

10th/10^e

Student Symposium
Colloque Étudiant



Hosted by: University of Montreal

Tenu à: Université de Montréal



Roger-Gaudry Pavillion

Pavillon Roger-Gaudry

Sept. 8, 2014

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If anyone is interested in being a part of the student committee or helping to organize this event next year, please email Petr at csacs.chemistry@mcgill.ca or talk to one of the people thanked above.

Les personnes intéressées à participer au comité étudiant ou à l'organisation de cet événement l'an prochain sont invitées à communiquer par courriel au csacs.chemistry@mcgill.ca ou à parler avec une des personnes remerciées ci-haut.

Schedule

- **9:00-9:50: Registration, breakfast and poster setup, Honour Hall**
- **9:50-10:00: Opening remarks, M-415**
- **10:00-11:20: Student talks (x4), M-415**
- **10:00-10:20: Oleksandr Bushuyev (McGill University),**

Photomechanical Azobenzene Crystals: Mechanistic Insights into Their Transformations

- **10:20-10:40: Lucie Giraud (Université de Montréal),**

Adhesion and Friction Between Supported Core Shell pH Sensitive Polymeric Nanoparticles

- **10:40-11:00: Frédéric Byette (Université de Montréal),**

Self-Assembled pH-Responsive Films Prepared from Mussel Anchoring Threads

- **11:00-11:20: Sirine Bayram (McGill University),**

Short Ligands Induce Chained Self-Assemblies and Plasmon Coupling in Silver Nanoparticles

- **11:20-11:30: Coffee break, Honour Hall**
- **11:30-12:30: Invited speaker - Prof. Aida, M-415**

Advanced Molecular Design of Functional Soft Materials

- **12:30-14:00: Lunch, Honour Hall**
- **13:00-14:00: Poster session 1 (even numbers), Honour Hall**
- **14:00-15:00: Student talks (x3), M-415**
- **14:00-14:20: Abbas Ghanbari (University of Montreal),**

Poly(2-hydroxybutanoic acid) Crystallization

- **14:20-14:40: Hu Zhu (University of Montreal),**

Mixed Solvent Induced Morphology Evolution in Dip-Coated PS-P4VP Thin Films

- **14:40-15:00: Ghulam Jalani (McGill University),**

Regeneration of cartilage and bone using hydrogels/upconverting nanoparticles hybrid materials

- **15:00-15:30: Coffee break, Honour Hall**
- **15:30-16:50: Student talks (4x), M-415**
- **15:30-15:50: Katherine Bujold (McGill University),**

Development of Sequence-Responsive DNA Cages for the Selective Release of Oligonucleotide Therapeutics

- **15:50-16:10: Marziye Mirbagheri (McGill University),**

Geometrical dependency of moisture transport rate in porous media

- **16:10-16:30: Elodie Rousset (University of Montreal),**

Ruthenium (II) quaterpyridine complexes and polynuclear assemblies for photocatalysed hydrogen production

- **16:30-16:50: Mohamed Amine Mezour (Université McGill),**

Directing the Assembly of Gold Nanoparticles with Two-Dimensional Molecular Networks

- **17:00-19:00: 10th Anniversary Banquet, Honour Hall**
- **17:30-18:30: Poster session 2 (odd numbers), Honour Hall**
- **18:30-18:45: Voting for best talk and poster, Honour Hall**
- **18:45-19:00: Announcement of the winners/closing remarks, Honour Hall**

Horaire

- **9h00-9h50: Enregistrement, déjeuner et installation des affiches, Hall d'honneur**
- **9h50-10h00: Discours d'ouverture, M-415**
- **10h00-11h20: Présentations orales d'étudiants (x4), M-415**
- **10h00-10h20: Oleksandr Bushuyev (McGill University),**

Photomechanical Azobenzene Crystals: Mechanistic Insights into Their Transformations

- **10h20-10h40: Lucie Giraud (Université de Montréal),**

Adhesion and Friction Between Supported Core Shell pH Sensitive Polymeric Nanoparticles

- **10h40-11h00: Frédéric Byette (Université de Montréal),**

Self-Assembled pH-Responsive Films Prepared from Mussel Anchoring Threads

- **11h00-11h20: Sirine Bayram (McGill University),**

Short Ligands Induce Chained Self-Assemblies and Plasmon Coupling in Silver Nanoparticles

- **11h20-11h30: Pause-café, Hall d'honneur**
- **11h30-12h30: Conférencier plénier - Prof. Aida, M-415**

Advanced Molecular Design of Functional Soft Materials

- **12h30-14h00: Dîner, Hall d'honneur**
- **13h00-14h00: Session d'affichage 1 (nombres pairs), Hall d'honneur**
- **14h00-15h00: Présentations orales étudiantes (3x), M-415**
- **14h00-14h20: Abbas Ghanbari (Université de Montreal),**

Poly(2-hydroxybutanoic acid) Crystallization

- **14h20-14h40: Hu Zhu (Université de Montreal),**

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- **15h00-15h30: Pause-café, Hall d'honneur**
- **15h30-16h50: Présentations orales étudiantes (4x), M-415**
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Directing the Assembly of Gold Nanoparticles with Two-Dimensional Molecular Networks

- **17h00-19h00: Banquet 10^e Anniversaire, Hall d'honneur**
- **17h30-18h30: Session d'affichage 2 (nombres impairs), Hall d'honneur**
- **18h30-18h45: Vote pour les meilleures présentations, Hall d'honneur**
- **18h45-19h00: Annonce des meilleures présentations / Discours de fermeture, Hall d'honneur**

Keynote Lecture – Conférence plénière

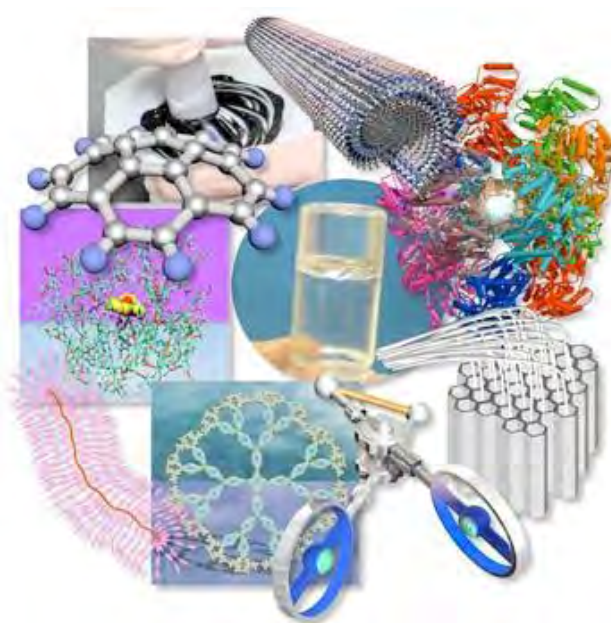
Professor Takuzo Aida

*Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo
Riken Center for Emergent Matter Science*

Advanced Molecular Design of Functional Soft Materials

Owing to a tremendous progress in supramolecular chemistry, one can now construct and tailor a variety of desired nanostructures, where assembling events involved mostly operate thermodynamically. On the other hand, if one may consider developing materials for practical applications, we certainly need to design kinetically preferred hierarchical structures. However, there is no rational molecular design strategy for this issue.

