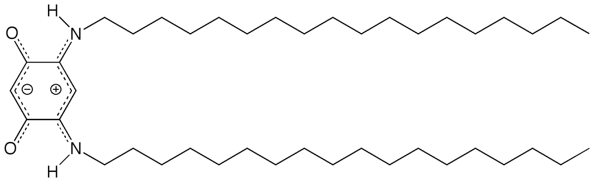

Fig. 1: Chemical structure of meta-dioctadecylaminobenzoquinone

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O-28

Unusual redox isomerism of bis-phthalocyaninates of lanthanides in monolayers at air/water and air/solid interfaces

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Exploitation of the phenomenon of redox isomerization can be a very perspective method for information storage on molecular level and for molecular switching devices. However, being extremely rare and affected by a multitude of factors, it remains almost unstudied in nanoscale and planar supramolecular systems.

This work is devoted to firstly revealed unusual process of orientation-induced and surface pressure controlled redox isomerization in bis-phthalocyaninates of lanthanides $(PcR_4)_2Ln$ (Pc= phthalocyanine, R=15-crown-5 or butoxyl) at air/water and air/solid interfaces. The reversible transformation Ce^{3+}/Ce^{4+} in such complexes was discovered earlier [1]. These transformations were confirmed by UV-Vis and X-Ray photoelectron spectroscopy. Unexpectedly, the study of the behaviour of a monolayer of bis-phthalocyaninates of Yb, Sm, and Eu, which can be found in two valence states: II and III, showed similar transformations. It was established that that reversible transformations $(PcR_4)^{-}2Ln^{2+} \leftrightarrow (PcR_4)^{2-}Ln^{3+}(PcR_4)^{-}$ can be performed upon cyclical compression-expansion of the monolayer on deionized water surface. The driving role of surface forces in these transformations was revealed. The existence of two redox-isomeric forms of europium bisphthalocyaninate was proved by XANES spectra of Eu cations in LB films transferred at different conditions. These spectra were recorded using synchrotron radiation at DESY in the scope of the project I-20180528. The presence of Eu^{2+} in LB films transferred at low surface pressure and its transformation to Eu^{3+} cations upon synchrotron source X-ray irradiation were testified. These results give us the direct confirmation of the redox-isomeric process that occurs upon spreading of the Eu phthalocyaninate solution onto air/water interface, and confirms that this redox-isomeric state is maintained upon transfer of the monolayer onto solid substrate.

The described redox isomerization drastically affects the electrochemical behaviour of the complexes, which is reflected in the form of an additional third peak on CVA in the range of potentials from -1 to +1 V. Correlations between reduction and oxidation peak positions of Pc2Ln and the ionic radius of the metal centre were demonstrated. It is shown that replacement of crown-ether substituents of phthalocyanine ring by more electron-donor butoxyl groups leads to stabilization of divalent state of Eu and Yb cations in bis-phthalocyaninates in monolayers and especially in LB films.

The present work was supported by RFBR grant no. 18-33-20187

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LB single component monolayers with stable 3D aggregates. Possible biosensor applications. Validity of Gibbs' phase coexistence rule at nanoscale.

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Single component monolayers from Diplamitoyl Phosphatidyl Ethanolamine head labelled with the fluorescent chromophore NitroBenzoxaDiazole (DPPE-NBD) were investigated at the air-water interface as Langmuir films and deposited on substrates as Langmuir-Blodgett (LB) films. When monolayers were deposited at surface pressures below the equilibrium spreading pressure (ESP) of 19.6 mN/m multilayer cylinders of mainly bilayer height and diameters in the 50 to 300 nm range were observed with Atomic Force Microscopy (AFM, Fig.1). These cylinders were stable for at least 2 months.

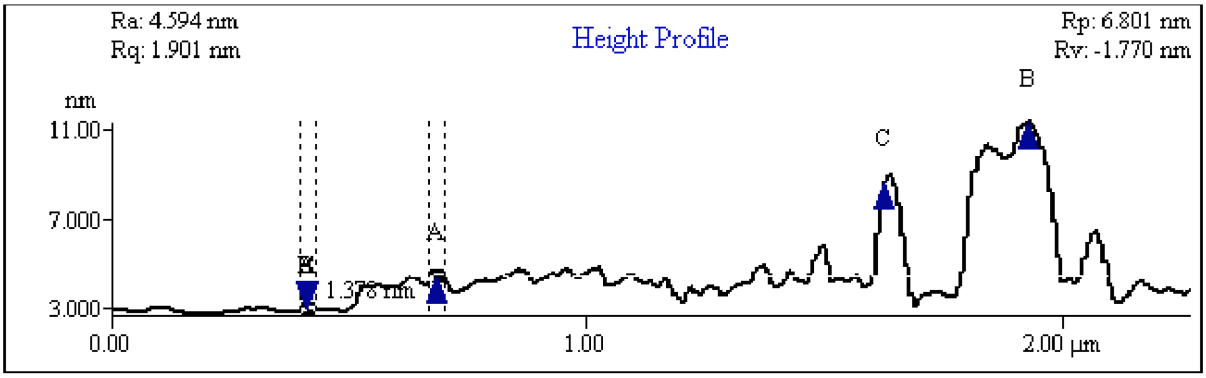

Fig. 1: Cross-section of a part of an AFM image of an LB monolayer from DPPE-NBD deposited in the phase coexistence region at 11 mN/m and 23° C from pure water subphase. Clearly the height difference of approximately 1.4 nm between the liquid-expanded and liquid-condensed phase can be seen. Also bilayer height or higher aggregates can be seen (indicated with arrows B and C) on the picture.

This well-developed 3D structure combined with only a monolayer thickness can produce very fast chemical sensors with enhanced sensitivity. The DPPE-NBD molecule behaves similarly as the DPPE phospholipid molecule and is an excellent bio compatible matrix for possible biosensor applications. NBD chromophore has high sensitivity to its surrounding. This combined with the discovered by us effects of fluorescence self-quenching in Langmuir films and its recovery on interaction with e.g. heavy metal ions [1, 2] can further increase sensitivity and/or selectivity of future biosensors.

Gibbs' phase coexistence rule for a single component system in thermodynamic equilibrium (below ESP) does not allow the coexistence of more than 2 phases. In our experiments we observe liquid-expanded, liquid-condensed phases and these 3D aggregates, which can be regarded as a 3rd phase. So this experiment might well show that this rule while true for thermodynamic systems composed of very large number of molecules is not valid at nanoscale for small (e.g. 1000) number of molecules.

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O-30

Langmuir monolayers as tool to predict the degradation of architectured macromolecules

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The next generation of polymer materials for medical devices will have tailored molecular architectures to encorporate multiple fuctionalities like degradability, shape memory capability, bio-instructivity and controlled drug release. The interplay of molecular degradation, water and fragment diffusion with the added complexity of the processed material's microstructure neccessitates a multi scale *in silico* approach to predict the device behavior during degradation *in vivo*. The success of such an approach depends on the availability of input parameters and models for the molecular degradation kinetics of the architectured molecules.

The Langmuir monolayer degradation technique is a powerful technique for the investigation of different aspects of the molecular degradation of amphiphilic macromolecules, including many polyesters used in biodegradable medical devices[1]. The absence of diffusion, the low number of molecules and the high reactant concentration make these experiments very fast yet relatively straightforward to analyse. The molecular degradation mechanisms, the kinetic parameters and the evolution of the molecular weight can be deduced with the aid of quantitative models. Complementary instrumental methods such as IR spectroscopy and interfacial rheology allow for studying the evolution of the material's morphology and mechanical properties *in situ*.

Here, we present quantitative models for the monolayer degradation of architectured molecules such as block copolymers, star shaped polymers and polymer networks. The models are compared to experimental results obtained with biodegradable (co)polyesters, and the predictions for the evolution of the molecular weight provided by the models are compared to results from *in situ* interfacial shear rheology. The insights gained on a molecular level will contribute to a deeper understanding of the structure-property relationships in degrading polymer materials to assure that they perform within the narrow safety margins that are imperative for medical devices.

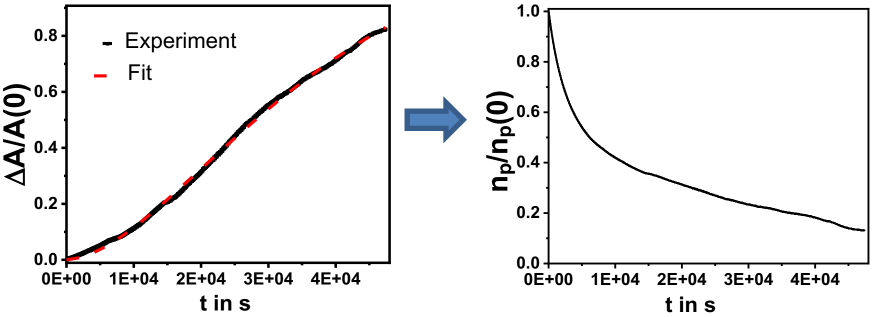

Fig. 1: Experimental poly(ε-caprolactone) degradation curve. The evolution of the degree of polymerization n_p *is deduced from the fitcurve.*

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O-31

Nano-structured films of semifluorinated alkanes “primitive surfactants”: formation and size of hemi-micelles by Molecular Dynamics

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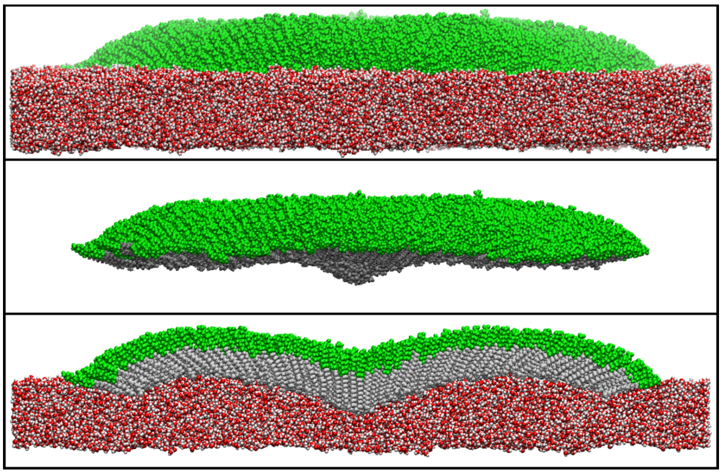
Perfluorinated chains (-$CF_2CF_2CF_2$-) are not only highly hydrophobic but also lyophobic, i.e. they segregate hydrogenated chains. Mixtures of alkanes and perfluoroalkanes are known to be highly non-ideal systems, exhibiting large regions of liquid–liquid immiscibility and large positive excess properties.

Semifluorinated alkanes ($C_nF_{2n+1}C_mH_{2m+1}$, FnHm) are diblock molecules in which a perfluorinated and a hydrogenated segment are covalently bonded together to form a single chain. Although not possessing a hydrophilic group, the simultaneous presence of the antagonist segments gives FnHm the required amphiphilicity to form various supramolecular structures. These are potential candidates for numerous applications, from medicine to smart-materials and tailored interfaces. Among them, the nano-structuration exhibited by Langmuir films of these so-called “primitive surfactants” is particularly striking [1,2,3]. A hexagonal 2D packing of domains (~30 nm diameter) is observed at the surface of water or an adequate solid substrate (Figure). In spite of all efforts, the origin and structure of the nano-domains have remained un-understood. The non-coalescence of the domains, even under compression, is particularly puzzling.



In this work Molecular dynamics simulations have been successfully used to model the formation, structure and size of the FnHm nano-domains. The simulated structures strikingly resemble the experimental. The ultimate aim is to understand, and thus control, how the simultaneous presence of mutually phobic hydrogenated and perfluorinated chains induces organization.

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Nanopores and nanogaps in graphene with chemical approaches: From biomolecular detection to water filtration

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DNA sequencing and biomolecular sensing are among the most envisioned applications of graphene[1], nonetheless each step towards these targets faces important challenges. Our research exploits chemistry: from the synthesis of graphene and porous 2D membranes, to handling, functionalization and application for 2D sensing devices. We recently introduced an innovative mixed cold/hot walls synthesis for CVD graphene[2] and developed bottom-up 2D organic films from polycyclic aromatic hydrocarbons structured by self-assembly as a network of molecularly precise nanopore arrays. Furthermore, we implemented polymer free transfer methods based either on the biphasic caging of graphene using cyclohexane[3] or lipid clamps[4], ensuring graphene films free of polymer residuals allowing the formation of graphene heterostructures made from graphene-lipid superstructures[5]. Interestingly, the chemical functionalization of graphene via the hydrogenation of the basal plane[6] and through the electrografting of diazonium salts at the edge[7], brings us to better understand the interplays between electrochemistry and quantum transport, both in terms of molecular selectivity and sensitivity of next generations of graphene field effect transistor sensors[8]. In sensing devices based on free-standing graphene, we discovered that graphene is hydrophilic in water[9-11], aiming now to understand the impact of water – conferring hydrophilic characteristics to graphene when suspended in water – on how graphene sensors in water operate in the presence of biomolecules (most particularly for nanopore and nanogap sensors). In the last part of my talk, I will present how we achieved the first dynamic tunneling graphene nanogap[12] at the intersection of two single carbon atoms. In the coming years, I believe that chemistry will play an increasingly larger role in the design of the next generation of graphene technologies[13-15].

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O-32

Redox-Induced Association of Ionic Amphiphiles to Ferrocene-Terminated Self-Assembled Monolayers

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Self-assembled monolayers (SAMs) of ferrocenylalkanethiolates, $Fc(CH_2)_nS$, chemisorbed to gold surfaces were originally designed for fundamental studies of long-range interfacial electron transfer across a well-defined and chemically tailorable organic layer.[1] Oxidation of the SAM-bound ferrocene to ferrocenium proceeds via coupled electron-transfer and ion-pairing reactions:

$$\begin{gathered} Fc_{SAM} \rightleftharpoons Fc^{+}_{SAM} + e^{-} \\ Fc^{+}_{SAM} + X^{-}_{(aq)} \rightleftharpoons (Fc^{+}X^{-})_{SAM} \end{gathered} \qquad (1)$$

The nature of the electrolyte anion X^- strongly affects the electrochemistry and stability of the ferrocene-terminated SAM in aqueous solution. Hydrophobic anions (e.g., PF_6^- and ClO_4^-) pair more effectively with the poorly-solvated ferrocenium cation than hydrophilic ones (e.g., Cl^- and F^-).

We have investigated the oxidation of $Fc(CH_2)_{12}SAu$ SAMs in the presence of ionic surfactants consisting of a hydrophobic hydrocarbon tail and hydrophilic anionic headgroup.[2,3] The idea is to combine the tendency of surfactants to aggregate at solid/liquid interfaces with the preference of SAM-bound ferroceniums to pair with lipophilic anions (Fig. 1). We show that the redox response in cyclic voltammetry (i.e., apparent redox potential, formal width at half-maximum of the anodic peak, and anodic-to-cathodic peak separation) is exquisitely sensitive to the surfactant aggregation state in solution. The surfactant adsorbs to the SAM surface by specific ion-pairing interactions between the anionic headgroups and the oxidized ferroceniums. A longer alkyl chain length results in an increased ability of the surfactant anion to pair with the ferrocenium, resulting in ferrocene oxidation at lower potential. Additionally, the chaotropicity of the anionic surfactant determines the reversibility of the ferrocene oxidation and ion pairing reactions. The use of ferrocenylalkanethiolate SAMs for the electrochemical detection of micelle formation and the redox-assisted assembly of solid-supported lipid films will be addressed in this presentation.

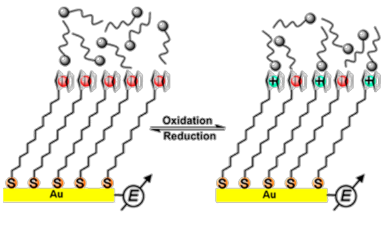

Fig. 1: Redox-induced aggregation of anionic amphiphiles at the solid/liquid interface.

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O-33

Highly Versatile Metal-Organic Frameworks

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The relationship between crystallization conditions, crystal structure and properties is a pivotal point in modern chemistry both for the investigation of fundamental aspects and for material design. The interest spans from the macro- to the nanoscale, and across the gamut of natural, laboratory-made, organic and inorganic systems.

In our study, we investigate the factors affecting the size and morphology of self-assembled metal-organic frameworks (MOFs).[1,2] In general, micro-nano crystals grown by modulator-free synthesis are polydispersed in size, exhibit non-homogeneous shape or simple polyhedral morphologies, usually reflecting the underlying geometry of the crystallographic structure. We developed an approach that results in the formation of monodispersed crystals with a large variability of morphologies, while keeping the crystallographic structure nearly identical.[3,4] No templates or modulators are used. The crystals generated include rare polyhedral shapes, hollow structures and unique morphologies not classifiable according to conventional rules (Fig.1) Interestingly, we prepared morphologically highly complex crystals from achiral components that exhibits single crystallinity and chirality at both the molecular structure and crystal morphology. The work provides new fundamental insights in the growth of uniform and chiral crystals, opening up opportunities for their use as 3D objects for nanotechnological applications.