Here we report some of our recent achievements related to this issue. The first topic focuses on how one can translate a tiny molecular motion into a macroscopic motion.^[1] We found that, by hot pressing using unidirectionally drawn Teflon sheets, a polymer brush containing triply connected azobenzene units in its side chains form a hierarchically ordered bimorph film, where all the cylindrical brush objects align homeotropically with respect to the film plane, and the film shows a macroscopic photomechanical motion. The second topic features the development of 'aqua material', characterized by an ultralow content of organic components and an ultrahigh content of water.^[2] This material can be prepared by mixing in water clay nanosheets and a dendritic molecular binder with sticky guanidinium ion functionalized dendron wedges on both sides of a poly(ethylene glycol) spacer, giving rise to the formation of a well-developed 3D network over a macroscopic length scale. The third topic features our quite recent achievement on the formation of a linear semiconducting heterojunction by stepwise supramolecular polymerization.^[3,4] This sequential control in supramolecular polymerization gives a clue for how to escape from a thermodynamic equilibrium. We also succeeded in designing the first columnar ferroelectric liquid crystal,^[5] ATP-responsive bionanotube,^[6] and a modular approach to complicated nanostructures.^[7]



References

1. Wang et al., *Nature* 2010, 463, 339
2. Hosono et al., *Science* 2010, 330, 808
3. Wei et al., *Science* 2011, 334, 340
4. Aida et al., *Science* 2012, 335, 813
5. Miyajima et al., *Science* 2012, 336, 209
6. Biswas et al., *Nature Chem.* 2013, 5, 613
7. Fukino et al., *Science* 2014, 344, 499

Talks – Présentations orales

1-Photomechanical Azobenzene Crystals: Mechanistic Insights into Their Transformations

Oleksandr Bushuyev, McGill University (Christopher J. Barrett)

A family of halogen-bonded azobenzene cocrystals with diverse photo-mechanical and thermochemical properties were prepared through halogen-bonded self-assembly. Cocrystallization of the same photomechanically-active azobenzene building block with different cocrystallization partners yielded a family of crystalline solids exhibiting a range of photo-mechanical properties, from those exhibiting isomerization without any changes to crystal shape to those undergoing a crystal-to-crystal isomerization accompanied by large-scale crystal bending. The latter permitted the use of variable temperature single crystal X-ray diffraction to in situ monitor structural changes in a crystal undergoing solid-state isomerization. The presented cocrystallization strategy thus opens a door to rapidly synthesize new photomechanical crystals and systematically explore factors of crystal structure and composition controlling photomechanical motion in the solid state.

2-Adhesion and Friction Between Supported Core Shell pH Sensitive Polymeric Nanoparticles

Lucie Giraud, Université de Montréal (Suzanne Giasson)

Charge, conformation, hydrophobicity, and hydrogen bonding all play significant roles in controlling adhesion and friction between polymer-coated surfaces in aqueous media, although the precise way in which they function is still debated. In order to elucidate the mechanisms underlying good lubricity in aqueous based systems, static and dynamic interaction forces between two pH-sensitive nanoparticle monolayers irreversibly attached onto mica surfaces were investigated using the Surface Forces Apparatus. The nanoparticles (NPs) were core-shell made of a polystyrene (PS) core covered with a polyacrylic acid (PAA) shell. The weakly charged polyelectrolyte shell (PAA) can undergo changes in the degree of ionization upon changes in pH or ionic strength allowing physico-chemical properties such as volume, surface potential and structure to be modulated.

Surface force measurements were carried out to assess the adhesion, friction and resistance to the compression and shear of the nanoparticles (NPs) under different pH. The normal and friction forces between two opposing NPs monolayers were strongly dependent on the pH. The range of the normal forces increased with pH suggesting an increase in the swelling of the immobilized NPs associated with an increase in the degree of ionization of the PAA. The normal forces were purely repulsive regardless of pH indicating the absence of adhesion. The friction forces significantly decreased with increasing the swelling of the NPs. Comparison between other reported studies suggest that the effective lubrication mechanisms involve the facility with which polymers under compression remain hydrated and hold a significant amount of water at the surfaces to be lubricated.

Such NPs are promising materials for designing smart materials whose surface properties (adhesion, friction, permeability) and interactions with the surrounding environment can be modulated in response to an external stimulus or signal.

3- Self-Assembled pH-Responsive Films Prepared from Mussel Anchoring Threads

Frédéric Biette, Université de Montréal (Christian Pellerin)

The byssus is a series of collagen-rich fibers securing mussels to solid surfaces immersed in seawater. The complex but elegant heterogeneous assembly of the various proteins in the threads is responsible for their remarkable mechanical properties combining strength and extensibility. Along with the well-known biocompatibility and biodegradability attributed to collagen-based materials, these mechanical properties are highly desirable to produce biomaterials for soft tissue engineering and drug delivery applications. In order to replicate the byssus natural features and properties, we prepared a soluble byssus protein hydrolyzate (BPH) that can generate water-insoluble self-standing films. Atomic force and scanning electron microscopy revealed the presence of self-assembled collagen-like fibrils at the surface of the films. Infrared spectroscopy analysis of the film formation showed that insolubility is caused by the self-assembly of polypeptides from the hydrolyzate into antiparallel β -sheets, aggregated β -strands and collagen triple-helix structures. The mechanical properties and water swelling measurements on the films can be reversibly pH-modulated by modifying the electrostatic interactions between the ~ 30 mol% of charged amino acids. Optimal mechanical properties and minimum swelling are obtained at the isoelectric point (pH 4.5). Higher or lower pH treatment reversibly decreases their stiffness and strength and increases their swelling ratio. Altogether, our results show that byssus proteins are an interesting sustainable feedstock for preparing new solid-state pH-tunable biomaterials.