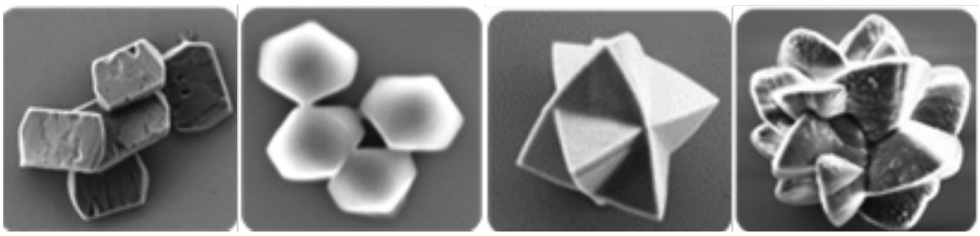

Fig. 1: MOF crystals obtained by additive free synthesis exhibiting varied and unconventional morphologies

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Kinetically driven self-assembly of semiconductor nanoplatelets

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Quasi-two-dimensional semiconductor nanoplatelets exhibit spectrally pure, directional fluorescence due to their highly anisotropic shape. In order to make directional light emission accessible in applications, nanoplatelets have to be collectively oriented in the solid state. Existing methods use excess surfactants to control their self-assembly into ordered films at liquid interfaces. The usage of such additives could be detrimental for optoelectronic applications. Here we report the effective control over the collective orientation of nanoplatelets in self-assembled films by exploiting exclusively the solvent evaporation rate. This kinetically driven self-assembly method yields well-defined monolayer films with controlled nanoplatelet orientation (either all oriented “edge-up” or “face-down”) without depositing additives. The absence of additives enables strong electronic coupling between the nanoplatelets making these films suited for optoelectronic applications. The strong coupling is apparent from contact-free photoconductivity measurements on monolayers that demonstrate a clear orientation dependent conductivity in self-assembled NPLs, as opposed to the purely excitonic response of isolated nanoplatelets in a dispersion. The orientation dependence originates from the orientation-dependent inter-nanoplatelet coupling strengths. The ability to assemble nanoplatelets in highly ordered monolayers with varying electronic properties paves the way for new applications in electro-optic devices.

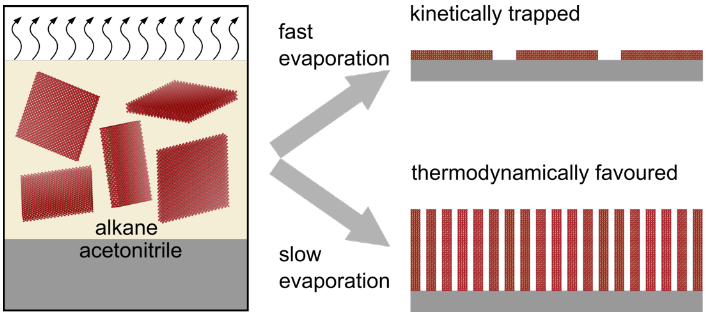

Fig. 1: The collective orientation of semiconductor nanoplatelets at liquid interfaces can be achieved by evaporation kinetics.

DNA SAMs on flat gold: a combined Atomic Force Microscopy and Spectroscopic Ellipsometry approach

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Single stranded oligonucleotide films are the building blocks for most DNA surface-based biosensors. A detailed control of the organization and optical properties of the receptor layer is a crucial issue for the development of a robust sensor. We propose a combined approach which couples optical spectroscopy and scanning probe nanolithography to investigate the structural and optical properties of DNA films. For ultrathin films, thickness and refractive index are highly correlated properties. The combined approach can be exploited to disentangle the correlation as we have shown for self-assembled monolayers (SAMs) formed by alkanethiols with different functional molecular tails [1,2].

Here we exploit molecular self-assembly of a 22-bases, single-stranded DNA bound through an alkyl thiol (C6) linker on flat Au films. Before hybridization of complementary DNA strands, the C6-ssDNA SAM was post-treated through exposure to mercaptohexanol (MCH), in order to replace weakly-adsorbed DNA molecules and to increase molecular order.

By AFM nanolithography, regularly defined micro-areas have been depleted from molecules under a high tip load. From the depth of the shaved area an accurate estimate of the film thickness could be obtained. A statistical analysis on several samples and patches showed a net increase of the SAM thickness upon MCH exposure (3).

By in situ SE dynamic scans we could monitor in real time the interaction of the C6-ssDNA layer with MCH. SE data indicate that exposure of the C6-ssDNA film to MCH induces a significant increase of the optical thickness of the film, a process which begins immediately after admission of MCH into the cell and goes on slowly.

Feeding the SE data analysis with the SAM thickness obtained by AFM we could solve the refractive index/thickness correlation. The combined AFM/SE analysis provided reliable estimates of both the thickness and the refractive index of the biofilm in the NIR region (650-1300 nm).We show that the contribution of the thiol/Au interface has to be included in the optical model to obtain a reliable determination of the refractive index of the DNA SAM in liquid (3).

The careful, correlative characterization of the mixed C6-ssDNA/MCH SAM represents a key step towards the optimization of a robust detection scheme based on helix-helix hybridization.

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O-36

Siramesine-membrane related anticancer mechanism: mitochondria or lysosomal destabilization?

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Siramesine is a cationic amphiphilic drug and a σ-2 receptor ligand with an anticancer activity not completely correlated with its action at the receptor. There are two main theories for explaining the anticancer activity of siramesine, both correlated with its action at the lipid membrane but of two different organelles. Thus, one explanation is related to lysosomal membrane permeabilization [1] and the other with loss of mitochondrial membrane potential, along with reactive oxygen species (ROS) production [2]. Although both possibilities are based on solid explanations, no consensus has yet been achieved. This is the context where this study emerges. Hence, membrane models (phospholipid monolayers) mimicking the main lipid composition of the lysosomal and mitochondrial membranes were employed to unveil the interactions with siramesine. The most abundant phospholipids in the membranes of the lysosomes are phosphatidylcholines along with small amounts of phosphatidylethanolamines, sphingomyelins, cholesterol and others in vestigial amounts. The intra-lysosomal membranes are enriched in bis(monoacylglycerol)phosphate (BMP), which is almost absent in the outer-lysosomal membrane, being this lipid also reported as a marker of late endosomes. The most abundant lipids in the mitochondrial membranes are phosphatidylcholines and phosphatidylethanolamines and the major differences between inner and outer membranes lay on the amount of cardiolipin and phosphatidylinositol. The outer mitochondrial membrane has in its constitution phosphatidylinositol, while the inner mitochondrial membrane has in its constitution cardiolipin.

Langmuir isotherms, Brewster angle microscopy (BAM) and grazing-incidence X-ray diffraction (GIXD) studies were performed to molecularly characterize siramesine-lipid membranes interactions.

Siramesine has shown to be able to interact with lipid membranes in a composition dependent manner. In particular, siramesine strongly interacts with lipid membranes containing anionic lipids. This preference for anionic lipids can be on the basis of the anticancer drug activity of siramesine, since the membranes of mitochondria and of the intra-lysosomal vesicles present in their lipid composition anionic phospholipids. In general, siramesine seems to prefer lipid membranes with anionic phospholipids (-1 charge) and with simple geometry (two hydrocarbon chains) that allow the establishment of an electrostatic complex between the drug and the lipids.

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Graphene oxide incorporated in Langmuir-Blodgett films of penicillinase and phospholipids to enhance penicillin detection

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Graphene Oxide is a single-layer sheet of graphite oxide which has attracted interest because it can be used as a semiconductor or insulator and its electronic and optical properties can be tuned easily. In this sense, it is an interesting compound to be incorporated as an adjuvant to enhance sensing properties of devices, especially ultrathin films based on enzymes.

In this work, we immobilized graphene oxide in Langmuir-Blodgett (LB) films of phospholipids and the enzyme penicillinase to investigate its influence on the biosensing properties towards penicillin. This enzyme was chosen because it can be employed in penicillin sensing considering its importance as an antibiotic with reported resistance. Previous works on phospholipid-enzyme has demonstrated the feasibly of using LB films for detecting penicillin [1,2].

The phospholipid employed was dimyristoylphosphatidic acid (DMPA) and dissolved in chloroform. Aliquots of DMPA were spread on the air-water interface, and solutions of penicillinase as well as dispersions of graphene oxide (both in water) were inserted in the aqueous subphase of DMPA monolayers. The mixed films were characterized with surface pressure-area isotherms, polarization-modulation reflection-absorption spectroscopy (PM-IRRAS) and Brewster Angle Microscopy (BAM). The monolayers were compressed to 30 mN/m and transferred to solid supports using the LB technique. The LB films were characterized with PM-IRRAS, fluorescence spectroscopy and quartz crystal microbalance. The catalytic activity of the immobilized enzyme towards penicillin was measured using UV-vis spectroscopy, and sensing properties using electrochemical measurements.

The insertion of graphene oxide in the enzyme-DMPA monolayer shifted the isotherms to higher lipid molecular areas, evidencing the expansion of the film due to the compound incorporation. PM-IRRAS spectra showed that the amide I and II bands of the enzyme were preserved upon graphene oxide incorporation and the gauche conformers related to methylene group stretching mode increased due to the configurational disorder. BAM revealed a homogeneous pattern of reflectivity of the air-water interface, suggesting a low degree of topographical aggregation. Co-transfer of penicillinase and graphene oxide together DMPA could be attested using PM-IRRAS and fluorescence spectroscopies. UV-vis spectroscopy showed that graphene oxide increases the catalytic activity of penicillinase and the best performance was achieved with thinner films. Electrochemical measurements attested the sensing properties towards penicillinase exhibiting regular and distinct output signals over all concentrations used in this work.

As conclusion, these results may be directly related not only to the nanostructured system provided by the ultrathin film, but also to the thickness of the active layer and to the surface morphology that allowed the preservation of catalytic activity and a fast analyte diffusion due to an adequate molecular accommodation.

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K-6

Light Responsive Soft Nano-Objects

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Azobenzene molecules are considered as molecular actuator that can convert optical energy in mechanical work. In this talk I will show several interesting examples where azobenzene can be used in order to actuate matter on large time and length scales, we will discuss photosensitive polymer films and polymer brushes, photoresponsive microgels [1-2] and light triggered manipulation of the microparticles trapped at a solid/liquid interface.

In the first part of my talk I will show how using a home made set-up combining an atomic force microscope (AFM) and two-beam interferometry it is possible to address two major points concerning the experimental efforts in understanding surface relief grating (SRG) formation in azobenzene containing polymers: (i) how is the orientation of the electric field vector within the interfering electromagnetic fields related to the topographical pattern within the SRG; (ii) how can one measure locally the opto-mechanical forces emerging during topography change. We will discuss three distinct systems: polymer films, polymer brushes, and azobenzene containing polymer nanoparticles. Tracking the topography change *in-situ*, while at the same time changing polarization and phase of the impinging interference pattern, we were able to answer these questions [3-6].

In the second part of my talk I will show how using azobenzene containing surfactant one can manipulate and even induce self-propulsion of microparticles trapped at a solid/liquid interface. Depending on applied wave length one can either remove or gather particles [7]. The physical origin of our approach is related to so-called light driven diffusioosmosis [8]. During irradiation of a solution of azobenzene containing surfactant with focused light, there is a formation of local fluid flow at a solid/liquid interface. The corresponding forces are sufficient to swiftly clean the illuminated area from particles trapped at the interface. When the colloids are turned into Janus particles, their self-propulsion can be initiated in the solution of azobenzene containing surfactant under global/homogeneous illumination with blue light. We discuss how to establish light-driven hydrodynamics as a useful and versatile tool for investigating collective motion of self-propelled particles and aggregation.

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O-38

Growth Mechanism, Morphology and Coverage: a Concentration-dependent Study of Layer-by-layer SURMOF Formation

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For many applications of metal-organic frameworks (MOFs) beyond gas storage, it is inevitable to grow MOF films on surfaces. One of the most powerful methods to produce such surface-anchored metal-organic frameworks (SURMOFs) is the successive immersion of substrates into solutions of the precursor metal salts and organic linkers, which is often referred to as layer-by-layer (LbL).[1] Functionality of the substrates and also deposition temperature are reported to have decisive impact on properties like coverage or the orientation of the SURMOF with regard to the substrate surface normal.[1]

We are exploring further influence factors on SURMOF formation using the LbL method. In this study, we focus on the concentration dependence of the LbL process, using the example of $Cu_2(F_4bdc)_2(dabco)$ SURMOF[2] on pyridine-functionalized gold surfaces (F_4bdc = tetrafluorobenzene-1,4-dicarboxylate and dabco = 1,4-diazabicyclo-[2.2.2]octane).

We will present and discuss the results of LbL experiments with varying concentrations of the precursors Cu(II)acetate and F_4bdc/dabco in ethanolic solution.

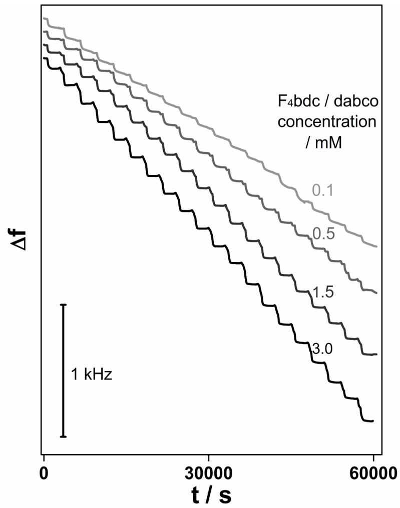

Fig. 1: Relative mass changes on quartz crystal microbalance substrates coated with a gold layer and functionalized with a pyridine-terminated self-assembled monolayer upon layer-by-layer $Cu_2(F_4bdc)_2(dabco)$ SURMOF deposition at room temperature. Cu^{2+} solution concentration was kept constant at 1 mM, organic linker solution concentrations were varied. Frequency curves are shifted in height.

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O-39

Mono and Multimolecular Micellar Films from Branched Poly(ionic liquid)s and Polyelectrolytes

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We review recent results from our research group on assembly of various polyionic compounds including traditional linear macromolecules, amphiphilic poly(ionic liquid)s, star and hyperbranched species as well thermally-responsive hyperbranched materials with end poly(N-isopropylacrylamide) (PNIPAM) blocks [1]. We study their assembling behavior in solution, within Langmuir monolayers, and within layer-by-layer multilayers at variable pH conditions, surface pressures, and temperature by combining *in situ* light scattering, atomic force microscopy, neutron reflectivity, and small-angle neutron scattering.

We discuss the resulting molecular assemblies, mesoscale aggregation, organized micellar structures, and gradient interfacial morphologies, as driven by amphiphilic balance, ion pairing, ionized state of different fragments, limited aggregation, and low-critical solution temperature (LCST) transition [2-3]. Thermally-dependent conductivity and viscoelasticity was considered for selected polyionic liquids [4]. Finally, dual-responsive behavior of organized multilayered films with orthogonal responsive properties (thermal and pH) was demonstrated for polyelectrolyte star block copolymers (Fig. 1) and models of structural reorganization within ultrathin films have been proposed based upon neutron reflectivity monitoring of internal morphology across LCST [5].

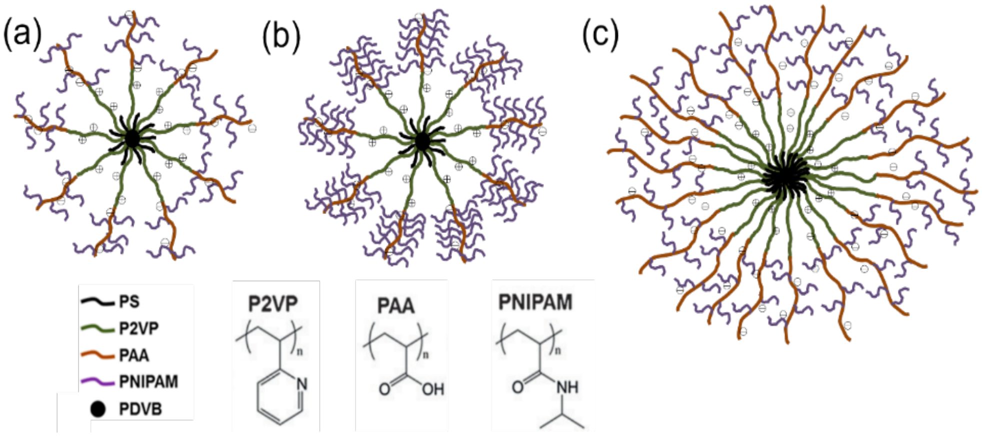

Fig.1: Star-graft block-copolymers with the responsive blocks [6].

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Photo-oxidation and cross-linking of a polybutadiene monolayer at the air-water interface

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In-situ cross-linking of polymer monolayers at the air-water interface (Langmuir monolayers) can allow their stabilization at the interface and their transfer onto solid substrate as stable ultra-thin coating [1]. Here we study the 2D cross-linking of 1,2-polybutadiene (PB) widely used in many elastomer materials. PB monolayers were first characterized by surface pressure-area isotherms, Brewster angle microscopy and in-situ Sum Frequency Generation (SFG) spectroscopy. Through the simultaneous presence of light and oxygen, the PB is shown to undergo an oxidation phenomenon which stabilizes the monolayer at the air-water interface. In the dark or under inert atmosphere, only 3D aggregates are evidenced. This is in agreement with several studies showing the high surface-sensitivity of thick PB films to oxidation either under a controlled oxygen flow or in ambient atmosphere [2-4].

Subsequently, radical cross-linking of the PB monolayer induced by UV-irradiation was demonstrated through thermodynamical characterizations and SFG. The monolayer compressibility decreases after UV irradiation, from 29 to 22 m.N^{-1}, indicating a large change in the polymer chains organization. The PB cross-linking reaction is also evidenced by SFG through the decrease of the C=C band intensity at ~1660 cm^{-1}, assigned to the pendant vinyl, as a function of the irradiation time. This successful cross-linking of PB monolayer provides a basis to synthesize interpenetrated polymer networks involving two different polymers.