4- Poly(2-hydroxybutanoic acid) Crystallization

Abbas Ghanbari, University of Montreal (Robert E. Prud'homme)

Poly(2-hydroxybutanoic acid) [P(2HB)] is a biodegradable polyester with a chiral carbon in the skeletal chain which yields two stereoregular enantiomers, namely poly(S-2-hydroxybutanoic acid) [P(S-2HB)] and poly (R-2-hydroxybutanoic acid) [P(R-2HB)]. In practical applications understanding the crystallization behavior of biodegradable materials is essential for regulating the biodegradability, as well as the physical properties. Therefore, in this work, we investigate the isothermal crystallization of synthesized P(S-2HB) using differential scanning calorimetry (DSC), polarized optical microscopy (POM), and in situ atomic force microscopy (AFM). To form a comprehensive picture of P(S-2HB) crystallization, the nucleation, growth kinetics, and morphologies of the crystals were examined in detail. An equilibrium melting temperature T_m° of 130.3 °C is obtained according to the Hoffman-Weeks method. The lamellar and radial growth rates exhibit a bell-shaped temperature dependence with a maximum around 400 ± 50 nm/min occurred at crystallization temperature equal to 79 ± 1 °C. Analysis of the growth rates using the Z-test of Lauritzen and Hoffman-Lauritzen model shows that crystallization occurs in Regime II, end surface free energy Δ_e of P(S-2HB) growing crystal is 60 ± 10 ergs/cm², and the work of chain folding q is between 18 and 24 kJ/mol, which is in the range of moderately stiff chains without bulky side-groups.

5- Short Ligands Induce Chained Self-Assemblies and Plasmon Coupling in Silver Nanoparticles

Sirine Bayram, McGill University (Amy Blum)

The controlled organization of plasmonic nanoparticles into highly anisotropic 1D arrays and networks offers a platform to attune the flux of surface plasmons. Extended planar nanoparticle assemblies are capable of subwavelength optical guiding, which can result in the miniaturization of integrated optical, photonic and biosensor devices.[1] We herein report a facile, green and aqueous method to generate extensive 1D self-assembled superstructures of metallic silver nanoparticles by controlling the degree of nanoparticle surface passivation and polarization by either of the three ditopic ligands: cysteine, cysteamine and dithiothriitol. UV-Vis reveals the characteristic surface plasmon band of silver colloids (SP) centered at 390 nm as well as a low-energy longitudinal plasmon band (LP) that is suggested to arise from uniaxial coupling of the isotropic surface plasmons.[2] The plasmon coupling is reinforced by the Hydrogen-bonding offered by the end moieties of the ligands chosen. The spontaneous formation of the chains is due to the alignment of dipoles within short inter-dipole distances to minimize the enthalpy cost as well as the disorder provided by the branched domains. Transmission Electron Microscopy (TEM) is also used to unveil the morphologies of the superstructures that self-assembled in the form of discrete chains, branched and looped chains as well as interconnected chain networks. The stability of the assembled structures colloids seems to depend on the degree of aggregation as revealed by TEM and LP: SP magnitude ratio. Simulations of the extinction spectra of random chains of silver nanoparticles suspended in water were performed using discrete dipole approximation (DDA) and Comsol methods. Simulation data agreed with the experimentally observed persistence of the transverse plasmon band and the appearance of a longitudinal band whose position and broadness are influenced by the number of chain particles, the polarizability of the particles and the inter-particle distance.

1. W. L. Barnes, A. Dereux, T. W. Ebbesen, *Nature*, 2003, 424, 824.

2. S Lin, M Li, E Dujardin, C Girard, S Mann, *Advanced Materials*, 2005, 17, 2553

6- Mixed Solvent Induced Morphology Evolution in Dip-Coated PS-P4VP Thin Films

Hu Zhu, University of Montreal (C. Geraldine Bazuin)

Polystyrene-*b*-poly(4-vinylpyridine) (PS-P4VP) thin films were dip-coated from mixed-solvent solutions of methanol and THF where the methanol/THF ratio was varied systematically. The selectivity of methanol for P4VP and of THF for PS induces a morphology evolution in the thin films, starting from the dot morphology using pure THF, then evolving successively to stripes, to lamellae, back to stripes, then back to dots with increasing methanol in solution. The evolution was associated with a phase inversion from P4VP nanostructures (dots, cylinders) in a PS matrix using pure THF to PS nanostructures (cylinders, dots) in a P4VP matrix in methanol-rich solutions. This was supported by rinsing experiments in selective solvents and by the distinct periodicities of the dots and stripes on either side of the lamellar morphology. Since the dot morphology observed by AFM can correspond to

either spheres or vertical cylinders and the stripe morphology to either horizontal cylinders or vertical lamellae, cross-sectional TEM investigations were performed. In addition to the influence of the mixed solvent composition on the thin film morphology, its interplay with the effect of other factors was determined, particularly the dip-coating rate (varied from 1 to 80 mm/min), which, along with the solvent, determines film thickness and nanostructure orientation.

7- Development of Sequence-Responsive DNA Cages for the Selective Release of Oligonucleotide Therapeutics

Katherine Bujold, McGill University (Hanadi Sleiman)

Recent advances in DNA nanotechnology have enabled the self-assembly of finely tuned DNA nanostructures that show great potential for drug delivery. Here, we present progress towards the development of a 3D DNA cage that can selectively target prostate cancer cells. We demonstrate the self-assembly of a dynamic and robust DNA nanocube that can be selectively unzipped from a 3D prismatic structure to a flat two-dimensional structure in the presence of a specific sequence of nucleic acids. Using the tpc-hpr fusion mRNA gene product (found uniquely in the LNCaP human prostate cancer cell line) as a trigger, we show the selective opening of this cube and its internalization in cancer cells by confocal microscopy. We also demonstrate early work towards the encapsulation a siRNA targeting prostate cancer within the construct and its specific release in LNCaP cells using antisense oligonucleotides (AON) that target Bcl proteins. Finally, the addition of dendritic DNA (D-DNA) chains on the exterior of the structure was found to modulate its uptake profile so that it may reach its target without the use of transfection agents.

8- Regeneration of cartilage and bone using hydrogels/upconverting nanoparticles hybrid materials

Ghulam Jalani, McGill University (Marta Cerruti)

Lanthanide doped upconversion nanoparticles (UCNPs) are exciting alternatives to the conventional fluorophores because of their ability to convert low energy NIR light to high energy light spanning from UV to NIR region via an ultrafast sequential two photon absorption. These UCNPs show deeper tissue penetration, narrow emission bands, low signal to noise ratio, low cytotoxicity and good physical and chemical stability. In this study we have developed a new nanocomposite system consisting of a bioactive, nontoxic, fast thermogelling, highly stiff injectable hydrogel from chitosan and hyaluronic acid via ionic and covalent co-crosslinking with an ability to encapsulate live cells and $\text{LiYF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}@\text{SiO}_2$ UCNPs at physiological conditions. We use the UCNPs for in-vivo tracking of hydrogel degradation and on-demand drug delivery. The in-vivo tracking of hydrogel degradation products and on-demand drug release via non-invasive optical method with deep tissue penetration holds a great potential for bioimaging, controlled drug delivery and tissue engineering.