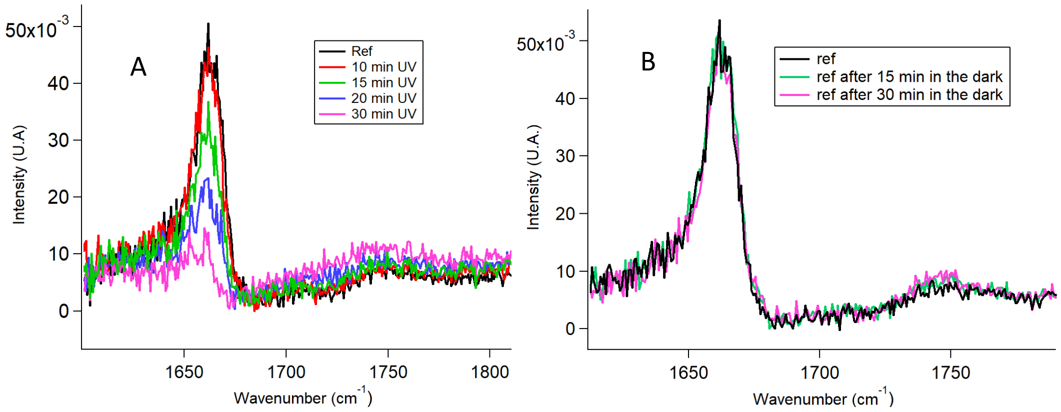

Fig. 1: SFG spectra (ssp polarization) as function of time for a PB monolayer maintained at 10 mN/m A. during UV irradiation. B. Reference experiment without UV irradiation

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Posters

P-1

Functionalized Nanomembranes for Structural Analysis of Proteins by Electron Cryo-Microscopy

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Here we present a method to create thin, biofunctionalized and selective membranes for structural investigations of proteins *via* electron cryo-microscopy (cryo-EM). To create this membrane, a bottom-up approach was applied (Figure 1). A biorepulsive polymer (polyglycerol) with thiol groups at one end was synthesized and then deposited on a gold surface.[1] The lose polymer brushes were crosslinked and then functionalized with a derivative of nitrilotriacetic acid (NTA). Before the transfer process, the thin film was treated with polymethylmethacrylate (PMMA), the gold layer was etched off and the free membrane was transferred onto a TEM-grid.

Afterwards, the NTA-functionalized membrane was treated with aqueous $NiSO_4$ solution to load the NTA moieties with Ni^{2+} ions. This permits to selectively bind proteins tagged with a histidine sequence to the membrane and to be analyzed by cryo-EM.

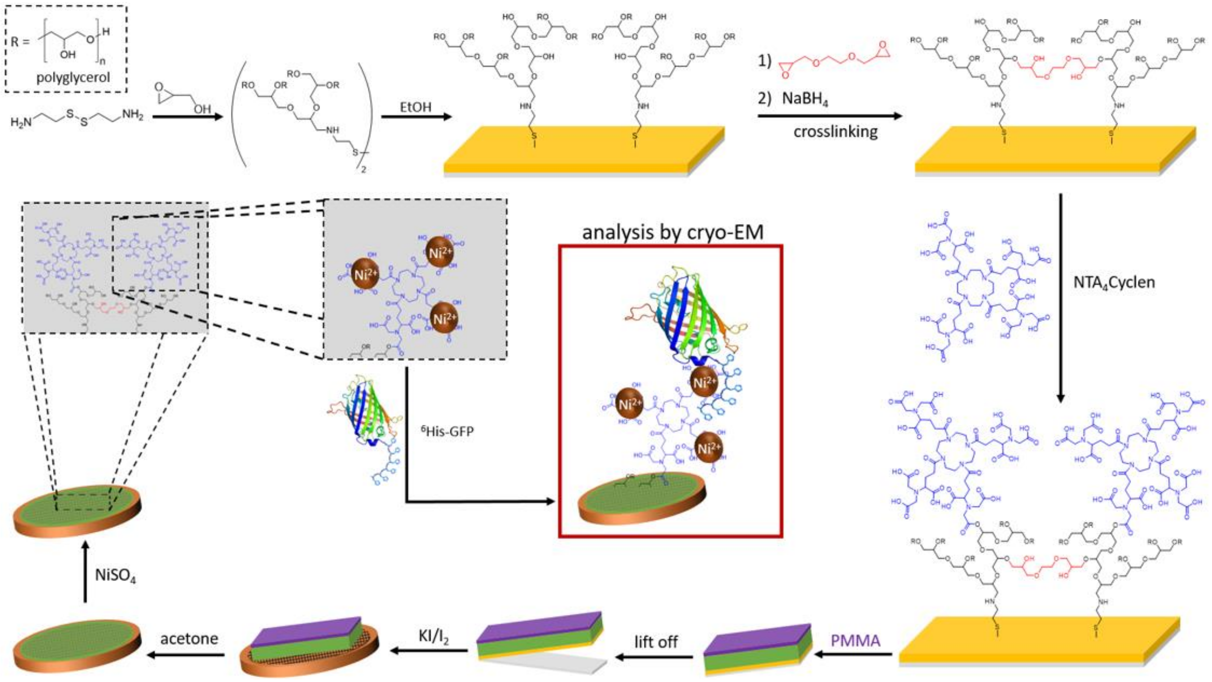

Fig. 1: Bottom-up process for manufacturing NTA-functionalized membranes. A biorepulsive polymer layer is deposited via thiol groups onto a gold surface and stepwise crosslinked and functionalized. After a multi-step process, the free membrane can be loaded with Ni^{2+} ions and histidine-tagged proteins be selectively attached to be analyzed by cryo-EM.

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Langmuir films for biosensing applications

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The specific and sensitive detection of pathogenic microorganisms remains a current scientific challenge and a practical problem of enormous significant. New advances in diagnostic and sensing technologies that can serve as alerts for bacterial contamination of food and water, enable highly selective and sensitive microorganism detection. Understanding the adsorption behavior of microorganisms on thin monolayers can provide a generic approach for the construction of the bacterial sensors. One of the current bacterial microorganisms' detections is based on culturing the microorganisms on agar plates followed by standard biochemical identification, which takes hours. Another bacterial detection approach is based on different kinds of biosensors, which in case of polymeric imprints change the shape of the microorganisms and results in its lack of detection. Due to the mentioned limitations, we suggest a different approach that takes into account a natural bacterial environment, such aqueous medium and the detection operation is harmless for microorganisms.

Our study aims at developing a technology for sensing microorganisms based on Langmuir-Blodgett technique. We suppose that the detection of the microorganisms is achieved by electrostatic interactions between the flexible amphiphilic layer and charged nucleocapsids. By using the Langmuir technique, we can measure the adsorption of nucleocapsids at the lipid monolayer at different pH, buffer and time conditions. By using Brewster's angle microscopy and atomic force microscopy, we will characterize the adsorbed structures at the interface and transferred to solid surfaces.

The research approach relies on the development and characterization of various Langmuir layers and their interactions with microorganisms.

Thermo-responsive microgels as transducers applied to ion-detection: synthesis, characterization and functionalization

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Stimuli-responsive polymers have attracted considerable scientific interest because of their ability to undergo conformational or solvation state changes under the influence of an external stimulus such as temperature, pH, light, magnetic and electric field or solvent composition [1]. These polymers can be prepared in various architectures (as micro-/nanoparticles, thin films, membranes, brush polymers, micelles …) and have found application in diverse fields, including tissue engineering, drug delivery and as (bio)sensors. In the field of sensors, stimuli-responsive polymers are often used as transducers between the environment to be analyzed and the detection platform [2].

In this study, we aim to develop a transducer film based on a thermo-responsive polymer for iron detection. The first step is to synthesize a poly(N-isopropylacrylamide-co-acrylic acid) (PNIPAM-co-AAc) microgel via free radical precipitation polymerization using a thermo-responsive monomer (NIPAM), a co-monomer (AAc) and a crosslinker (N,N'-methylenebisacrylamide) (BIS). This polymerization yields microgels which exhibit a Lower Critical Solution Temperature (LCST), identified as the temperature at which the microgel undergoes a transition from a swollen state to a collapsed state [3]. In this work, dynamic light scattering (DLS) is used for the characterization of particle size and the study of transition reversibility. Visible spectrophotometry (transmittance) allows for the determination of the LCST and the study of the thermo-responsive behaviour.

In order to vary microgel size, the monomer concentration was varied between 35 and 140 mM. A monomer concentration of 50 mM leads to microgel particles with a diameter of 750 nm in the swollen state (15°C, < LCST) whereas the size decreases to 230 nm in the collapsed state (60°C, > LCST). Higher monomer concentrations lead to larger particles. In order to change the LCST, the AAc concentration was varied from $1.5\%_{mol}$ to $10\%_{mol}$ and the crosslinker concentration from $1.5\%_{mol}$ to $5\%_{mol}$. However, all of these syntheses produce microgels with a LCST around 30-32°C. The transition from swollen to collapsed state shows excellent reversibility for all samples and increasing the crosslinker proportion influences the swelling/deswelling amplitude and the transition sharpness.

The second step of the project consists of depositing the microgel on a glass substrate coated with a gold thin layer functionalized with cysteamine. Different parameters (pH, concentration, temperature, dipping duration) were varied in order to optimize microgel deposition. Atomic Force Microscopy (AFM) is used to observe the surface of the microgel to determine the optimal coating conditions.

In order to produce a sensor, the thermo-responsive microgels will be functionalized with a specific chemical group able to bind the targeted analyte and combined with plasmonic nanostructures designed to detect the refractive index change resulting from polymer collapse.

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Fluorinated Benzene Derivatives with Dipolar Headgroups for the Fabrication of Electron Injection Layers

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For the fabrication of semiconducting electronics based on organic molecules, the contacting between metal electrodes and organic semiconductors is of major importance. In this context, injection layers (IJLs) are essential to improve the charge carrier transfer. [1-2] An efficient method to produce IJLs is the formation of self-assembled monolayers (SAMs). A series of fluorinated benzene derivatives with internal dipole moments was synthesized (Fig. 1). By immersing Au(111) substrates into ethanolic solutions of these molecules, polar SAMs were formed via covalent attachment of the S/Se groups to the metal surfaces. Orientations and structures of the monolayers were investigated by ellipsometry, infrared reflection-absorption spectroscopy and scanning tunneling microscopy.

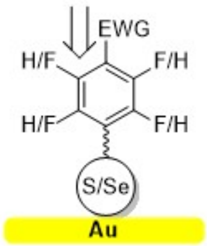

Fig. 1: Molecules synthesized in this study. The arrows indicate the directions and magnitudes of the dipole moment contributions of the electron withdrawing group (EWG)

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P-5

A study of host-guest interaction between organic vapors and a novel calix[4]arene Langmuir-Blodgett thin film

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Calix[n]arenes, as the third generation hosts, are known to be excellent Langmuir film forming materials [1,2]. In this study, 5,11,17,23-Tetra-(tert-butyl)-25,27-di-(3-aminomethyl pyridine acetamide)-26,28-dihydroxy calix[4]arene (C16) was used as a chemical sensor material. The C16 Langmuir-Blodgett (LB) thin films were fabricated as a LB thin film chemical sensing element. Surface Plasmon Resonance (SPR) technique was used to characterize the C16 LB thin films. Fitting the experimental SPR curves of C16 LB thin films were actualized to determine the film thickness and refractive index using Fresnel formula algorithm *via* the Winspall software (developed by Wolfgang Knoll). To study the interaction of host-guest mechanism, C16 LB thin film chemical sensing element was exposed to acetone, benzene, ethyl acetate, chloroform and methanol vapors. After intermolecular interactions between the LB thin film and volatile organic compounds (VOCs) molecules, poor bonding ended and the VOCs molecules removed from the host molecules. It is shown that the LB thin film has reproducibility property and the swelling process was analyzed by well-known Fick's Equations [3].

$$\left(\frac{M_t}{M_\infty}\right) \cong \left(\frac{I_{rf(t)}}{I_{rf(\infty)}}\right)^{-1} = 4\sqrt{\frac{D}{\pi d^2}}\, t^{1/2} \qquad (1)$$

where, M_t and M_∞, represent the penetrant mass sorbed into the deposited film at time t and at equilibrium state, respectively. $I_{rf\,(t)}$ and $I_{rf\,(\infty)}$ are the intensities of reflected light at any time, t and saturation point in I_{rf}, respectively. D is the diffusion coefficient and d is the thickness of slab. In this approach diffusion coefficients for swelling were confirmed to the square root of time and were correlated with the VOCs. The response times, selectivity and reproducibility performance parameters of C16 LB thin film were measured for each VOCs. This study indicates that the LB thin film is highly sensitive to chloroform and acetone vapors than others. The average response times of chloroform and acetone are 0.650 s, 0.914 s, and the average recovery times of chloroform and acetone are 1.300 s, 1.156 s, respectively. Consequently, it became evident that C16 LB thin film can be used as a sensing material against specific organic vapors at room temperature.

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P-6

2D Polymer Networks at the water-air interface based on Nitrile Butadiene Rubber and Polyethylene Glycol-based copolymer.

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Interpenetrating Polymer Networks (IPNs) are widely investigated in many applications. These materials are obtained by cross-linking generally two polymers in a blend, using two different cross-linking pathways. The resulting materials interestingly exhibit combined properties of the two composing polymers. For instance, the 3D Nitrile Butadiene Rubber/Polyethylene Glycol (NBR/PEG) IPN is a well-known material in many applications, such as ionic membranes in some ionic actuators in where the PEG network serves as an ionic liquid reservoir, whereas the NBR network ensures convenient mechanical properties [1]. In order to miniaturize these devices, it is necessary to reduce the membrane thickness. For that, the Langmuir technique is well suited to obtain ultrathin films at the water-air interface. In this work, we are interested in the synthesis of pure PEG-based copolymer (PEG-PPG-PEG) and NBR networks at the water-air interface. The PEG-based network is formed by acid-catalysis in the presence of a cross-linker in the water subphase, while the NBR is cross-linked by UV photo-irradiation. The first thermodynamic measurements show that for both systems the monolayers undergo a contraction at constant surface pressure of 10 mN/m (Figure 1a) reflecting signs of their cross-linking. In addition, the recompression isotherms (Figure 1b) obtained after 2 hours at 10 mN/m to ensure the cross-linking reaction show a higher compressibility modulus than the reference isotherms. The next steps consist of characterizing the monolayers with Sum Frequency Generation spectroscopy in order to follow up *in situ* the evolution of the cross-linking reaction across the time. Finally, reaching the pure polymer networks will permit studying the 2D NBR/PEG-based IPN to obtain ultrathin membranes.

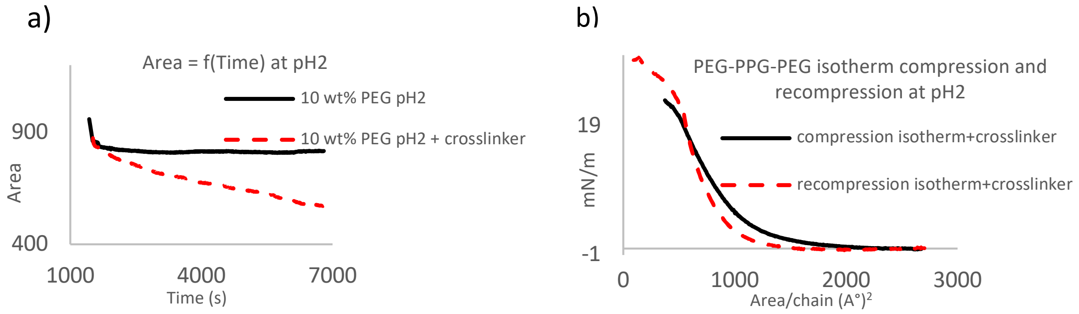

Figure 1 : a) Areas vs time with and without cross-linking for PEG-based monolayers. **b)** Compression isotherms of PEG-based copolymer in presence of the cross-linker in the subphase obtained either immediately or after 2 hours at 10 mN/m to ensure the cross-linking reaction (recompression isotherm).

Reference : [1] V. Woehling et al. / Sensors and Actuators B 256 (2018) 294–303

Lifetime of disinfection agents: active chlorine content and surfactant degradation

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Here we present an analytical study in which we investigated the time-dependent decrease of active chlorine content in surfactant-containing hypochlorite solutions and identified the surfactant degradation products.

For investigations, a model system was designed on the base of surfactants with short aliphatic chains added to hypochlorite solutions. We measured the time-dependent active chlorine content in surfactant-containing hypochlorite disinfectants and identification of degradation products was realized by NMR-Spectroscopy and GC-MS, followed by synthesis of identified compounds and analysis for confirmation.

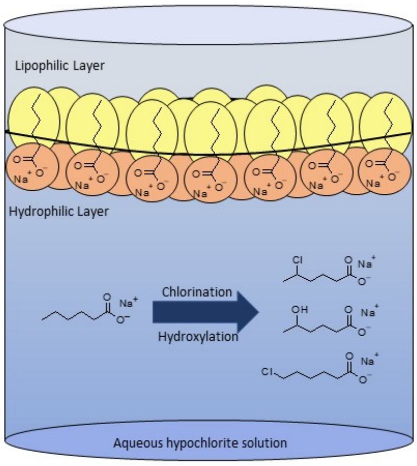

Fig. 1: Model system based on sodium caproic acid added to hypochlorite solution for investigation of the lifetime of surfactant-containing disinfectants and identification of degradation products.