9- Geometrical dependency of moisture transport rate in porous media

Marziye Mirbagheri, McGill University (Reghan Hill)

Moisture transport in porous materials is of interest in many industrial and engineering domains as civil, chemical and biochemical engineering and wood, pharmaceutical, food and paper industry. Many chemical reactions, biological processes and material preservations depend on moisture transfer rate. Thus having a good understanding of this process and the ability to control it is crucial.

Depending on the structure and type of the medium various mechanisms dominate this phenomenon including bulk, surface and Knudsen diffusion for pure diffusive mass transfers. In many works all of these mechanisms are taken into account in one effective diffusion coefficient, in which the porous medium is treated as a continuous phase.

The present mechanisms determine how the effective diffusivity is influenced by geometrical parameters of porous structure as volume fraction, porosity, tortuosity, surface area fraction, etc. In the absence of surface and Knudsen diffusion, for instance, effective diffusivity and particle size have a monotonic relation, whereas, addition of interfacial exchange kinetics and surface diffusion to the system will alter this to a non-monotonic variation.

This study investigates influential parameters when diffusion in dispersed and continuous phases is coupled with interfacial phenomena.

10-Ruthenium (II) quaterpyridine complexes and polynuclear assemblies for photocatalysed hydrogen production

Elodie Rousset, University of Montreal (Garry S. Hanan)

Radial architectures allow fine topological control of functional molecular structures. Assemblies based on the coordination of metal centres enable a fine-tuning of the properties by careful choice of building blocks. We present here the complete study of a family of complexes $\text{Ru}(\text{bpy})_x(\text{qpy})_{3-x}$ (where $\text{bpy} = 2,2'$ -bipyridine, $\text{qpy} = 4,4':2',2'':4'',4'''$ -quaterpyridine and $x = 1,2,3$). Theoretical calculations were performed to support the interpretation of the photophysical properties. The complexes display longer-lived excited state lifetimes and improved quantum yields in comparison to reference $\text{Ru}(\text{bpy})_3$ which suggests that these complexes are good photosensitizers. Preliminary results for hydrogen production will be discussed for these complexes and radial assemblies of RuRe_6 and RuCo_6 systems.

11-Directing the Assembly of Gold Nanoparticles with Two-Dimensional Molecular Networks

Mohamed Amine Mezour, Université McGill (Bruce R. Lennox)

The precise organization of nanoparticles into well-defined patterns at surfaces and interfaces offers for versatile approaches to the development of novel technologically important materials. Among the various existing nanopatterning methods, molecular self-assembly has gained increasing attention as a highly accurate, efficient, and low-cost 'bottom-up' approach. In the present study, lamellar patterns resulting from the adsorption of three p-dialkoxybenzene derivatives on HOPG have been investigated as molecular templates for directing the assembly of thiol-capped gold nanoparticles (AuNP). STM characterization at liquid-solid interface reveals the periodic arrangement of AuNP on top of the SAMN, in epitaxial relation with the latter and long-range order. The templating process is driven by van der Waals interactions of the alkyl chains of the SAMN and AuNP, plus the matching of the alkyl chain lengths. The templating effect demonstrated here opens a new avenue to explore the assembly of new object such as quantum dots, proteins, chromophores.

Posters – Présentations par affiche

1- A Visible-Light-Mediated Synthesis of Carbazoles

Shawn Parisien-Collette, University of Montreal (Shawn Collins)

The photosynthetic preparation of N-aryl- and N-alkyl-bearing carbazoles utilizes continuous flow, visible light, and a Cu- or Fe-based photosensitizer. The method is mild and efficient, and allows the straightforward synthesis of a variety of carbazoles with different substituents, heterocycles, and complex carbon architectures.

2- Synthesis, Crystal Structure and Photophysical Properties of Novel Pyrene/Helicene Hybrid

Anne-Catherine Bedard, University of Montreal (Shawn Collins)

Synthesis of a novel helically chiral aromatic resulting from fusion of pyrene and 5-helicene has been accomplished using photoredox catalysis as the key step. Flow chemistry was investigated for the synthesis of the target compounds and its photophysical properties were investigated.

3- New Complexes of Hydroxyamidine/ α -Aminonitrone (AMOX) Ligands for discrete supramolecular assemblies

Mathieu Leblanc, University of Montreal (Garry S. Hanan)

N,N'-Disubstituted hydroxyamidines, also known as α -aminonitrones (AMOXs), display high steric and electronic modularity, as a wide range of substituents can be introduced on the α -carbon and/or on the nitrogen atoms. Hence, they afford precise electronic tunability, facilitated by the delocalization on the amidine backbone. They are excellent bidentate ligands that form stable 5-membered rings with metal ions. In our research, we exploit these properties by investigating their incorporation into supramolecular assemblies, based on coordination chemistry and/ or hydrogen bonding, by introducing a bridging substituent on the α -carbon which opens a second coordination site on the ligand. The properties of the metals used will dictate the function of the final assembly (eq.: light-harvesting properties with Ru, Re, Ir or magnetic properties with Co, Fe or Mn). The type of assembly is induced by the coordination geometry of the metal ion, in combination with the coordination vectors of the ligand (e.g.: tetrahedral metal + parallel coordination vectors = grid type assembly). Herein, we present the synthesis and characterization of bis-AMOX ligands, and their precursors.

4- Rhodium Paddlewheel Complexes as Hubs for Chromophore Assemblies

Daniel Chartrand, University of Montreal (Garry S. Hanan)

In our general objective of forming discrete assemblies of multi-chromophoric units for homogenous solution photocatalysis studies, we use stable rhodium amidinate dimers as structural backbone for

polynuclear assemblies. Multiple grafting approaches were tested and we were able to prepare assemblies of one to four rhenium chromophores.

These were tested for photocatalysis of Hydrogen with a cobalt catalyst to study if the chromophore assembly still remained active versus free chromophores.

5- Electronic Excited State Redox Properties for BODIPY Dyes Predicted from Hammett Constants: Estimating the Driving Force of Photoinduced Electron Transfer

Richard Lincoln, McGill University (Gonzalo Cosa)

Here we formulate equations based solely on empirical Hammett substituent constants to predict the redox potentials for the electronic excited state of boron-dipyrromethene (BODIPY) dyes. We utilized computational, spectroscopic, and electrochemical techniques toward characterizing the effect of substitution at the positions C2, C6, and C8 of the 1,3,5,7-tetramethyl BODIPY core. Working with a library of 100 BODIPY dyes, we found that highest occupied molecular orbital (HOMO) energies calculated at the B3LYP 6-31g(d) level correlated linearly with the Hammett σ_m value for substituents at position C8 and with Hammett σ_p values for substituents at positions C2 and C6. In turn, we observed that LUMO energies correlated linearly with Hammett σ_p at position C8 and with Hammett σ_m at positions C2 and C6. Focusing on a subset of 26 dyes for which reduction potentials were either previously available or measured herein and ranged from -1.84 to -0.52 V (a full 1.3 V), we found a linear relationship between redox potentials in acetonitrile and HOMO and lowest unoccupied molecule orbital (LUMO) energies determined via density functional theory (DFT). A linear correlation was thus ultimately established between redox potentials in acetonitrile and Hammett substituent constants. Combining this with equations derived for the linear relationship existing between the zero vibrational energy of the excited BODIPY and Hammett substituent constants enabled us to provide the parameters toward predicting the oxidizing/reducing power of photoexcited 1,3,5,7-tetramethyl BODIPY dyes in their singlet excited state.

6- Texture Transformation Process for Confined Nematic Liquid Crystals

Alireza Shams, McGill University (Alejandro D. Rey)

Nematic liquid crystals inside micro-capillaries exhibit a large variety of textures with point defects, line defects and loop defects, whose stability is dictated by factors such as geometry and temperature. In this work, we present theoretical studies of pattern formation of nematic liquid crystals disclination under capillary confinement including a branching processes from $m=+1$ disclination line to two $m=+1/2$ disclination curves that describes the nucleation and growth regime of the textural transformation from radial to planar polar textures. It is found that the branching and disclination shape adjust to the capillary confinement by regulating their tension-to-bending stiffness ratio in such way that the resulting branch angle is close to $1/3$. The disclination loop growth is a result of the tension/bending elasticity balance and the loop dilation rate depends on the curvature and normal velocity of the disclination. We also found in a conical capillary, the cone aperture increases the bending stiffness but decreases the curvature of the disclination. These competing effects lead to a

decrease in total disclination curvature, increase in elastic energy and volume of the branching region. These new findings based on the 'nematic elastica' are also useful to predict other novel structures that arise in different geometries of interest and can be used to assess the Frank elasticity of the nematic liquid crystal.

7- Multiple shape memory effects of polymers with cholic acid and photo-crosslinking cinnamate group

Kaojin Wang, University of Montreal (Julian X. Zhu)

A series of methacrylate-based copolymers with oligo(ethylene glycol) and cholic acid pendant groups were synthesized via free radical polymerization. They show broad and tunable glass transition temperatures (T_g), which result in the dual and triple shape memory effects. The fixity and recovery ratios for the dual-shape memory are up to 99% and 89%, respectively.

8- Rheological and electroacoustic spectroscopies of nanoparticle doped hydrogels

Vahid Adibnia, McGill University (Reghan Hill)

Hydrogels, generally defined as cross-linked polymer networks that are swollen by water, form an important class of soft matter that are often biocompatible. Embedding hydrogels with nanoparticles can significantly enhance the hydrogel properties, providing, for example, improved mechanical performance, and novel biological and physicochemical characteristics. Characterizing nanoparticle properties and understanding the particle-hydrogel interactions is vital for optimizing the properties and performance of nanoparticle-hydrogel composites. While rheological spectroscopy of nanoparticle-doped hydrogels can involve characterization of dynamic mechanical properties at test frequencies in the range of about 0.001 to 100 Hz, electroacoustic spectroscopy is a powerful, non-invasive diagnostic that can encode the particle dynamic electrophoretic mobility at MHz frequencies. The mobility spectrum can help unravel the many combined influences that a polymer network has on the nanoparticle dynamics. This study experimentally examines the rheological and electroacoustic response of nanoparticle-doped hydrogels. A commercial rheometer is used to systematically explore how particle concentration influences gel storage and loss moduli. Using a commercial ESA instrument, we show how the applied electric-field frequency influences the nanoparticle mobility. These data help to elucidate nanoparticle interactions with hydrogels, also furnishing insights that will help to establish more general properties of the interactions at the nanoscale.

9- Development of Novel Materials containing Cholic Acid and Porphyrins

Edgar Aguilar, Université de Montréal (Julian X. Zhu)

The interest in cholic acid has been rising in recent years due to its important applications in fields like medicine and materials science. This is mainly due to its amphiphilic properties. On the other hand, porphyrins are well known from their broad absorption spectra. They are also useful in large application fields such as electronic devices and medical technologies.

In this work, we decided to join the properties of cholic acid and porphyrins in order to make a novel compound, which possesses a porphyrin core and multiple units of cholic acid molecules attached around it.

The first part shows the total synthesis and characterization of the novel compounds, obtained by click-chemistry reactions. This technique has been explored in recent years due to its soft conditions, easy workout and high yields. In order to use click chemistry, we synthesized cholic acid molecules bearing an azide function, and porphyrin molecules possessing alkyne sites. The characterization was made by ¹H and ¹³C NMR, mass spectrometry, and UV-vis.

Taking into account the amphiphilic properties of the cholic acid molecule, we tested the final compound in inclusion experiments with pyrene as a probe.

10-Dental Materials containing Bile- and Amino-acid derivatives

Eric Habib, Université de Montréal (Julian X. Zhu)

Traditional resin composites commonly used for dental restorative materials contain monomers that have demonstrated toxicity in multiple studies, in addition to containing the oestrogenic compound bisphenol A. Here we demonstrate the synthesis and properties of a new class of resin monomers based on methacrylated bile acids or amino acids. The physical properties and polymerization conversion rates of these monomers show promise and could lead to a new generation of resin composites for dental materials.

11-Synthesis and Characterization of Novel Biocompatible Polymers made from Bile Acids

Élyse Champagne, University of Montreal (Julian X. Zhu)

Materials used in biomedical applications need to be biocompatible and ideally biodegradable. Bile acids are naturally occurring compounds found in humans that possess these qualities, amongst others, such as tunable flexibility and thermal shape memory, once polymerized. Previously, shape memory polymers were synthesized based on these molecules using Ring Closing Metathesis (RCM) and entropy-driven ring opening metathesis polymerization (ED-ROMP).[1] However, the resulting polymers were lacking biocompatibility because of the Grubbs' catalyst first and second generation persistence. We have synthesized a cholic acid-based polymer using Candida Antarctica Lipase B (CALB) enzymatic polymerization to replace the ED-ROMP step, which greatly decreases the ruthenium contamination (310 to 12 ppm)[2]. For now, the obtained polymer was characterized by Nuclear Magnetic Resonance (NMR) and Thermogravimetric Analysis (TGA). The missing peaks at 6.4 and 6.2 ppm and the degradation temperature of about 340 °C tend to prove the structure obtained.[2] Indeed, previous literature shows matching results. Future goals involve determining the thermo-mechanical properties of the resulting polymer, using Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA), and further reducing the metal contamination by completely eliminating Grubbs' catalyst from the synthetic route.