P-8

Continuous fabrication of luminescent organic nanoparticles by visible laser processing of dye solution microdroplets

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We adopt the liquid-phase laser processing by a visible pulse laser resonant excitation [1], which is expected not to damage the organic material, but efficiently invoke the molecular vibration via strong electron-phonon coupling of π-conjugated organic dyes MEHPPV, leading to nanoparticle (NP) formation, after exposed to and cooled by insoluble water [2]. Fluorescence optical microscopy revealed that a large volume of fluorescent NPs were successfully fabricated. Dynamic light scattering apparatus revealed that NPs have unimodal size distribution in 100nm - 300nm. However, there are several issues to be solved in this original method. The first issue is irregular suspension of the microdroplets: the hand-held homogenizer produced standing sonic waves with peak intensities positioned in a lattice. The difficulty of holding the dye solution injector tip at these peak positions brought about inhomogeneous suspension of dye droplets. It led to broad distribution of resultant NP size after laser processing, which is inadequate for application, e.g. printing ink to form a display pixel in a high-resolution static-image flexible digital signage device [3]. Furthermore, the second issue is that, while the laser irradiation, NPs randomly diffused over the water in a beaker, crossing the laser beam for short time in a Brownian motion. It led to broad distribution of irradiation time among dye droplets, sometimes bringing about large irregular aggregates. The third issue is that if we took too much time for microdroplets suspension, the produced heat evaporated the chloroform and formed a solid MEHPPV film on the water surface which hindered the laser irradiation. Instead of this two-step fabrication [2], microdroplet suspension and laser irradiation, we propose a novel procedure which performs these two-steps simultaneously: we have devised a continuous fabrication machinery which utilizes a glass capillary as a container (Fig. 1): dye solution injected into the water flow in the capillary is dispersed as microdroplets by an ultrasonic agitation. The laser beam is guided through the capillary with a beam diameter larger than the capillary diameter. All the dispersed dye microdroplets are laser processed with the same intensity and for the same duration of time while the microdroplets travel through the whole length of the capillary. This mechanism assures that every dye microdroplet is homogeneously laser processed and converted to solid NP, expecting homogeneous and narrow distribution of resultant NP size.

Preliminary results using this novel machinery suggested an improvement in the narrow distribution of resultant dye NP size. This machinery enables a continuous and large volume production of dye NPs with homogeneous size for industrial production.

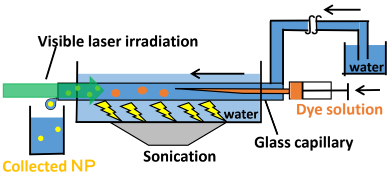

Fig. 1: Continuous NP fabrication by simultaneous suspension and laser irradiation to microdroplets flowing through a glass capillary.

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P-9

Silver Nanowire Forest Grown from Gold Nanoparticle Seeds Chemically Bound on SiO_2 Layer

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Utilizing only solution processes, we have fabricated nanowires (AgNWs) forest on large-area Si wafers with surface SiO_2 layer for optical applications: similar technique applied to plastic sheets will give rise to transparent and flexible sheets with controlled surface reflectance in a predefined spatial pattern. If we utilize nanocoiled AgNWs with specific handedness, and hence with specific chirality, the resultant surface-coat will function as a circular polarization filter and the coated films, therefore, function as high efficiency anti-reflection coatings because of the existence of high density free electrons in AgNWs.

AgNWs were epitaxially grown by a polyol solution process from gold nanoparticle (AuNP) crystal seeds [1, 2] that were chemically crosslinked via thiol residues to Si wafer (Fig. 1). Since the surface SiO_2 layer does not hinder this crosslinking, AuNP crystal seeds are expected to be anchored to any plastic sheets actually. AgNW spatial patterning, which may be required for the optical application of the AgNW forest, will be controlled e.g. by the location of nanoholes of anodized aluminum oxide ultrathin film, through which AuNPs penetrate and are crosslinked to the underling plastic sheets prior to the AgNW growth. In the present study, we used Si wafers as substrate particularly for SEM observation. To control the density of AuNPs crosslinked to Si wafers in order to avoid the AuNP aggregation and subsequent fuse, Si wafers with surface SiO_2 layer were dipped in the 1:1 mixture of thiolated (trimethoxysilyl)propanethiol and nonfunctional trimethoxy(methyl)silane (1/80 diluted with toluene) for 2 hrs: Fused AuNPs without clear crystal facets would not promote an epitaxial growth of AgNws. AuNPs were prepared by a polyol process [2] in solution, and crosslinked to the surface-treated Si wafer (Fig. 1). AgNWs were grown from these AuNP seeds at 175°C in ethylene glycol. Even after 10 min ultrasonic cleaning, crosslinked AgNWs were successfully confirmed to be fixed to the wafer through the SEM observation (Fig. 2). AgNWs had clear straight profile and had similar diameter. Since AgNWs with few μm length will suffice for optical application, we can reduce the length and obtain higher density AgNws by using concentrated AuNP suspension. Increase in the concentration of (trimethoxysilyl)propanethiol may also be effective to the realization of dense and vertical growth of crosslinked AgNWs.

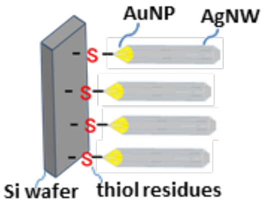

Fig. 1 Schematic of AgNWs epitaxially grown from AuNP seeds which were crosslinked to a Si wafer via thiol residues.

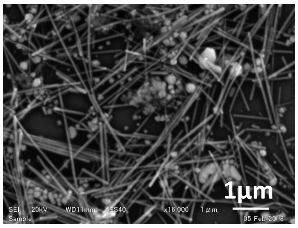

Fig. 2 SEM image of AgNWs grown and crosslinked to the surface-treated Si wafer.

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Fabrication of Nanopillar Arrays on Si Wafer Surface: Selective Si Etching Assisted by Au Nanoparticles Deposited Through Arrayed Nanoholes in Anodized Aluminum Ultrathin Film

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Mimicking the nanopillars on the surface of cicada wing that are flexible and durable although very thin [1], nanopillar arrays were fabricated on a Si wafer surface by selective Si etching assisted by Au nanoparticles (NPs): to realize a large area flexibility of thin Si wafer, Si nanopillars, hence Au NPs, should be homogeneously placed on the Si wafer surface, which was realized by homogeneously located arrays of nanoholes in anodized aluminum ultrathin (AAU) film, through which Au NPs were deposited.

AAU film should be thin enough with similar thickness as the nanohole diameter (ca. 70 nm) so as to let the AuNPs penetrate through: we employed high purity (> 99.999%) Al plate with enough thickness of 0.5 mm as the starting material for easy manipulation while keeping surface smoothness, and obtained ca. 300nm thick AAU films with regular nanohole arrays by detaching them from both sides of the two-step anodized Al plate via a chemical procedure [2]. SEM observations assured that homogeneous array of 70 nm nano throughholes with 100 nm spacing was successfully fabricated in the AAU film (Fig. 1(a), (b)). Two methods were tried to deposit Au or Ag NPs on the Si wafer through these AAU film nanoholes: (1) vacuum sputtering of Au NPs and (2) solution phase chemical crosslink of Au NPs to thiol-containing silane-coupled Si wafers. For the method (1), DC sputtering through an AAU film did not deposit Au NPs on the underlying Si wafer. SEM image (Fig. 1(c)) indicates thick deposition of an Au layer only on the AAU film surface, suggesting that there was no penetration of Au atoms through the film nanoholes. For the methods (2), 20 - 30 nm Au NPs, which were prepared by a polyol solution process [3], were crosslinked to the Si wafer surface. The Si wafer became yellowish white, and then became black after selective etching of Si beneath the Au NPs presumably letting Au NPs buried into the etched holes. SEM observation assured that about 20 - 40 nm high-density holes were formed successfully on the Si wafer surface (Fig. 1(d)). Preliminary bending measurement suggest that Si wafers with surface nanoholes endured one-point-five-times higher strain than bare Si wafers with the same thickness, however they have similar Elastic modulus.

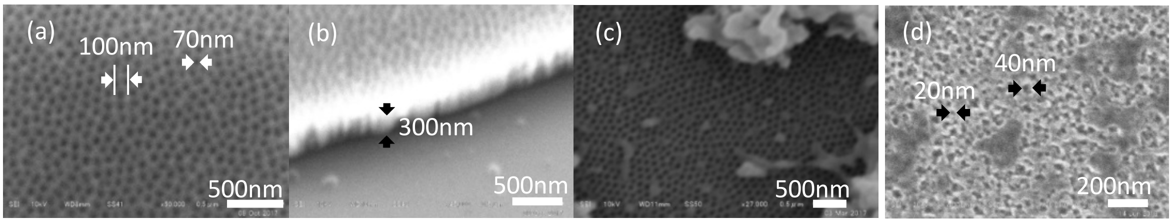

Fig. 1:SEM images of (a) the upright, (b) oblique view and (c) Au-sputtered AAU film with nanohole arrays, and the Si wafer after selective etching assisted by surface deposited Au NPs.

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Increase of the internationalization rate of Quantum Dots by fluorinated organic ligand

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Fluorescent inorganic quantum dots are highly promising for biomedical applications as sensing and imaging agents. However, the low internalization of the quantum dots, as well as for most of the nanoparticles, by living cells is a critical issue which should be solved for success in translational research. In order to increase the internalization rate of inorganic CdSe/ZnS quantum dots, they were functionalized with a fluorinated organic ligand. The fluorinated quantum dots displayed an enhanced surface activity, leading to a significant cell uptake as demonstrated by in vitro experiments with HeLa cells. Experimental and computational results of Langmuir monolayers of the DPPC phospholipid as a model cell membrane with in vitro experiments for analyzing the mechanism of internalization of the fluorinated CdSe/ZnS quantum dots, were combined. Surface pressure-molecular area isotherms suggested that the physical state of the DPPC molecules was greatly affected by the quantum dots. UV–vis reflection spectroscopy and Brewster Angle Microscopy as in situ experimental techniques further confirmed the significant surface concentration of quantum dots. The disruption of the ordering of the DPPC molecules was assessed. Computer simulations offered detailed insights in the interaction between the quantum dots and the phospholipid, pointing to a significant modification of the physical state of the hydrophobic region of the phospholipid molecules. This phenomenon appeared as the most relevant step in the internalization mechanism of the fluorinated quantum dots by cells. Thus, this contribution sheds light on the role of fluorine on the surface of inorganic nanoparticles for enhancing their cellular uptake.

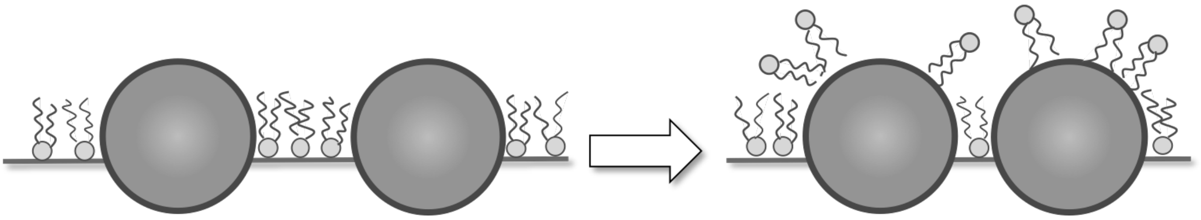

Fig. 1: Fluorinated Quantum Dots interacting with lipid membrane under compression

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P-12

Influence of the Anion on the Deposition of Cu-containing Surface Mounted Metal-Organic Frameworks (SURMOF)

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Metal-Organic Frameworks (MOFs) have gained increased academic attention since their first mentioning in the midst of the 1990s. The combination of metal ions coordinated to organic ligands opens a wide field of functional highly porous materials for a variety of applications. Many of those require the deposition of the respective MOF material on a functionalized surface (SURMOF). However, the mechanisms of MOF fomation, as well in bulk but especially on the surface, are still under discussion. In our study we investigate the influence of the anion of the Cu^{2+} source on the liquid phase epitaxy (LPE) of pillared layer SURMOFs[1] to gain further insight into the crystallization process. For instance, it is already known that the use of $Cu_2(OAc)_4$ for LPE leads to the formation of mixed ligand clusters which may lead to complex phase mixtures.[2] As a result of our study we could show that the anion plays a cruical role in the SURMOF deposition regarding the resulting crystal phase and coverage of the surface, thus competing temperature and template effects due to surface functionalization.

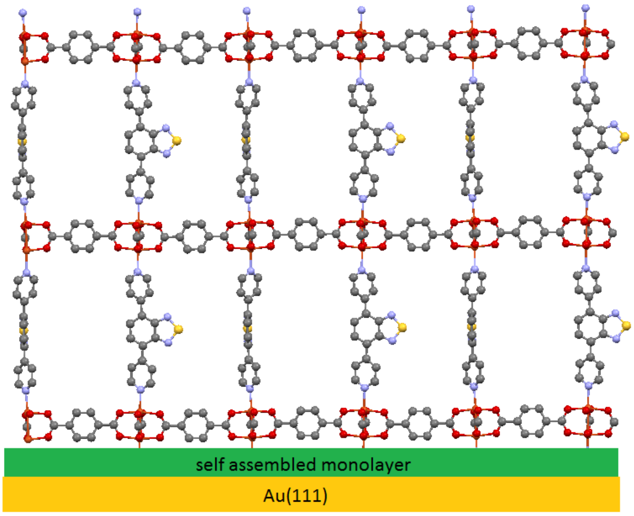

Fig.: Schematic representation of a pillared layer SURMOF on Au(111) surface functionalized with a self assembled monolayer.

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Surface mounted metal-organic frameworks with dipolar N-heterocyclic ligand precursors

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Metal-organic frameworks (MOFs) are two to three-dimensional coordination polymers consisting of metal ions and multifunctional organic ligands. Due to their high surface area and stability as well as the numerous possible functionalizations, that are only limited by the potential of organic synthesis, MOFs are interesting materials for various applications such as sensing.

For this, we have synthesized new organic pyridine terminated ligand precursors with an intrinsic dipole moment perpendicular to their molecular axis using palladium-catalyzed C-C cross coupling reactions. These ligands are used to prepare pillared-layer MOFs [1] with mixed linkers. The MOFs are intended to be deposited on suitable and accordingly functionalized substrate surfaces to form surface mounted metal-organic frameworks (SURMOFs) for sensing applications.

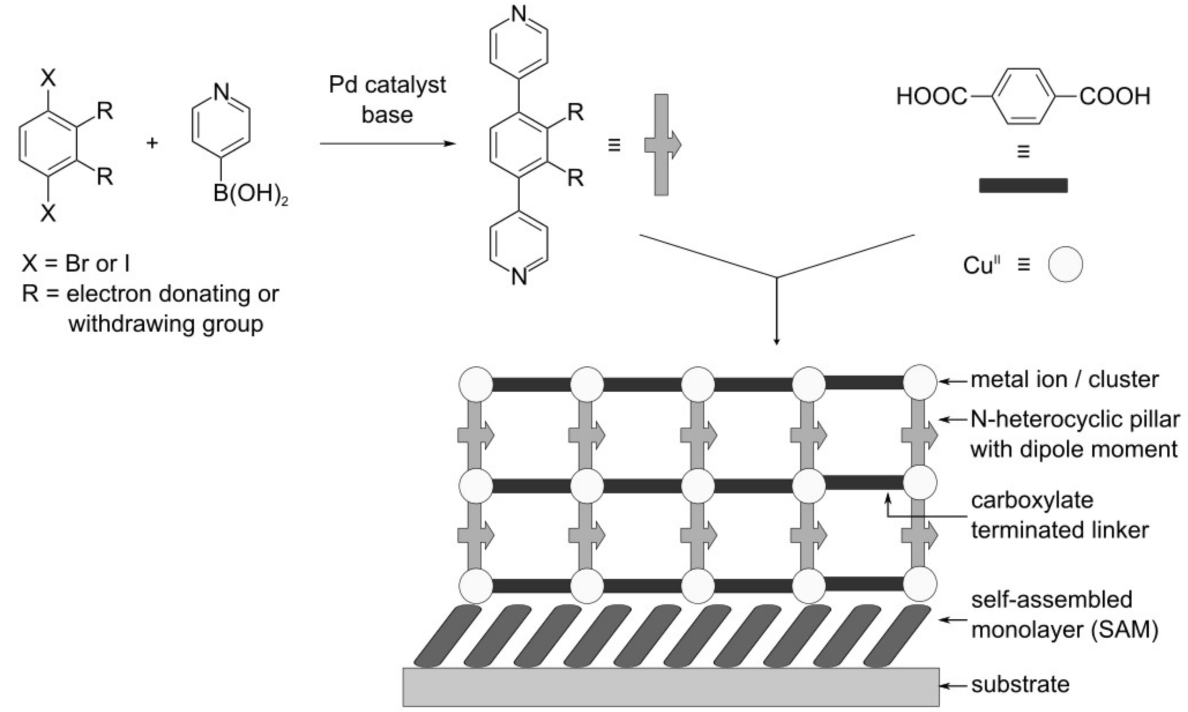

Fig. 1: Schematic overview of the synthesis of pyridine terminated dipolar pillar precursors and the resulting SURMOF that is grown on a SAM-functionalized substrate surface.

References

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Antibiotic release from well-ordered mesoporous titania films produced via evaporation induced self-assembly.

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Most implants used in biomedical technology are manufactured from titanium, a material which does not cause any intervention to the body functions. Good osteointegration is the best property of a successful implant. However, implants are highly susceptible to microbial attack and colonization, since their surfaces are incapable of suppressing bacterial growth. Microbial infections are therefore the most common cause of implant failure [1]. The development of an implant coating loaded with antimicrobial agents would be an effective way to improve the success rate of implants. This would lead to topical antibiotic administration in the surgical region [2]. Mesoporous titania coatings on titanium implants have been found beneficial in this respect. They are usually produced using electrochemical anodization.

In the present work we have produced mesoporous titania thin films on glass substrates via evaporation induced self-assembly [3], using different titanium alkoxides and polymeric templates (P123, F127, KLE, PS-b-PEO) we have loaded these films with antimicrobial agents and tested their uptake and release from the films as a function of the film structure.

The existence of long-range order in the mesoporous films and the crystallinity of the TiO_2 films was evaluated by X-ray diffraction (XRD) and X-ray reflectivity (XRR). The surface topography of the films was studied using atomic force microscopy (AFM). The antibiotic uptake and delivery from the mesoporous thin films were monitored using high liquid performance chromatography (HPLC), UV-visible absorption and fluorescence spectroscopy.