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12-New Bile Acid Dimer - Synthesis and Molecular Modeling

Nicolas Levaray, Université de Montréal (Julian X. Zhu)

Bile acids are natural amphiphilic compounds that exist in the digestive tract of humans and animals. They possess a convex hydrophobic face and a concave hydrophilic face. Due to the amphiphilicity of bile acids, these materials are capable of responding to changes in polarity of the media by exposing either their hydrophobic or hydrophilic face. Our group has previously synthesized dimers, trimers and tetramers based on cholic acid. These oligomers can form reversible pockets for binding and encapsulating metal ions and hydrophobic or hydrophilic species. Different covalent bonds including triazoles, esters, amides or ureas were used to link the cholic acid moieties. We have synthesized new dimers based on cholic acid linked together through a shorter bridge in one case, and a longer linker in another case. The formation of host-guest pockets is investigated by using polarity-sensitive probes such as pyrene or coumarin 343. In an effort to obtain a better understanding of the host-guest interaction, the two dimers were designed to have simple linear spacers to simplify molecular modeling.

13-Tailoring the reaction path in the on-surface chemistry of thienoanthracenes

Laurentiu E. Dinca, INRS Varennes (Federico Rosei)

The systematic study into the behavior of different tetrathieno-anthracene (TTA) isomers on different transition metal surfaces can provide insight into the mechanisms underlying the chemistry of these molecules, leading to an improved understanding of how to tailor molecule/substrate pairs to produce desired products. More precisely, by investigating for any existing correlations between isomerizations within the molecule (specifically, the positioning of the thiophene moieties), and the chemical nature of the reaction products (radicals) we may be able to gain some degree of predictive control over these surface-confined reactions. Of particular interest are to predict selectivity for intra- or intermolecular reactions and to facilitate strategies to identify and design precursors capable of targeting specific reactions.

14-Complex thermoresponsive behavior of diblock polyacrylamides

Yong-guang Jia, University of Montreal (Julian X. Zhu)

Diblock thermoresponsive copolymers poly(N-n-propylacrylamide)-b-poly(N,N-ethylmethylacrylamide) (PnPA-b-PEMA) of various block lengths were synthesized by sequential reversible addition-fragmentation chain transfer (RAFT) polymerization. The work aims at

understanding the complex thermoresponsive behavior of block copolymers whose aqueous solutions change, with increasing temperature, from a transparent solution to a cloudy and then to a clear and finally to a turbid liquid. The thermoresponsive behavior depends on the polymer concentration and is reversible with certain hysteresis. Dynamic light scattering and atomic force microscopy results help to assign the first cloud point to a transition from unimers to micellar clusters. The longer PnPA block relative to the PEMA block and the hydrogen bonding between the PnPA and PEMA blocks are determining forces for the formation of micellar clusters. Further rise in temperature leads to restructuring and dissociation of these loose clusters into smaller micelles due to further dehydration of the PnPA block and disruption of hydrogen bonds between the PnPA and PEMA blocks, resulting in an optically clear solution. A second cloud point appears again when the micelles start to aggregate. A pseudo-phase diagram was obtained for N-substituted polyacrylamides, providing guidelines towards the rational design of thermoresponsive copolymers showing two or more responsive temperatures.

15-Integration of amphiphiles with DNA nanostructures: orthogonal assembly languages working together

Tom Edwardson, McGill University (Hanadi Sleiman)

The selective association of hydrophobic side-chains is a strong determinant of protein structure. We have observed a parallel mode of assembly in DNA nanotechnology by using small, simple and DNA minimal nanostructures as scaffolds for site-specific positioning of hydrophobic groups. Dendritic DNA amphiphiles (D-DNA) were synthesized, containing an addressable oligonucleotide portion and a hydrophobic alkyl dendron at the 5' terminus. It was found that anisotropic organization of these hydrophobic domains on the 3D scaffold results in a new set of assembly rules; dependent on spatial orientation, number and chemical identity of the D-DNA on the cubic structure. When four amphiphiles are organized on one cube face, the hydrophobic residues engage in an intermolecular 'handshake' between two cubes, resulting in a dimer. When eight amphiphiles are organized on the top and bottom faces of the cube, they engage in a 'handshake' inside the cube. This produces a monodisperse micellar core within the DNA nanostructure, which can encapsulate small molecules and release them in the presence of a specific DNA sequence.

Expanding on the synthetic aspect of this work, a new approach to produce sequence-controlled polymers attached to DNA has been developed. We report a stepwise solid-phase synthesis for the generation of completely monodisperse and sequence-defined DNA-polymer conjugates. These polymeric modifications to DNA display self-assembly and encapsulation behavior which is highly dependent on sequence order. These novel DNA conjugates are promising candidates for targeted drug delivery applications. Combining the highly specific recognition of the oligonucleotide sequence with the orthogonal association of rationally designed hydrophobic moieties can lead to a variety of structures with diverse biological applications.

16-Structure Characterisation Method for Biological Plywoods

Oscar Aguilar Gutierrez, McGill University (Alejandro D. Rey)

The twisted plywood architecture is a ubiquitous biological and synthetic fibrous composite structure, analogous to that of cholesteric liquid crystals. Twisted plywoods can show ideal or non-ideal structures and are formed via equilibrium or non-equilibrium liquid crystal self-assembly processes. A

key to the structure characterisation of plywood films is the specification of the local and global helix vector $h(x)$ and pitch $p(x)$ of the cholesteric order. Previous extensive work demonstrated that oblique cuts of the plywood give rise to arc-patterns that depend both on the unknown incision angle and the unknown pitch $p(x)$, thus making the precise 3D cholesteric reconstruction ambiguous. We present an efficient method based on geometric modelling and new visualisation software that determines unambiguously the important characteristics of biological plywoods.

17-Block Random Copolymers: Design, Synthesis, and Application

Mohammadtaghi Savoji, University of Montreal (Julian X. Zhu)

Synthesis of thermo-responsive block copolymers from random copolymers allows tuning the phase transition temperatures of individual blocks and introducing multiple cloud points in a single polymer. The same technique may also be applied for other stimuli, and both pH- and thermo-responsive diblock random copolymers have been designed. The dual stimulus-responsive diblock random copolymer was synthesized by a sequential reversible addition-fragmentation chain transfer (RAFT) polymerization. A well-defined block copolymer in the form of $AnBm-b-ApCq$ was prepared where A, B and C are N-n-propylacrylamide (nPA), 2-(diethylamino)ethyl methacrylate (DEAEMA) and N-ethylacrylamide (EA), respectively. This polymer shows interesting 'schizophrenic' behavior in aqueous solutions. Most recently, we found that different types of aggregates may be obtained in aqueous solution by adjusting block composition and length in preparation of diblock random copolymers. They may also switch between different morphologies under controlled conditions, all in aqueous media. Hence, both micelles and vesicles may form by proper selection of block ratio, temperature, and pH without adding any organic solvent. This stimuli-induced morphological change is promising for encapsulation and release of molecular probes in aqueous solution.

18-Chain mobility and glass transition in polymer nanocomposites

Lili Zhu, McGill University (Bruce R. Lennox)

The properties of polymers which are confined at nanometer length scales differ greatly from the properties in the bulk. Many literatures have been reported in order to get a generality of nano-confinement effect. Despite of these researches, the confinement effect on polymeric chain behaviors is still a difficult subject in condensed physics, which is mainly due to the difficulties in the interface characterization for nanomaterials. In this study, we utilized 1H solid-state nuclear magnetic resonance (1H SSNMR) to characterize the structure and the mobility of the polymers/gold nanoparticles (Au NPs). Then the glass transition temperature (T_g) of polymers/Au NPs with varied molecular weight and particle size was measured. The change trend of the molecular mobility was found to be consistent with the deviation in T_g . On the basis of the experimental results, we demonstrated that the surface confinement dominates molecular mobility as well as T_g . Moreover, the core-shell model for the confinement on Au NPs was proposed. This work is essential to better understand the confinement effect and can be extended to investigate the dynamic properties of polymer composites with more complex structures, such as NPs with binary polymer brushes.

19-Grafting of Polymeric Ligands and Phosphonic Acids onto ZrO₂ and TiO₂ Nanomaterials

Magali Chever, McGill University (Linda Reven)

This work looks at the grafting of small molecules and polymeric ligands onto metallic inorganic nanosurfaces of sphere and rod-like shape. The grafting serves primarily to modify the material's surface and the goal is to optimize the formation of stable and strongly bound inorganic-organic composites. Spherical ZrO₂ nanoparticles (4 nm diameter) were synthesized following a non-aqueous method with benzyl alcohol as solvent; while anatase TiO₂ nanorods (16x2 nm dimensions) were obtained from a low temperature (80 °C) hydrolysis of titanium isopropoxide (TTIP) in oleic acid. The concentrations reported are 0.18 mmol ZrO₂/mL and up to 1.21 mmol TiO₂/mL. Carboxylic acid-functionalized polystyrene (PS) was grafted onto ZrO₂ in a proposed brush-like manner and stable attachment was confirmed by FT-IR data. A graft density of 0.24 chains/nm² was obtained by TGA analysis for the PS mono-layer brush and DLS measurements confirmed a 22.4 nm hydrodynamic diameter. Attachment of phenylphosphonic acid (PPA) and PPA/1-dodecylphosphonic acid (DDPA) mixtures was done on the TiO₂ nanorods. Solid-state NMR (¹H-, ³¹P- and ¹³C- NMR) spectra of samples were obtained to confirm attachment of the ligands and investigate the ratios of the mixtures used, with the future goal of determining the special distribution of the ligands on the inorganic NP core.

20-Nanoparticle/liquid crystal hybrids based on hydrogen bonding interactions

Mahdi Roohnikan, McGill University (Linda Reven)

The goal of this research project is to develop stable nanoparticle/liquid crystal (NP/LC) composites based on hydrogen bonding interactions. Hydrogen bonding is relatively strong non-covalent interaction, promoting stability, yet is still reversible, allowing the annealing of defects. Most work on LC nanocomposites has been based on thermally unstable gold nanoparticles. Here highly stable monodispersed metal oxide nanocrystals (ZrO₂, TiO₂) synthesized by a non-aqueous hydrolysis method, will be dispersed into benzoic acid based LCs. Doping LCs with metal oxide NPs can improve their electro-optical properties such as the switching speed in response to electrical fields. Reciprocally, LCs can reversibly template the NP spatial arrangement and provide electrical control over the NP optical properties. In the metal oxide NP- benzoic acid LC model system, hydrogen bonds will be formed between pendant COOH groups on the surface of functionalized NPs and LC host molecules. The interaction between the LC and the unfunctionalized metal oxide NPs will also be investigated. Solid-state NMR, polarized optical microscope (POM) and transmission electron microscopy (TEM) will be the main analysis tools to study interactions, mesomorphical behavior and the dispersion properties of these nanocomposites.

21-Surface Probe Microscopy (SPM) Facility Centre for Self-Assembled Chemical Structures

Beatrice Lego, Université McGill (Amy Blum)

The CSACS-SPM facility offers access to equipment to the academic and industrial scientific community. Our three AFM instruments are equipped with a variety of accessories that allow experiments in controlled atmospheric environment, in liquid, in humidity environment and at variable temperatures:

- MultiMode NanoScope IIIa (Digital Instrument)
- MultiMode 8 (Bruker)
- MFP-3D (Asylum Research)

The CSACS SPM Facility offers service on:

- Atomic Force Microscopy (AFM) (available modes: Contact, Tapping or Alternative, automated Peak Force, Non-contact)
- Scanning Tunneling Microscopy (STM)
- Force measurement
- Magnetic Force Microscopy (MFM)
- Student training
- Sample analysis services

The facility has expertise, but not limited to, on imaging biological samples (DNA nanostructures and origami, biological cells), nanoparticles, organic monolayers, nanofibers, metallic substrates. Properties that are commonly determined are: topography, roughness, feature size, molecular organization and self-assembly, depth profile, elastic modulus.

22-Production of Nanoelectrodes for the Quantitative Analysis of Dissolved Mn²⁺ and Crown Ether Capture Efficiency in Lithium Ion Batteries

Samantha Gateman, McGill University (Janine Mauzeroll)

LiMn₂O₄ is a popular cathode material because it has a low material cost, environmental advantages and good electrochemical performance at room temperature. However, it exhibits fast capacity fading during cycling at high temperatures, which hinders its practical application.[1] Most research agrees that the leading factor to this complication is the dissolution of Mn²⁺ into electrolyte solution, and subsequent anode poisoning. Several methods such as anion and cation substitutions in the cathode material have been developed to minimize the manganese dissolution.[2] An alternative approach proposes to coat a separator with cation chelating agents, such as crown ethers, to trap the manganese cations, thus preventing their migration to the anode.[3] We present the use of a Hg/Pt nanoelectrode to measure the concentration of Mn²⁺, and to determine the efficiency of capture of a Mn²⁺ chelating

agent. The nanoprobe is produced through the assembly of a Pt/quartz laser-pulled disk nanoelectrode. A spherical cap of Hg was formed upon the Pt disk by electrodeposition from a mercuric ion solution.[4] The nanoelectrodes were characterized by steady-state voltammetry, scanning electrochemical microscopy, environmental scanning electron microscopy, and energy-dispersive X-ray spectroscopy. The optimal conditions for Mn^{2+} detection by anodic stripping voltammetry (ASV) were investigated, and the probes were calibrated for sensitivity to Mn^{2+} ions. Quantitative detection of Mn^{2+} was achieved for concentrations ranging from nano- to micro-molar. The nanoprobe manufactured will aid in the high spatial resolution mapping of Mn^{2+} released from battery materials during the charge and discharge cycling, allowing the efficiency of treatments, which inhibit Mn^{2+} dissolution, or capture Mn^{2+} to be determined.