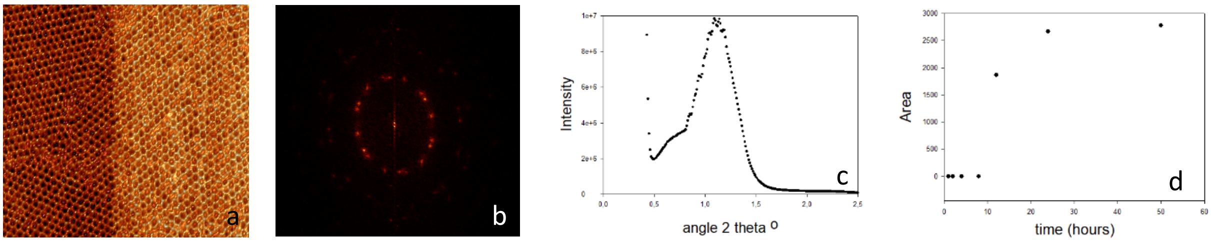

Figure 1: a)AFM image b) FFT analysis method for AFM image c) low-angle XRD patterns and d) release of Vancomycin from as-synthesized KLE-templated titania film (a-d).

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Investigation of the polymer thin film behaviour within the combinatorial laser-induced forward transfer

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Combinatorial laser-induced forward transfer (cLIFT [1]) is a newly developed method for the generation of high-throughput peptide microarrays. As a variant of the commonly known laser-induced forward transfer (LIFT) process, it allows for the flexible creation of high-precision minute amounts of peptides in the microarray format, as well as for other applications in materials science and combinatorial chemistry.

Within this particular process, a laser locally heats a donor slide, which carries a chemical building block inside a protective polymer film. Due to the irradiation, material transfers selectively from the donor to an acceptor slide. Subsequently, the reaction can proceed on the functionalized acceptor slide, e.g. *via* heating. Finally, repeating the lasing process with different donor slides generates combinatorial patterns of chemical building blocks. Furthermore, to use the full potential of this method, we developed a system that generates combinatorial patterns automatically with a repeatable precision of below 5 µm [2].

Because the cLIFT method is a rather novel technique, where the transfer mechanism appears fundamentally different from the published LIFT principle, it is still poorly understood. Therefore, we investigated the behavior of the polymer thin film during and after laser irradiation. We analyzed the exact expansion of the polymer thin film (Fig. 1, a-c) as well as the contact with the acceptor slide through high-speed imaging (Fig. 1, d), which proves for the first time that the cLIFT method can be classified as a contact problem. Thus, we characterized the method allowing the utilization of standard numerical approaches for a quantitative analysis to obtain a deeper understanding of the fundamental process.

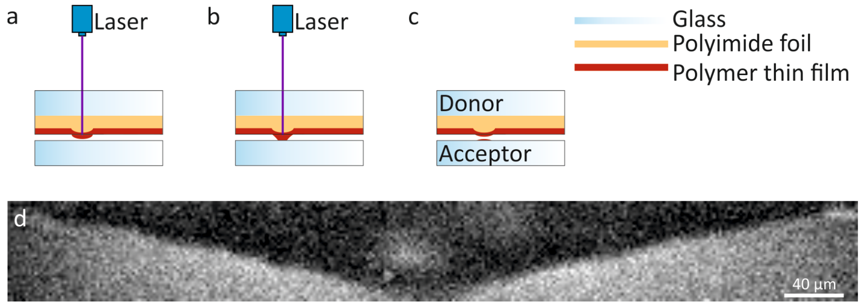

Fig. 1: The laser irradiation causes the expansion of the polymer thin film, following a smooth Gaussian bell distribution, (a) until the film reaches the acceptor surface. Then, the acceptor surface blocks the thin film movement in z-direction and forces it to spread on the surface with a distinct contact angle (b). Finally, the thin film compresses after the laser heating stopped and a minute amount of material remains on the acceptor slide (c). Optical micrograph of the donor-acceptor contact (d).

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P-16

Surface passivation of silicon with covalently bound organic monolayers

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The surface passivation of semiconductor materials plays a crucial role in the production of high-efficiency photovoltaic cells. We have used a modification of a two-step halogenation/Grignard route, involving chlorination-alkylation reaction [1]. The reaction is air sensitive due to the natural formation of oxide on the silicon surface and therefore a glove box will be used which has been shown to work really well for these types of synthesis [2-4]. This method has been shown to allow the introduction of small alkyl chains whilst retaining excellent chemical and electrical properties and has been found to produce monolayers for a wide range of silicon substrates; Si (100), Si (111) silicon nanowires and porous silicon.

The surfaces were characterised with XPS, AFM and FT-IR in order to measure and confirm the presence of the covalently attached organic layers. We have characterised the electron-hole pair recombination lifetime using time resolved fluorescence and will present preliminary results of the effect of the organic passivation on the silicon substrates.

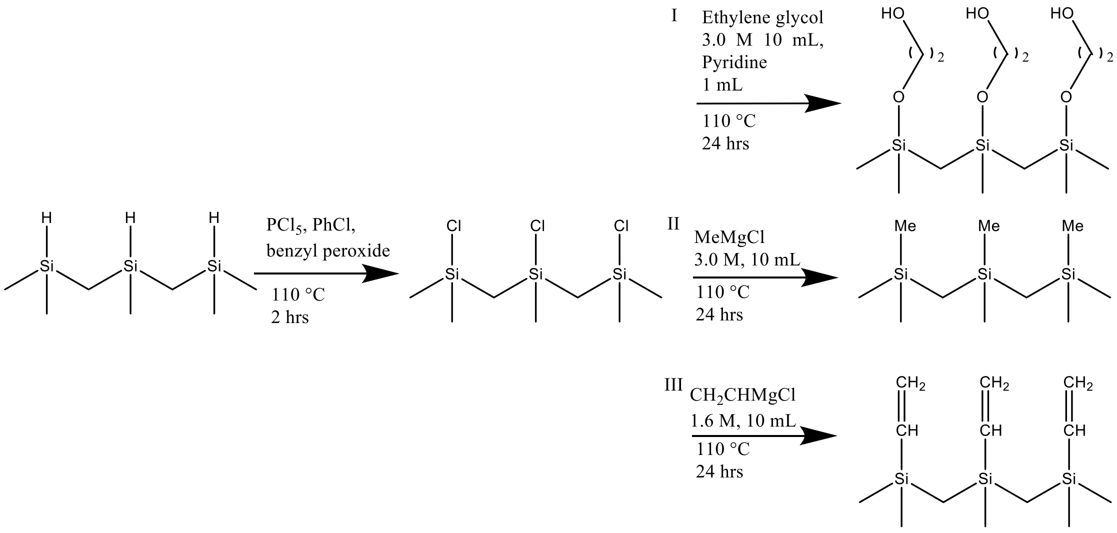

Fig. 1: Reaction schemes for I) diol-terminated silicon surface II) methyl-terminated silicon surface III) vinyl terminated silicon surface.

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Effect of the pesticide acephate on Langmuir monolayers: A PM-IRRAS study

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The function of the cell membranes is mainly driven by their lipid composition. The Langmuir technique is a good method to mimic these structures and also give information about interaction with analytes of interest. To get the complete information about the molecular level interactions, the in-situ polarization-modulated infrared reflection absorption spectroscopy (PM-IRRAS) technique has been used to characterize the monolayers on liquid/air interface. The main goal of this study was the investigation of the interaction between lipid films and the acephate pesticide, based on π-A isotherms and mainly in PM-IRRAS spectra. Acephate, an organophosphorus insecticide, was chosen as analyte due its potential toxicity shown by in vivo and in vitro studies and carcinogenic potential in humans. Since this pesticide is widely used in agricultural fields, there is concern that it becomes an emerging pollutant. Once this agrochemical contaminates the human being, it affects the cells, damaging the protection of these structures (the cell membrane). To mimic the cell membrane, dipalmitoyl phosphatidylcholine (DPPC) (a saturated zwitterionic phospholipid) was used, since it represents the phosphatidylcholines, the most frequently found compound in mammalian cell membranes. Besides, four other lipids with chemical groups similar to those found in DPPC polar head group were used to investigate, specifically, charge effects in the interaction between acephate and lipid monolayer: DODAB - dimethyldioctadecylammonium bromide (with a positive quaternary ammonium in its head); DHP - dihexadecyl phosphate (with a negative phosphate group); DPPA -1,2-dipalmitoyl-sn-glycero-3-phosphate (with glycerol and phosphate); and DPTAP -1,2-dipalmitoyl-3-trimethylammonium-propane (with glycerol and choline in its head).

The π-A isotherms of DPPC showed no profile changes or displacement to different molecular areas in the presence of acephate in the subphase. However, for lipids with positive quaternary ammonium in its polar head (DODAB), as well as glycerol and choline (DPTAP), it was observed a displacement to smaller molecular areas, increase of collapse pressure and appearance of an inflexion point.

The PM-IRRAS spectra confirmed the effects in π-A isotherms: it was observed a shift in the peaks 943 cm^{-1} and 913 cm^{-1}, relative to the positive headgroup of DODAB and DPTAP, respectively. Therefore, chain order parameters were noticed for DPTAP, suggesting a higher lipid packing of the hydrocarbon chains. Although DPPC π-A isotherms have not shifted, the presence of the pesticide affected the choline and phosphate groups of the lipids, confirmed by the peak shift of PM-IRRAS spectrum of DPPC film at 953 cm^{-1} and 1076 cm^{-1}, respectively.

These effects can be attributed to the fact that the acephate molecules preferentially interact with the positively charged headgroup, decreasing the repulsion between the lipid molecules and, therefore, allowing a closer packing of the monolayer.

Acknowledgment: FAPESP (2018/23123-4), CNPq, CAPES.

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Conformational changes induced by histidine aqueous solutions on LS films of ethane-bridged bis-porphyrins

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Ethane-bridged bis-porphyrin derivatives play a preeminent role for the detection of various analytes in sensing applications [1]. The central metal ion is able to rule specific molecular arrangements upon analyte binding. Three bis-porphyrin compounds: a free base (metal free), Ni complex, and Cu complex, have been tested for histidine detection in aqueous media. Histidine is involved in various biological processes, including such deadly disease as lung cancer [2]. The conformational changes of bis-porphyrins, induced by histidine binding, can be detected by monitoring the Soret band position. The spectroscopic characterization, at the air-water subphase interface, indicates that, in the presence of histidine, the Ni and Cu metallated derivatives undergo conformational changes. This behaviour was confirmed when these two derivatives were deposited onto the solid support by the Langmuir-Schaefer (LS) technique [3]. A prototypal Surface Plasmon Resonance (SPR) detection system for histidine based on these two porphyrin LS films was developed. The Cu substituted compound based SPR system allows the histidine sensing down to nanomolar concentration. Furthermore, a SPR response of the Ni bis-porphyrin shows a semilogarithmic dependence on the histidine concentration up to 10^{-6} M proposing the use of these two porphyrins in a sensor array for the monitoring of histidine levels in plasma.

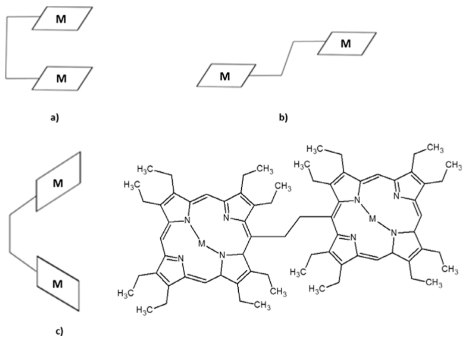

Fig. 1: (a) syn- (b) anti- and (c) tweezer conformers (d) chemical structure of bis-porphyrins. M represent the metal central ions or two protons in the porphyrin unit.

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Simulation of Langmuir Monolayers of Fluorinated Surfactants

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Fluorinated amphiphiles have been attracting much attention as they are known to be effective surfactants. The particularity of fluorinated carboxylic acids ($C_nF_{2n+1}COOH$) is their ability to form stable monolayers on a water surface, which contrasts to the behaviour of their hydrogenated analogue molecules, especially when the number of carbons in the molecule is lower than ten atoms [1,2]. Despite the fact that long acid chains containing more than 12 carbon atoms are considerably difficult to synthesize, their promising potential applications render them interesting to be studied. Molecular Dynamics (MD) simulations can be considered a great tool to analyse the behaviour of these monolayer systems by modelling their interactions at air/water interfaces [3].

In recent work, simulations of systems with a limited number of fluorinated amphiphiles deposited in water at low surface pressures and ambient temperatures show stiff and highly ordered domains with an unequivocal tendency to aggregate [4,5,6].

We performed MD simulations by using the All-Atom force field based on the Optimized Potentials for Liquid Simulations (OPLS-AA). The non-bonded molecular interactions contain a repulsion and a dispersion term that are modelled by the Lennard-Jones potential and the electrostatic interactions between two charged particles is expressed by means of specifying the atomic partial charges. To the existing force field a few of these parameters were changed in order to perceive if those alterations would better translate the expected behaviour.

The influence of the previously mentioned parameters is made by the analysis of the system's evolution by the change in their aggregation state. Moreover, we observed the coexistence of a tilted and vertical phases. Additionally, the Grazing Incidence X-ray Diffraction and X-ray Reflectivity spectra was obtained in order to compare the simulation results to the experimental ones. Furthermore, the influence of changing the force field parameters was extended to different fluorinated chain-lengths.

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P-20

Formation of multilayer graphene films by carbonization of polyimide Langmuir-Blodgett films

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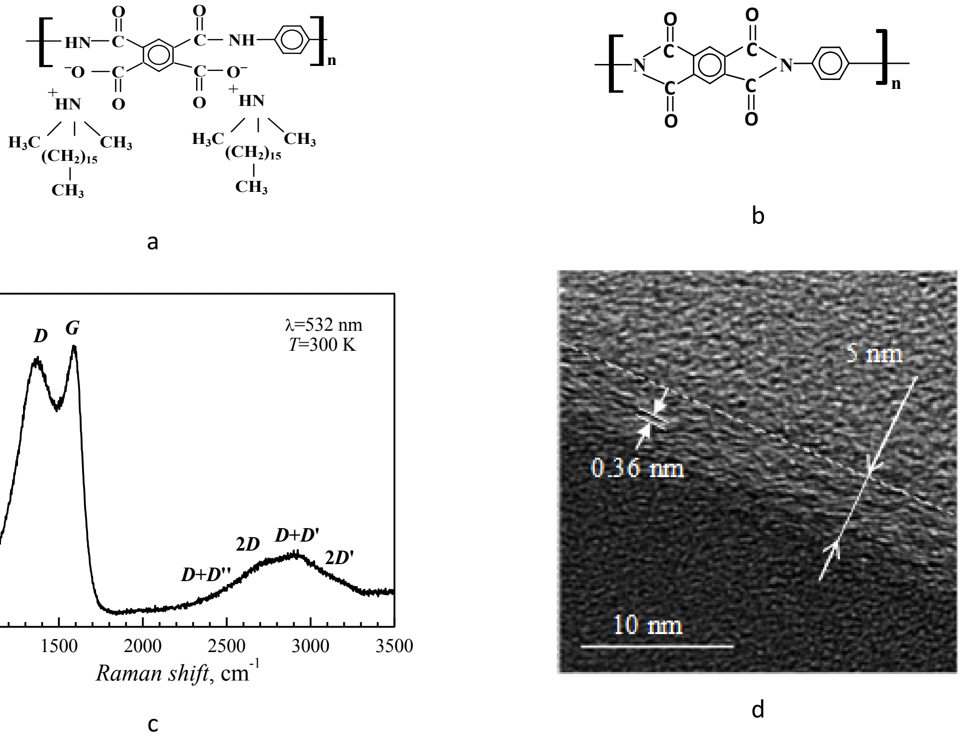
Despite the recent progress in fabrication of graphene layers on solid substrates, no appropriate method has been proposed for preparing high quality graphene films directly on dielectric and semiconductor substrates without transfer from a metal surface. This paper is the first report on forming multilayer graphene films on a quartz glass substrate by carbonization of the Langmuir-Blodgett (LB) films of polyimide (PI). The LB films of polyamic acid tert-amine salt (Figure a) containing 20, 10 or 5 layers were formed on quartz glass substrates. These films were converted to PI (Figure b) films by heating them to 400°C. Carbonization of PI films was carried out at 1000°C in vacuum. The Raman spectrum of the carbonized polyimide film (20 layers) was typical for grahite-like films (Figure c). Using the method of transmission microscopy, it has been shown that the film 5 nm thick consists of "stacks" of layers with a distance between the layers of 0.36 nm (Figure d), which is close to the interplanar distance in the graphite structure (0.34 nm). The surface resistance of the 5 nm film was 1.2 ± 0.2 kΩ, and the transmittance was 87% at $\lambda = 550$ nm. With the film thickness decreasing the surface resistance increased up to 18 kΩ, and the transmittance increased to 94%. But the analysis of the Raman spectrum showed that thinner films of multigraphene have more perfect structure.



a

b

c

d

Figure: Structure formulars of polyamic acid tert-amine salt (a) and polyimide (b); Raman spectrum (c) and cross-section (d) of carbonized polyimide film (20 layers).

SIRIUS: a Multipurpose Scattering and Spectroscopy Beamline devoted to the Study of Solid and Liquid Surfaces at the SOLEIL Synchrotron

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The SIRIUS beamline at the SOLEIL synchrotron (France) is devoted to the study of surfaces and interfaces by X-ray scattering and spectroscopy in the range of tender to hard X-rays (1.4 - 13 keV) [1, 2]. The main communities of SIRIUS users are either interested in soft matter systems, and in particular in soft interfaces (air-liquid interfaces, biomimetic systems, Langmuir monolayers, polymer layers, nanoparticles at interfaces ...), or in semiconductor/magnetic nanostructures (III-V materials, quantum wells, metallic or oxide multilayers ...). Most of the existing grazing incidence techniques are available on the beamline: diffraction and wide angle scattering (GIXD/GIWAXS), small angle scattering (GISAXS), fluorescence in total reflection (TRXF) or excited by Standing Waves (SWF), and surface absorption spectroscopy in diffraction conditions (DAFS/GIDAFS) [3].

We will present the main characteristics of SIRIUS and several research projects carried on the beamline. SIRIUS is equipped with two diffractometers allowing for a large versatility in the sample environment. A first diffractometer can handle cumbersome and heavy sample environments, while simultaneously allowing for various detection strategies thanks to two detector arms [1,2]. Experiments at low energies with limited absorption of the incident and scattered beams can also be carried using a second 4-circle vacuum diffractometer [4]. We will describe examples of research work in various fields: coupled measurements using fluorescence, diffraction and scattering in soft matter (Langmuir monolayers [5], meta-materials [6]), and in hard condensed matter (in-situ monitoring of Atomic Layer Deposition [7]), as well as recent work of SAXS measurements through hydrophobic surfaces mounted on a Surface Force Apparatus [8]. We will thus show the potential of SIRIUS for in-situ use of coupled techniques (using X-ray but also UV-visible spectroscopy) on diverse materials in various conditions.

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Imaging Ellipsometry in the field of Graphene and 2D-materials: From Flakesearch to Fast Full Wafer Characterization

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Recent progress in large area manufacturing of Graphene demands quality control and characterization tools of 2D-materials. The combination of imaging from microscopy (magnify microstructures) with the sensitivity for thin films (<0.1 nm – 10 µm thickness) of ellipsometry, makes imaging ellipsometry (IE) a powerful method to characterize thin-nest layers, e.g. monolayer of Graphene or few-layer of hexagonal Boron-Nitride. By using the contrast mode of IE we demonstrate a noncontact, fast characterization of cover-age, layer-numbers, defects and contamination of 2D-Materials. The sensitivity for thin films overcomes the contrast issues usually associated with conventional microscopes. So it is possible to visualize a Graphene mono-layer on a native 4" Silicon-wafer, without any requirements of further sample preparation as needed in optical microscopy. The Graphene layer can be seen in dark in the Figure 1. A scan of the complete 4" wafer only takes 47 minutes and reveals defects and contaminations of 10 µm. The imaging aspect allows a direct quantitative analysis of the sample as shown in Figure 2. To expand the capabilities of the proposed method the characterization of various materials is done on different substrates. The mapping of Graphene on Copper can be done without destroying the foil and enables a reuse of the catalyst foil is possible. Additional ellipsometric measurements are shown to characterize the Cupperoxide layer underneath the Graphene. The feature of ellipsometric measurement enables further methods as e.g. flakesearch [2] or optical characterization of 2D-materials [3]. Large area and spectroscopic investigations of hBN will be shown. Summing up we show that IE is applicable to a wide range of 2D-layered structures and a promising tool to fill the gap in 2D metrology for fast full wafer analysis and the characterization of hBN.

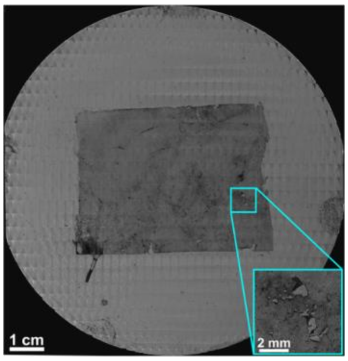

Fig. 2: Full 4" wafer scan recorded in the contrast mode within 47 minutes to detect cracks, foldings and impurities of 10 µm of the Graphene.

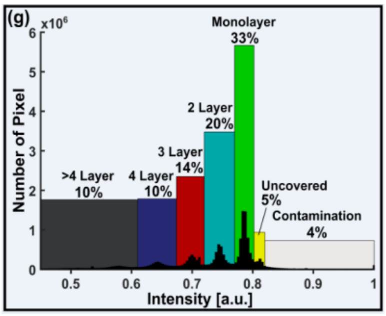

Fig. 1: Quantitative histogram analysis to calculate the coverage and contaminations of Graphene.

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Disentangled Deposition of Luminescent Electrospun Nanofibers Doped with Organic Dyes

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Luminescent organic nanofibers were fabricated by electrospinning the solution mixture of viscous polar polymer and rhodamine 6G dye [1]. SEM observations revealed that large volumes of nanofibers were successfully fabricated with constant diameter about 100 nm along the whole length of nanofibers. Fluorescence optical microscopy revealed that homogeneously luminescent nanofibers were deposited on a rotating cylindrical electrode with reduced entanglement at the rotating speed of 3000 through 3600 rpm, opening a novel usage as detached separate nanofibers: when intentionally embedded in commercial textiles, they will function as e.g. forensic tracking owing to the invisibility to naked eyes. As the present research aims to disperse the organic dye homogeneously over the whole length of the resultant nanofiber, dye aggregate nor dye crystal formation [2-4] should be avoided. As a demonstration, four types nanofibers were fabricated doped with either Rhodamine 6G, Rhodamine B, Rhodamine 101, or pseudo-isocyanine dye Nk1420 and were easily distinguished based on their photoluminescence.

The morphological observations indicated that the sufficient Coulomb force from the imposed electric field and the mechanical tension by the rotating cylinder were both necessary for the straight nanofiber depositions (Fig. 1). When the two conditions were fulfilled, straight nanofibers were electrospun on the cylinder, irrespective of the doped dye, at the line velocity of as much as 8m/s, without being torn into short fragments. This fact indicates a practical and speedy production was attained of disentangled nanofibers with 100 nm diameter typically. At the rotating speed of 3600 rpm, most of the nanofibers were deposited parallel to the rotating direction (vertical in Fig. 1, as A-A, B-B, *etc.*), although small fluctuations of the deposited direction suggest that whipping instability still remained in the electrospinning process. On the other hand, some rare fibers showed exceptionally curved profile (shown by arrows), which may be caused by a breakage of nanofibers in midst of the deposition process and therefore may be avoided through further improvement of the spinning condition.

The nanofibers which are indiscernible with the naked eye, but detectable by portable spectrometer, open up a novel security application of nanofibers: a small amount of electrospun nanofibers doped with designated selection of different dyes can be woven into conventional fibers of white T-shirt. The resultant T-shirts, white in appearance, but with weak photoluminescence at designated selection of luminescence peaks, can be distinguished by a simple spectrometer for security inspection.

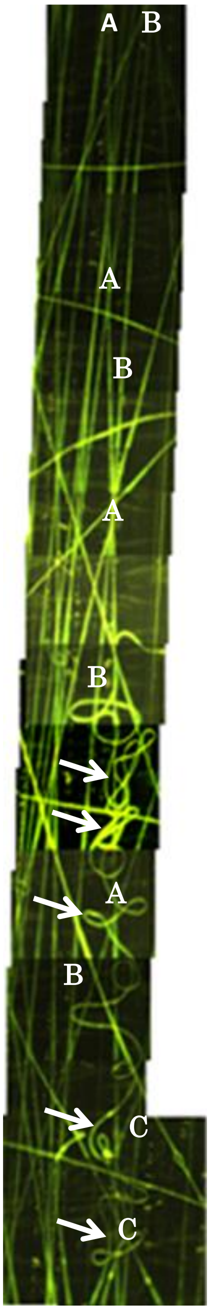

Fig. 1 Superimposed fluorescence images of Rhodamine 6G doped nanofibers electrospun on a cylindrical electrode rotating at 3600

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GRAPHENE OXIDE SHEETS ON FLEXIBLE INSULATING POLYMERIC FOLDS

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Graphene-based materials are of great interest for flexible electronics and energy devices [1]. An appealing and low cost approach consists on drying graphene oxide (GO) suspensions on flexible surfaces, prior reduction of reduced-graphene oxide (rGO) by laser thermolysis. Controlling and rationalizing the heterogeneities emerging during the drying process is of primary importance since this influences the film properties and needs to be fully understood for such particular colloids [2].

Herein, we have first examined the structure of thin films obtained by liquid deposition after drying aqueous dispersions containing different GO concentrations on pure Polyethylene Terephtalate (PET) and/or pure Polyoxydiphenylene-pyromellitimide (Kapton) folds. The local structures have been investigated by means of optical and atomic force microscopies in different positions onto the dried surfaces.

Laser thermolysis has been performed on different positions of the previous surfaces to form rGO as a function of the laser exposure time. The changes in local structure have been also followed by optical and atomic force microscopies. In order to rationalize the link between GO concentration, local structure and efficiency of thermoysis, electric contacts as been made at different positions in order to check out the resulting conductivity.

Using these results, we were then able to built efficient electrodes rGO-based for flexible supercapacitors with very good properties as well as transparent rGO-based surfaces which can be further incorporated in flexible 2D solar cells.

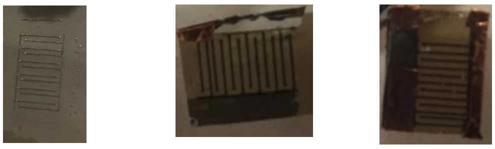

Fig. 1: Pictures showing different geometries of electrodes made of GO dried on PET.

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Nanoscale Spatially Resolved Chemical Analysis of Phase Separation in Pulmonary Surfactant (PS) Monolayers by Resonance-Enhanced AFM-IR Spectroscopy

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The pulmonary surfactant (PS) arrangement constitutes an excellent example of dynamic membrane polymorphism, forming a monolayer at the air/water interface along with associated bilayer reservoirs in water [1]. The key function of lung surfactant is to maintain the surface tension to enable breathing while preventing alveolar collapse. PS composition is around 91% phospholipids, 5-8% neutral lipids (mostly cholesterol), and 1-4% proteins [2]. The design of synthetic PS preparations is primarily aimed at efficiently treating acute respiratory distress syndrome (ARDS). Studies have showed that cholesterol and surfactant proteins play an important role in modulating the structure of surfactant membranes [3].

Microscopy, surface spectroscopy and analytical techniques have provided crucial information with regards to the chemical composition and surface activity of in vivo surfactant structures [3]. The architecture and behaviour of such structures can be further elucidated, at least in part, through the biophysical study and comprehension of model membranes. Planar-supported lipid monolayers formed by the deposition of pre-formed Langmuir monolayers onto solid surfaces are commonly used as model systems for probing membrane-related phenomena. AFM has become one of the most influential tools for the biophysicochemical characterisation of lateral phase separation of surfactant membranes [2].

We use resonance-enhanced atomic force microscopy (AFM)–infrared (IR), a technique coupling an atomic force microscope with a pulsed tunable IR laser source, to obtain high spatial resolution chemical analysis and morphological correlation of a synthetic PS monolayer (INFASURF®) transferred onto ultra-flat template stripped gold substrate by the Langmuir-Blodgett technique.

Preliminary results demonstrate that the deposition of the PS monolayer onto Au substrate produces a local enhancement effect that allows the measurements to be made on a nanometer thick monolayer. AFM-IR provides a better comprehension of the chemical composition correlated to structural phase separation.

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Multi-scale molecular modelling of silk-like proteins

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Proteins form in nature a wide variety of high performance, superior characteristics materials, such as e.g. spider silk. Silk fibers have very high mechanical strength and toughness, and several functionalities that rise from a hierarchical assembly of the proteins in the fibers. Recently, we associated the occurrence of liquid-liquid phase separation and the resulting formation of a bicontinuous network as prerequisites for fiber formation for a solution of synthetic silk-like protein constructs [1]. The finding rises a number of fundamental questions related to mechanism of protein fiber formation in the system, the role of liquid-liquid phase separation in it, and about the molecular level structure and interactions related with the formation of the bicontinuous network in the protein material.

Here, we employ both coarse grained and atomistic detail molecular simulations to examine the factors responsible for the formation of the protein condensate. We identify the attractive sites in the protein constructs and assess the binding affinities via atomistic detail modelling to resolve potential molecular level mechanisms of condensate formation. A coarse-grained bead model of the system reveals the large-scale structural scaling response resulting from the atomistic level interactions. We compare the modelling results with our cryo-TEM image analysis, analytical ultracentrifuge data, and changes in diffusion response of the proteins. We discuss the meaning of the findings for design of synthetic silk-like protein constructs and using such constructs for protein based fibers.

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Organophosphonate self-assembly on titanium dioxide

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We studied the self-assembly on TiO2 surfaces of organic molecules bearing a phosphonate group as the head and an amine group as the tail with carbon chain lengths of 6 and 12 methylene units. Mechanically polished Ti foils (covered by the native oxide layer) have been used as substrates for the molecular deposition. Previous to deposition, the substrates were plasma-cleaned in order to enrich their surfaces with hydroxyl groups, suitable for phosphonate coupling. Effect of post-deposition annealing on the molecular binding has been evaluated.

Molecular deposition has been monitored by combining Atomic Force Microscopy (AFM), differential Spectroscopic Ellipsometry (SE), Angle Resolved X-ray Photoemission Spectroscopy (AR-XPS), and Grazing Incidence Reflectance Fourier Transform Infrared Spectroscopy (GIR-FTIR),

AFM analysis of TiO2 surfaces after phosphonate deposition shows the presence of irregular, partially coalesced monomolecular islands on the surface. SE allows for a non-destructive fast check of the layer deposition. The comparison of Δ curves with simulations indicates that, assuming a reasonable value for the refraction index of ~ 1.5, the decrease in Δ fairly corresponds to the formation of a monomolecular layer.

XPS and GIR-FTIR analyses prove the occurrence of molecular deposition. Deconvolution of the XPS O1s core level region shows the presence of the Ti-O-P component and confirms the covalent coupling of the molecules to the surface. Angle Resolved XPS data indicate that longer chain molecules exposed the amino group at the outer interface, while GIR-FTIR clearly indicates that the annealing increases their order.

Biomolecular nanopatterns through peptide self-assembly

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We have studied the surface nanopatterning induced by the deposition of biomolecules on surfaces with different hydrophobicity. We have considered two short peptides of 10 and 14 amino acids with predominant α-helix native structure, and albumin as a large globular protein. These biomolecules were deposited on highly ordered pyrolytic graphite (HOPG) and hydrophilic freshly cleaved mica.

HOPG treated with a diluted aqueous solution of insulin or methionine showed the formation of three-fold oriented nanopatterned rippled domains of 6.2 nm periodicity on the HOPG surface [1]. Ripples were then used as a template for the deposition of small aggregates formed by the different biomolecules. AFM inspection showed that the aggregates organized on the HOPG surface forming elongated structures perpendicular to the ripples. Occasionally, the presence of few fibrils aligned along the ripples was observed. Peptide deposition onto a freshly cleaved mica surface resulted in the presence of single layer and double layer islands oriented in a three-fold symmetry on the sample surface.

These results show that the interaction of biomolecules with different kinds of surfaces gives rise to nanopatterns with different structures. Tuning the nature of substrate-peptide interaction could modulate the peptide self-assembly mechanism and therefore open the way to the development of new hybrid materials.

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Detection of Thiabendazole Fungicide/Parasiticide by SERS

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Thiabendazole (TBZ) is a fungicide and parasiticide widely used in vegetables and fruits to prevent mildew and other diseases caused by long period transport. The TBZ is also used in the pharmaceutical industry as an anthelmintic in several species of animals, and also in the control of parasitic infection in human beings. This work aimed the detection of TBZ in aqueous media through surface-enhanced Raman scattering technique (SERS), for which, the localized surface plasmon resonances (LSPR) play a key role.

The procedure adopted to synthesize silver nanoparticles (AgNPs) was similar to that described by Leopold and Lendl [1] through reduction of silver nitrate with hydroxylamine hydrochloride. The UV-Vis spectrophotometer Varian, model Cary 50, was employed to obtain the extinction spectra of AgNPs colloid (with and without TBZ). The Raman and SERS spectra were recorded using a micro-Raman Renishaw spectrograph, model in-Via, laser line at 514.5 nm. TBZ SERS spectra were obtained by adding an aliquot of 980.0 μL of AgNPs colloid (stock suspension) in a cuvette followed by the addition of 20.0 μL of TBZ solution with the desired concentration. The SERS measurements were carried out focusing the laser beam inside the cuvette (1.0 mL) containing AgNPs colloid + TBZ. This procedure was repeated, independently, three times for each concentration, using one batch of AgNPs.

The extinction spectra show the TBZ induces the aggregation of AgNPs in the colloidal suspension, which is dependent on TBZ concentration. The latter favour enhancing the TBZ Raman signal (SERS spectra in Fig. 1a), leading to TBZ detection at ppb level (limit of detection = 0.16 ppb). It is important to mention that the application of SERS as an analytical tool (Fig. 1b) is not a straightforward step due to the dependence of the enhancement factor on size, shape, and aggregation of the AgNPs. These results pave the way to detect TBZ from fruit and vegetable skins at low concentrations.

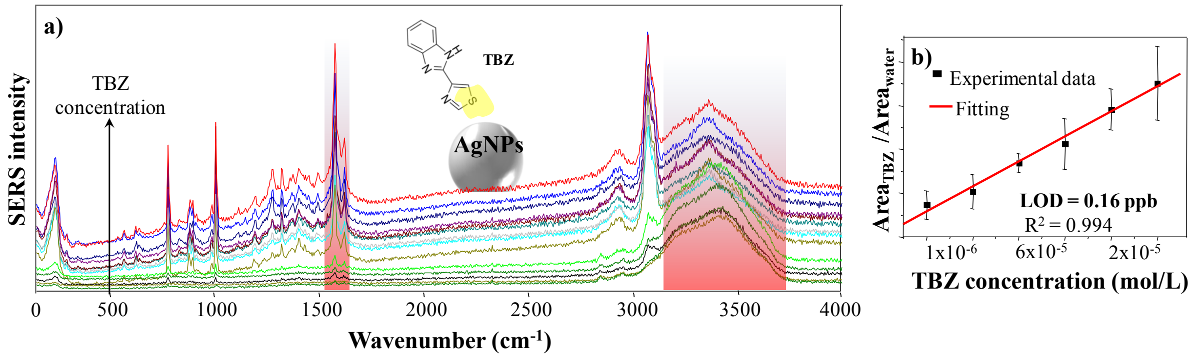

Fig. 1: a) SERS spectra of TBZ adsorbed on AgNPs colloid (inset); b) analytical curve; LOD: limit of detection.

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Hybrid graphene oxide/polysaccharide nanocomposites with controllable surface properties and cell adhesion

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The build-up of thin coatings with desirable and precisely tunable properties is of primary importance in medical applications. We demonstrate that the composition of the hybrid nanocomposites comprising polysaccharide matrix and graphene oxide (GO) exerts a strong effect on their surface properties and biocompatibility.

The in situ build-up of the hybrid films, followed by quartz crystal microbalance,have shown that after the deposition of GO-layer(s) the exponential growth typical for hyaluronic acid / chitosan films is impaired by the hindered chitosan interpenetration (hyaluronic acid is a non-diffusing specie). Incorporation of GO-layers into the highly hydrated hyaluronic acid / chitosan matrix does not affect the final thickness, but has a dramatic effect on the surface morphology and roughness dependent on both the number and the localization of GO-layers into the polymer matrix.The surface roughness of the hybrid multilayers increases systematically with the number of incorporated GO-layers, although single freestanding GO-sheets are extremely flat. We consider that GO affects the internal structure of the natural interpenetrating hyaluronic acid / chitosan multilayers.

The surface roughness in turn tunes the hydrophilicity and protein adsorption. Relatively weak effect of chemical cross-linking of the polymer matrix on the physicochemical features is found, since it affects mainly the bulk and to a lesser extent the surface of the films.

An important finding is the relationship between the films composition and thrombogenicity and cell (human umbilical vein endothelial cells) adhesion. Generally, the platelets and endothelial cells adhesion on the hybrid films originates from the concurrent impact of two factors – the number of GO-layers and their location into the polymer matrix. Approaching the GO-layer to the surface of the film and increasing the number of GO-layers increase its ability to adhere platelets and endothelial cells. The physicochemical features and biological response of the studied thin hybrid films provide an opportunity for various biomedical applications as surface coatings of blood contacting materials.

Synergy in the interaction of amoxicillin and methylene blue with dipalmitoyl phosphatidyl choline (DPPC) monolayers

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Understanding molecular-level mechanisms in the action of emergent pollutants is essential to correlate with their possible impact on living organisms in the environment and on human health. In this study, we investigate the interactions between two widely used compounds classified as emerging pollutants and Langmuir monolayers of 1,2-dipalmitoyl-sn-glycerol-3-phosphocholine (DPPC) that represent a simplified model of the lipidic structure of cell membranes. The pollutants studied were the antibiotic amoxicillin (AMX) and methylene blue (MB), a pharmaceutical drug also used as a dye in industry. AMX and MB were found to expand the surface pressure isotherms of DPPC, also affecting its morphology according to Brewster angle microscopy images. Significantly, when these compounds were mixed (MIX), monolayer expansion increased. The synergy in MIX activity was confirmed with in-situ polarization-modulated infrared reflection absorption spectroscopy (PM-IRRAS) measurements, which indicated that electrostatic interaction with DPPC head groups was considerably stronger than for either AMX or MB. An adduct formed between AMX and MB in MIX also caused the DPPC monolayer thickness to increase, as inferred from measurements with grazing-incidence X-ray scattering out of the specular plane (GIXOS), in contrast to the decreased thickness induced by AMX or MB. That a mixture potentiates the interaction between contaminants and cell membrane models may be relevant for cocktail effects on living organisms.

Acknowledgments

Brazilian agencies: FAPESP (2013/14262-7 and 2017/06534-8), CNPq (304836/2018-4), and CAPES.

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Perylene Bisimide Based Langmuir-Schaefer Films for Singlet Oxygen Photo-releasing in Photodynamic Therapy Applications

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Perylene bisimide (PBI) derivatives are a class of dyes with excellent optoelectronic properties, high chemical and thermal stability and high fluorescence quantum yield [1]. Therefore, these compounds are intensively used for different applications such as photovoltaic cells, selective sensing devices for aromatic amines or toxic gases [2].

In this work, an amphiphilic-asymmetric PBI derivative, the 2-(2-methoxyethoxy)ethyl)-9-(tridecan-7-yl) perylene bisimide derivative, was used as photosensitizer due to its high efficiency in singlet oxygen production upon photoexcitation processes [3]. This compound was immobilized onto a solid support, by Langmuir-Schaefer (LS) technique, to achieve a preliminary medical device for photodynamic therapy (PDT) applications able to induce death of some cancer cells.

First, the PBI solutions, at different concentrations, were characterized by spectroscopic measurements in order to select the opportune concentrations to spread onto a water subphase in a Langmuir trough. Then, physical-chemical and morphological characterizations of the obtained floating films were performed directly at the air/water interface by recording the Surface Pressure vs Area per Molecule curves, by Reflection Spectroscopy and by Brewster Angle Microscopy. The PBI was successfully transferred onto quartz substrates and the resulting multilayer PBI-LS films were characterized by UV–Vis absorption, fluorescence and polarization–modulation infrared reflection–absorption spectroscopy to study the supramolecular aggregation states of PBI and its optical properties.

The results showed that the photochemical behaviour of the PBI were well preserved even when immobilized, exhibiting a high efficiency in the singlet oxygen production upon light excitation. Therefore, the PBI-LS films were assessed in *in vitro* tests on human cervical carcinoma C13 cell line and their dark- and photo-toxicity was measured. This study revealed absence of cytotoxicity in dark conditions and a high photo-cytotoxicity toward cancer cells, making the PBI-LS films very promising photoactive devices for PDT application.

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Lyotropic Colloid-Stabilized Nanostructured Microemulsions At Surfaces

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Aqueous dispersions of lipid-based lyotropic liquid crystalline phases stabilized by nanoparticles have been extensively studied during the last decade [1-7] as potential nanocarriers for cosmetics or medical applications for example. However, their behavior and organization at liquid or solid surfaces are unknown despite the potential applications in film form.

We use a new approach, where the metastability of the dispersed microemulsions is used to observe their adsorption behavior at water-air interfaces. The thermodynamical behavior (isotherms of adsorption) is studied along with compression-decompression cycles. These measurements are coupled with Brewster microscopy to determine the structural features of the films at different densities and number of cycles. To check out the thermodynamic equilibrium of the structures observed, the results are compared to ones obtained by direct deposition the objects at the interface. We compare our new approach to structures obtained on solid substrates through spin coating and drop casting methods. We characterize the latter surfaces by atomic force microscopy (AFM) as a function of the concentration of deposition. All the structural results are rationalized and the processes are compared to determine the best approach to the formation of organized films made of lyotropic colloid-stabilized nanostructured microemulsions.

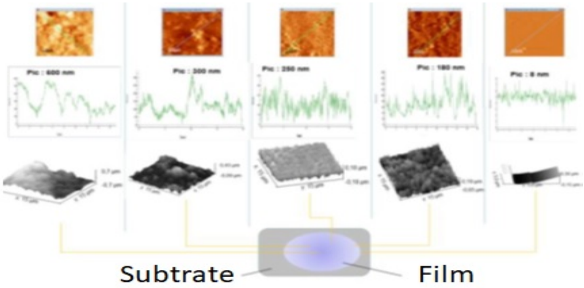

Fig. 1: Example of the different structures obtained by drop casting as viewed by AFM along the films.

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The Interaction of the TRPML1 N-terminus with biomembranes

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The transient receptor potential mucolipin 1 (TRPML1) ion channel is located both in the plasma membrane and in the lysosome. Its N-terminus is partly disordered and not always reported in the available TRPML1 cryo-EM structures [1]. It contains binding sites for PI(4,5)P_2 (plasma membrane lipid) and PI(3,5)P_2 (lysosomal lipid) [2].

We use different peptides that constitute the N-terminus: A "long" peptide (hsML1-N2-66), representing the complete N-terminus, and a "short" one (hsML1-N37-66), representing only the part which contains the PIP_2 binding sites.

We combine surface-specific vibrational sum frequency generation (SFG) spectroscopy with surface pressure measurements in order to get information on the adsorption of the peptides to a biomembrane and their conformation/orientation. We also investigate the role of interfacial water in the peptides/membrane interaction. We test the influence of POPG and PIP_2 on lipid binding and on secondary structure formation to get an idea on the specificity of these lipids for TRPML1 channel's N-terminus.

By testing different lipids and their mixtures we find that "short" and "long" peptides adsorb to these lipid monolayers, whereas the "front" one does not. The observation of the Amide I peak on the SFG spectra is observed for both "short" and "long" peptide in the case of POPG/POPC=60:40 and POPC/PIP_2=95:5 monolayers indicating a predominantly α-helical structure and orientation at the interface. It is also apparent that these peptides' SFG signal is enhanced in presence of negatively charged lipids. By monitoring the CO stretching vibration we obtain information on the effect of the peptide binding on the order in the phospholipid monolayer. In order to look at the membrane hydration we collected SFG spectra in OH-stretch region and observed that the injection of the "short" or the "long" peptide leads to the decrease of the OH-stretch peak intensity which is due to a perturbation or replacement of water molecules by these peptides when they interact with the membrane. The combination of these observations with those obtained from CD spectroscopy, Laurdan (fluorescent dye) assay, and NMR experiments provides a good understanding of the interaction of TRPML1 N-terminus with biomembranes.

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Ionic Liquids at the air-water interface

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Room temperature ionic liquids [ILs] are an important class of new solvents often considered as environmentally friendly media for chemical processes [1]. Accordingly, a large number of applications in several fields of science and technology have been proposed [1, 2]. ILs consist solely of ions which bulky and irregular shape, often comprising hydrocarbon chains and rings, inhibits solidification near room temperature [1]. The peculiar physicochemical properties of ILs are often associated with their mesoscopic organization or local order and with the formation of nanostructured domains resulting from the self-aggregation of the apolar and polar components of the ILs into domains [2]. However their complex relationship with water was not studied extensively in the literature, especially in presence of a large amount of water and at interfaces, despite the impact of its dispersion on environmental issues. We have used the Langmuir techniques at the air/water interface to study in a first approach the stability of n-alkyl-3-methyl imidazolium cation ($C_n$mim) associated with different anions at the air/water interface [3], and study in a more detailed manner the behavior of the more stable cation anion couple: $[C_n\text{mim}]^+[\text{Ntf2}]^-$. As depicted in figure 1, we have evidenced a time evolution of the monolayer at the air/water interface that we studied with different techniques from ⍰-A isotherms to x-ray fluorescence at grazing incidence.

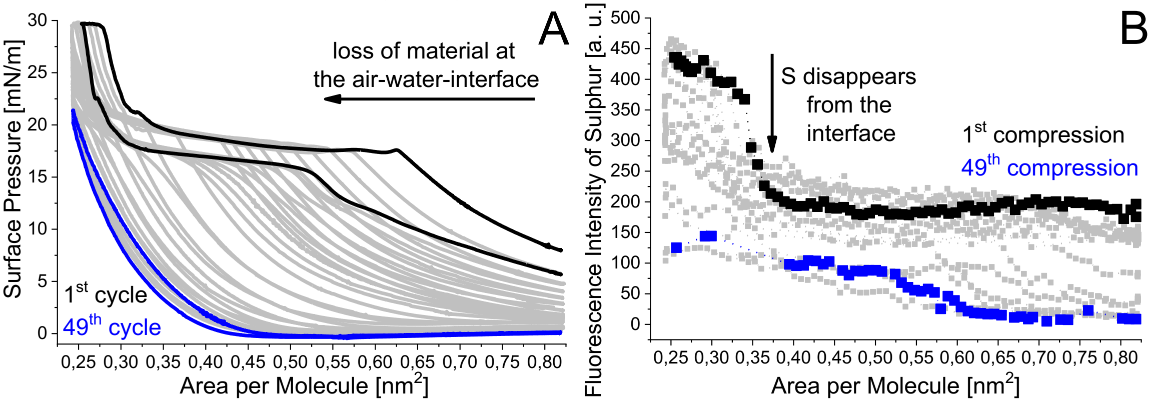

Figure 1: A) Evolution of the ⍰-A isotherms for 49 compression-decompression-cycles of $[C_{20}\text{mim}]^+[N(Tf)_2]^-$at 20 °C and B) Corresponding evolution of the x-ray fluorescence intensity of the sulphur K_α line coming from the NTf2 anion along 49 compression-decompression-cycles.

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Stretchable polymer gel films with high ionic Seebeck coefficient for highly sensitive temperature sensors

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Thermoelectric material enables direct conversion of heat into electrical signals. Hence, they can be used for heat flux and temperature sensors [1]. These applications are based on the Seebeck effect of the materials, i.e., the creation of a voltage across the material subject to a temperature gradient. The magnitude of Seebeck coefficients is different in different materials. For insulator materials with large energy gaps, their Seebeck coefficients are high, of 1 mV/K or higher. But the low electrical conductivity makes it difficult to perform reliable thermos-voltage measurements. For the poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) polymer films, the electrical conductivities are high, while the Seebeck coefficients are low, in the range or tens of µV/K.

Recently, another type of thermoelectric materials were emerging for thermoelectric applications for their ultrahigh Seebeck coefficients, reaching around 10 mV/K. This special class of materials, electrolytes, also possesses high ionic conductivity which is enough to ensure the easy thermos-voltage measurements. However, typical electrolyte materials are not stretchable, limiting their applications in the future stretchable wearable electronics.

In this work, a type of highly stretchable polyurethane (PU) was applied as the polymer matrix and ionic liquid (IL) was introduced as the ionic conductive filling phase. PU was dispersed in the water, and certain content of IL was added through high speed stirring. Then the dispersion was casted and dried overnight to obtain a uniform polymer electrolyte film. Thermoelectric properties, mechanical properties, ionic conductivities of the polymer film samples were tested. The results showed that the films are with high ionic Seebeck coefficients, and can be applied as highly sensitive temperature sensors.

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From Langmuir Blodgett to Grafted Films

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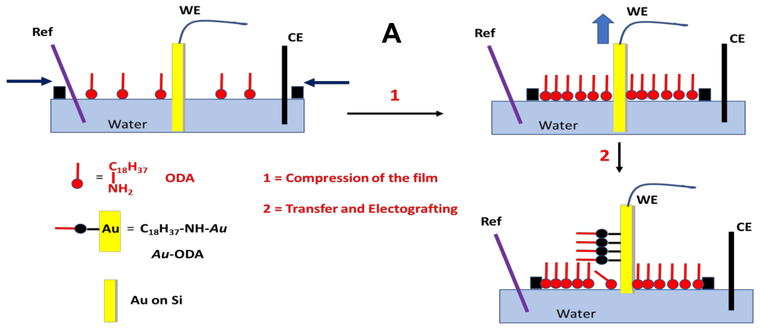
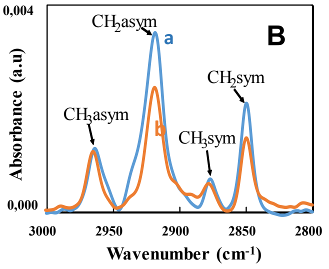
A new type of surface thin film is described; a compact crystalline monolayer film strongly attached to a gold surface was obtained by transfer of a Langmuir Blodgett (LB) film of octadecylamine (ODA) or alcohol (ODOH) to an Au or Pt surface and simultaneous oxidative electrografting of this film still in contact with the aqueous subphase.

Several methods are available for the functionalization of metallic surfaces with organic films: Langmuir films, thiols on gold, silanes and phosphonic acids on oxidized surfaces, electroreduction of diazonium salts on metal oxidized or not, electrooxidation of amines and alcohols on carbon, Pt and Au[1]. These different methods can be classified according to the strength of their attachment to the surface but also according to whether they provide organized or disorganized films. At one end of the classification, Langmuir-Blodgett films are only adsorbed, that is they are weakly attached, to the surfaces on which they are transferred but are solid crystalline monolayer films. At the other end one finds electrografted films that provide strongly bonded multilayered disordered films. This poster presents a new method (Figure 1A) for the surface modification of metallic surfaces that combines the interesting feature of each method: the obtained film is *an organized monolayer as LB films, strongly bonded to the gold surface as electrografted films, which is able to resist ultrasonication.* The films are characterized by water contact angle, ellipsometry, XPS, IRRAS, AFM and grazing incidence X-ray diffraction (GIXD). In particular IRRAS spectra indicate an organized film similar to that obtained with the well-established thiols on gold (Figure 1B). GIXD revealed alkyl chain ordering of grafted ODA films. These films can find possible applications in the field of biosensors.



A) setup of the experiment.



B)alkyl signals of
a) Au-ODA
B) Au-S-$C_{18}H_{37}$

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Controlled self-assembly of Langmuir-Blodgett colloidal crystal films of monodispersed silica particles on non-planar substrates

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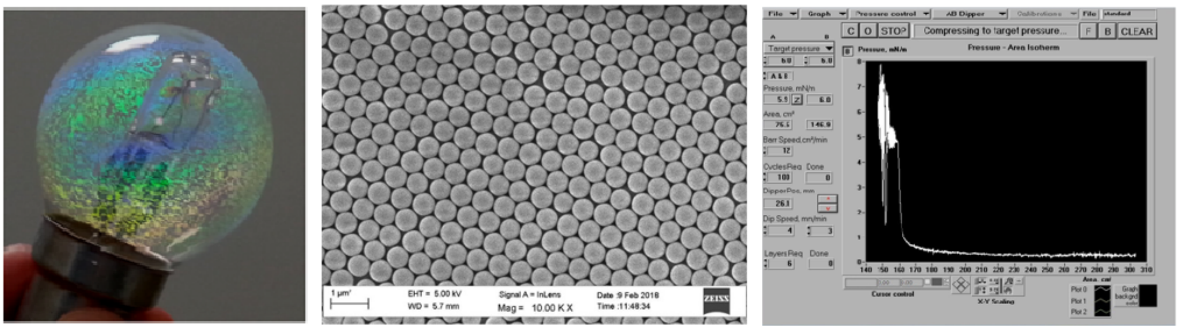
In this work we demonstrate the suitability of the Langmuir-Blodgett (LB) method for deposition of highly ordered colloidal crystal films of monodispersed silica particles onto non-planar substrates. We show that the barrier-controlled LB deposition method [1] can facilitate the high quality self-assembly of monodispersed silica particles into colloidal crystal films at the air-water interface and also allow for their successful transfer onto curved substrates such as light bulbs, flexible polymer foil rolls and light-guiding fibre cables. Such capabilities are important in terms of expanding the range of potential applications of colloidal crystal films that may emerge as a result of the ability to coat such materials onto various non-planar optical components and devices..

The figure below demonstrates that we have successfully adapted our LB method so as produce ordered colloidal crystal films on highly curved structures. In previous studies we have shown that such films, prepared from silica particles having diameters in the range 100 – 750 nm, are capable of acting as anti-reflective and/or diffractive layers [2,3]. However, as deposited these films lack the mechanical robustness that would be required for them to be used routinely in device applications.

In order to address this issue we have also examined different organic polymer materials and their infilling into the colloidal crystal films in order to form composite colloidal crystal - polymer films which exhibit greatly improved mechanical stability. We show here some possible materials choices for which the resulting composite films were able to display both the optical properties of the original colloidal crystal film and the enhanced mechanical robustness secured by the polymer film infilling, making them suitable for applications in optical devices.



Target pressure: 6.0 / 6.0
Pressure, mN/m: 5.9 / 6.0
Area, cm²: 76.5 / 146.9
Barr Speed,cm²/min: 12
CyclesReq: 100; Done: 0
DipperPos, mm: 26.1
Dip Speed, mm/min: 4 / 3
LayersReq: 6; Done: 0

Fig. 1: Shows the monodisperse silica particles film deposited onto a light bulb (on left), the scanning electron microscope image of the film's topology (in the middle) and the surface tension vs. area isotherm documenting the film's processing on a computer controlled Langmuir – Blodgett trough.

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Understanding the function of polyester-binding proteins: from bacteria to the air-water interface

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Biological structures provide inspiration for the design of polymeric materials with improved surface functionalities like bioinstructivity or anti-fouling properties for advanced medical applications. The ability of bacteria to tolerate exceptional amounts of polyhydroxyalkanoate (PHA) polyesters inside their cytoplasm, by coating them with surface-active amphiphilic proteins called phasins, has incited the functionalization of material surfaces with phasins carrying cell-directing elements [1]. Optimizing the physical adsorption of phasins requires deep understanding of the molecular arrangement during polymer-protein interactions to preserve their structural conformation while controlling surface coverage.

The Langmuir technique, combined with *in situ* Brewster Angle Microscopy (BAM) and Polarization Modulated Infrared Absorption Spectroscopy (PM-IRRAS) [2], was used to investigate i) the conformation, kinetics and stability of phasin PhaF (produced by *Pseudomonas putida* KT2440) at air-water and ii) its adsorption to Poly[(3-*R*-hydroxyoctanoate)-*co*-(3-*R*-hydroxyhexanoate)] (PHOHHx) and poly[(*rac*-lactide)-*co*-glycolide] (PLGA) copolyesters.

PhaF forms monolayers of 1-2 nm thickness, with an almost flat orientation of its α-helix at the air-water interface, which is maintained at 37°C. PhaF adsorption onto PHOHHx monolayers yields stable mixed-layers below π = ~15.7 mN/m, further penetration induces a phase separation and the collapse of the polymer layer. The adsorption kinetics of PhaF onto polyesters suggests that PHOHHx is more adequate substrate for functionalization than the less hydrophobic PLGA (Fig. 1). We envision that the optimal exposure of PhaF hydrophobic residues towards polyester surfaces, plus its ability to anchor nucleic acids or cell-adhesion-promoting peptides, can be exploited in the fields of drug delivery and gene transfection.

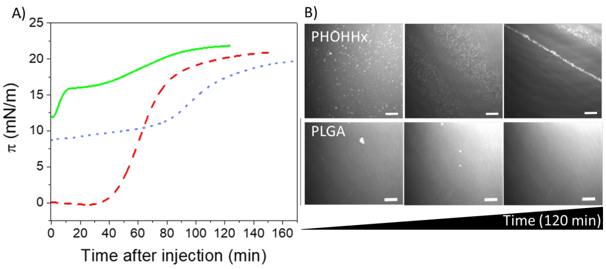

Fig. 1: A) PhaF adsorption onto water (dotted), PHOHHx (solid) and PLGA (dashed) B) BAM images of protein adsorption

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P-40

Reticulation of lipids self-assembly: electrical and mechanical correlation

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We present an original platform constituted of an engineered lipid monolayer which is used as the active sensitive layer and as ultra-thin gate dielectric in field effect transistor sensors. In living cells lipid membranes are known to constitute natural insulators which play an efficient role as barrier to both ionic and electronic transport across the membrane, associated with an electrical resistance of the order of several giga-Ohms in magnitude. However, despite excellent insulating properties, lipid bilayers and even more lipid monolayers have been poorly exploited in devices due to their inherent instability under application of an electric field, leading to damages caused mainly by an electroporation process occurring at low electric field. Furthermore a lack of mechanical stability is often observed.

We show that both the mechanical and chemical stabilities of lipid layers as well as their dielectric performances can be improved by changing the molecular structure of the lipids and by achieving intra-chain reticulations within the layer.

By studying mechanical rupture using nano-indentation and electrical breakdown, we demonstrate a relationship between the mechanical and electrostatic pressures. These results suggest a correlation between mechanical and electrical stabilities raising questions related to the rupture mechanism of the lipid layer and the role played by the molecular structuration and organization. We present our first experimental data (FTIR, X-ray diffraction, etc) of the reticulation impact on these properties.

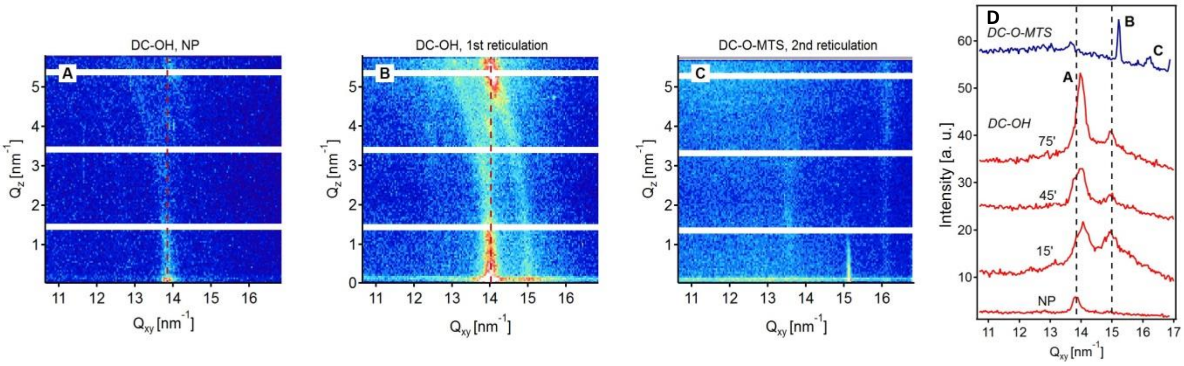

Figure 1 GIXD patterns for A) a non-reticulated DCOH lipid layer, B) after the 1st reticulation, C) after the 2nd reticulation. D) Evolution of in-plane spectra obtained at different time of reticulation using AAPH free radical.

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Funding: ANR-16-JTIC-0003-01 and SATT-Sud Est under contract N°147680.

P-41

Imogolite nanotubes partially transformed by decylphosphonic acid to form an interface active composite material

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The natural Imogolite clay ((HO)3Al2O3SiOH) with nano-tubular structure of 2-3 nm diameter is a promising candidate for polymer reinforcement, water treatment and other applications.[1] However, its hydrophilic external gibbsite like surface limits its use in hydrophobic environment. Among the different possible grafting functions for the outer surface, the phosphonic acid moiety is the most used. It shows strong reactivity with imogolite [1]. If the resulting products can be dispersed in a hydrophobic environment, the impact of the reaction on the tubular structure was never demonstrated and experimental evidence of grafted dispersed imogolite tubes with a brush-like layer on their exterior is still missing [2].

By combining different experimental techniques (SAXS, IR, MAS NMR, SEM and TEM) we systematically characterized the reaction product of imogolite and (decyl)phosphonic acid [3]. The product shows properties which were previously ascribed to grafted tubes [2], but no evidence for grafting is found. Instead, we observed the formation of a lamellar phase at the expense of the tubular structure, which forms a composite material with the remaining imogolite tubes (fig 1 A,B). This newly formed material has unusual interfacial properties able to stabilize water droplets in toluene (fig 1C). The exhibited reactivity can be explained by the surface chemistry of the imogolite. Beyond the particular case of imogolite reactivity, the approach described here opens an interesting synthetic strategy to form hierarchical materials from nanoparticles dispersion.

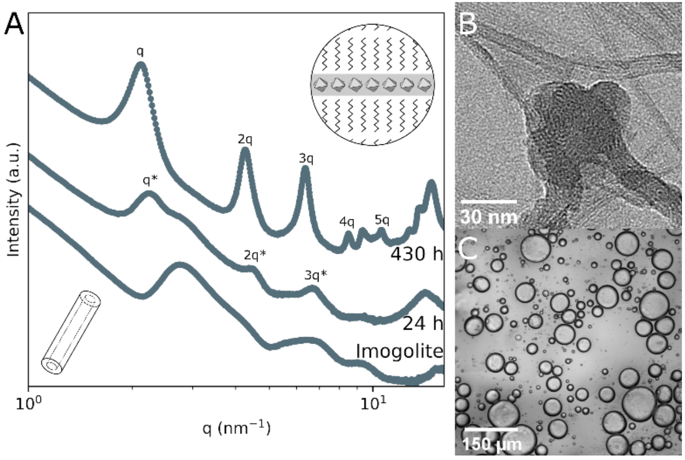

Fig. 1: (A) SAXS curves of dried imogolite and the product of the reaction with decylphosphonic acid. (B) TEM picture of lamellar phase within a network of aggregated imogolite tubes after the reaction. (C) W/O emulsion formed by the reaction product.

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Chemical bath deposited Al-doped ZnS thin films: Effect of Al content on their structural and optical properties

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Abstract

ZnS is one of the potential candidates as a window/buffer layer in solar cells and photovoltaic devices. It can substitute the highly toxic CdS buffer layer in heterojunction solar cells and enhance their blue response due to its wide energy band gap of 3.7 eV with a high optical transmittance of >85%. In order to achieve that purpose, its high resistivity (~ 107Ω.cm) must be reduced by several orders of magnitude. Without affecting its optical behavior, doping the ZnS by suitable dopants such as Al, Ga and Cu seems to be an effective way. In the present work, Al-doped ZnS thin films with different Al concentrations (2, 4, 6 and 9 %) were deposited on glass and Si substrates by chemical bath deposition using an aqueous solution containing ZnSO4, thiourea and ammonia. The Structural, Surface morphology and Optical properties were investigated as a function of Al content. The Raman analysis showed a pure cubic ZnS structure. SEM observations showed that all films displayed a granular morphology with grain size decreasing by increasing Al content. All films exhibited high transparency (over 70 %) in the visible spectrum. The optical band gap was estimated using optical transmission spectra and the obtained values range around 3.48 and 3.68 eV.

Keywords: ZnS thin films, Al-doping, Optical properties, structural, morphological and optical Properties

Formation of gold nanostructures for LSPR bio-sensing by microwave annealing

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LSPR bio-sensing is becoming the main stream bio-sensing technology nowadays because of the advantages of its relative experimental simplicity, high sensitivity, and suitability for a wide range of applications [1, 2]. Our recent work opened a possibility of utilizing LSPR phenomenon for detection of small molecules of mycotoxins in a combination with the method of total internal reflection ellipsometry (TIRE) and small-size bio-receptors such as half-antibodies and aptamers [2]. The key element in LSPR bio-sensing is metal nano-structures which can be produced by different methods. One of the simplest technologies of nano-structures formation is de-wetting of thin metal (gold) films typically achieved by annealing at temperatures of 500-550 °C for few hours [3]. In this work we report on the use of microwave annealing [4] of thin gold films for few minutes which gives very similar results, e. g. well-defined gold nano-islands on the surface of glass.

A series of samples of gold films (4, 5, 6, 8, and 10 nm in thickness) thermally evaporated on glass slides were subjected to annealing using either conventional oven (550 °C, 10 h) or microwave oven for 13 min. The microwave oven and ceramic kiln used for annealing are shown in Fig. 1a. The samples produced were characterized with SEM, XRD, and UV-vis absorption spectroscopy. As one can see from a typical SEM image in Fig. 1b, the microwave annealing has resulted in well-separated faceted gold nano-islands, larger than those obtained by thermal annealing. XRD measurements also show larger island dimensions and higher crystallinity for microwave annealed samples. UV-vis spectra in Fig. 1c show the transition from classical Drude dispersion for continuous 5 nm thick Au film to well-pronounced LSPR band in the visible spectral range for both types of nano-structured Au films. LSPR band for microwave annealed samples is slightly red-shifted in comparison with those thermally annealed which is in line with the differences in lateral dimensions of Au nano-islands.

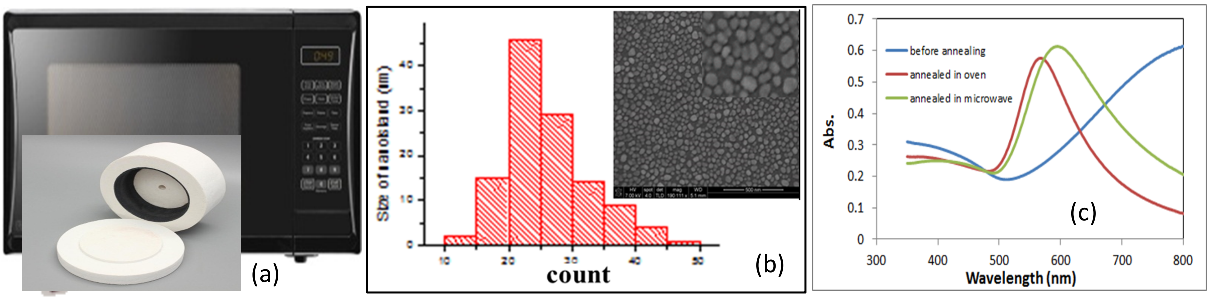

Fig. 1: Microwave and kiln (a); SEM image, size distribution (b) and UV-vis spectra (c) of Au nano-islands.

Comparison of the results obtained for the samples produced by conventional thermal annealing and microwave annealing showed the advantages of the latter in larger, more crystalline, and less size-dispersed gold nano-islands produced nearly 50 times quicker. The optical spectral properties of Au nano-islands produced by those two methods are similar and resulted in similar sensing characteristics (RIS, LDL) in LSPR/TIRE measurements.

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Hemi-micelles of semifluorinated alkanes at the air-water interface: influence of chain-length on the aggregate size by Molecular Dynamics

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Semifluorinated alkanes ($C_nF_{2n+1}C_mH_{2m+1}$, FnHm) are diblock molecules in which a perfluorinated and a hydrogenated segments are covalently bonded together to form a single chain. These so-called "primitive surfactants" are known to form nano-structures Langmuir films [1-2-3] in which a hexagonal 2D packing of domains (≈30 nm diameter) is observed at the surface of water or an adequate solid substrate (Fig. 1). The non-coalescence of the domains, even under compression, is particularly puzzling.

In recent work, we succeeded to model the formation, structure and size of the FnHm nano-domains using Molecular dynamics simulations. The simulated structures strikingly resemble the experimental ones.

In this work, we extended the previous methodology to investigate the influence of chain length of both the hydrogenated and fluorinated segments on the size and aggregation number of the hemi-micelles. The simulation results are able to reproduce the experimental data in remarkable agreement, including GIXD spectra.

In addition, first thermodynamic studies were performed to assess the properties of mixtures of FnHm, specifically stability and domain size as a function of composition.

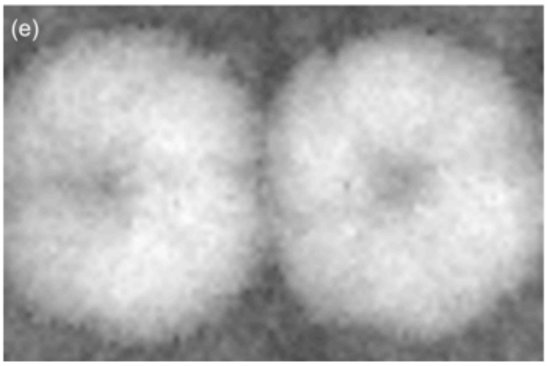

Fig. 1. Top-view topography (AFM-like) image of two simulated hemi-micelles of 1760 molecules, depicting a depression in the center (pit-centred micelle).

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