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23-Anti-asparaginase sensing to detect allergic reactions in leukemia treatment Production of Nanoelectrodes

Alexandra Aubé, Université de Montréal (Jean-François Masson)

Leukemia is a blood cancer affecting children with almost 50% of mortality rate. Multiple chemotherapeutic agents are currently used in treatment of leukemia in children and many treatment schedule include asparaginase, a well know and very effective therapeutic agent against leukemia. The issue with asparaginase is that approximately 30% of the patients develop asparaginase toxicity¹ which leads to the decrease of the treatment efficiency. Since the symptoms of the allergic reaction appear many days after the actual antibody production, it is of great interest to develop an assay that can allow rapid and simple anti-asparaginase detection to readjust the treatment as fast as possible to increase remission chances. We have developed a surface plasmon resonance (SPR) sensor to measure antibodies for asparaginase. SPR is a spectroscopic technique that allows real-time monitoring of specific molecules in complex matrix, when appropriate surface chemistry protects the sensor. Preliminary experiments show that anti-asparaginase can be detected in a high nanomolar range using a simple biosensor exploiting the chemistry of protein-protein specific interaction. Various forms of His-tag asparaginase were expressed and bound to the SPR sensor chip to capture anti-asparaginase. Different forms of asparaginase were compared to create the biosensor with the highest efficiency in detecting anti-asparaginase in complex matrix such as blood. To make the results comparable to clinical environment, bovine serum was used as a complex matrix for real time detection. By combining this approach with a peptide surface chemistry used to reduce non-specific binding developed in our group, a novel and very effective assay was developed and can easily be adapted to

clinical purpose. We collaborate with a local children's hospital handling most cases of leukemia in the greater Montreal. Thus, we envision that this assay could be a part of the routine tests done with the patients' blood and allow detection of anti-asparaginase antibodies.

24-Detection of Prostate Cancer Biomarker in Crude Serum by SPR

Julien Breault-Turcot, Université de Montréal (Jean-François Masson)

One limitation of analysis directly in a crude biological fluid comes from its complexity. The variety and concentration of proteins in biofluid such as serum can generate important interference on a sensor. For label-free technique, such as surface plasmon resonance (SPR), nonspecific adsorption will be quite a challenge. This interference can be reduced with an appropriate self-assembled monolayer (SAM) covering the metallic sensor. Peptide SAMs had previously shown to decrease nonspecific adsorption for bovin serum approximately to 10 ng/cm^2 . The peptide SAM use here will be the 3-MPA-HHHDD-OH, which molecule has at one extremity a thiol that can be linked to the gold surface and several COOH at the other extremity that can be used to immobilize a molecular receptor. This SAM provides an excellent platform for biosensing directly in crude serum. Another innovation involves the use of a micropatterned Au film instead of the continuous Au film generally used in SPR. A microhole array with a periodicity of $3.2 \mu\text{m}$ and a diameter of $1.6 \mu\text{m}$ has showed increased sensitivity to bulk refractive index and binding event on sensor. This new combination of surface chemistry/plasmonic material has been used extensively for IgG detection in buffer but also at pM level directly in crude bovine serum. Prostate specific antigen (PSA), a biomarker used for the diagnosis of prostate cancer, was also studied by using the plasmonic material/surface chemistry combination. The level of PSA in serum will increase for patient suffering from prostate cancer. Since PSA is a smaller protein than IgG, a secondary antibody was use in order to obtain a detection limit sufficiently low for diagnosis. Detection of the PSA-Anti-PSA complex was achieved in crude bovine serum at 0.1 nM , which is the PSA concentration found in serum for healthy patient.

To further decrease detection limits, the coupling of SPR sensing with fluorescence secondary detection is explored. The SPR instrument was fitted with a module to capture fluorescence. In that case, a fluorescent SAM formed on a gold film was analyzed with the SPR/fluorescence instrument. Afterward, the assay developed for PSA will be modified in order to allow monitoring by both SPR and fluorescence. In this case, the secondary antibody used will be tagged with a Fab fragment that is fluorescent. For this test, the microhole array that gives an increased SPR shift and an improved fluorescent emission will be used. Since the test developed could ultimately be used for analysis of clinical samples, the two detection technique will provide a better confidence in the results obtain and a reduction of the false positive rate.

25-Single Molecule Spectroelectrochemistry as a Tool to Visualising Redox Processes

Robert Godin, McGill University (Gonzalo Cosa)

Single molecule techniques are uniquely positioned for studying heterogeneous systems. The ability to distinguish distinct populations with different properties (rates, conformations, dynamics, etc.) is essential to fully understand processes and pathways in heterogeneous systems. Our laboratory is

utilizing combined electrochemistry and single molecule spectroscopy techniques (to give single molecule spectroelectrochemistry, SMS-EC) to visualize, map and study key redox processes in nanomaterials. In one case, we are studying the effect of externally applied potential has on the fluorescence of conjugated polymer nanoparticles and in another case how interfacial electron transfers between dye sensitizers and metal oxide semiconductor are modulated by the external potential.

Conjugated polymers have attracted much interest in material sciences due to their light harvesting and semiconducting properties and may be of exceptional use in optoelectronics. The precise control of chain conformation is needed in order to fabricate devices with the desired photophysical and electronic properties. We have discovered that the chain conformation of a conjugated polyelectrolyte (MPS-PPV) is very sensitive to the water content of H₂O/THF solvent mixtures. At low water content (0.5% H₂O v/v), nanoparticles are formed and can be studied by SMS-EC. We will show that sub-ensemble populations with differing responses can be identified, and hints at the heterogeneity of polymer/surface interactions.

I will also discuss our work in the field of dye-sensitized solar cells (DSSCs) which have shown great promise as a leading solar cell technology. We are studying the underlying electron transfers in charge injection processes from photoexcited dyes into mesoporous semiconductor electrodes. Utilizing SMS-EC, I will show the effect an applied bias to the semiconductor (filling or emptying electronic states) has on the dynamics of electron injection from sensitizing dyes. Our experimental conditions have the promise to directly measure important properties in functional nanostructured electrodes.

26-New Polyelectrolyte Multilayers for Cellular Growth

Kaïen Gu, McGill University (Christopher J. Barrett)

Polyelectrolyte multilayers (PEMs) are versatile thin films that can be rapidly and reproducibly manufactured and have been previously used in optical coatings, microelectronics, nanofluidics, and macromolecular encapsulation. PEMs are formed with a layer-by-layer (l-b-l) deposition technique whereby oppositely charged polyelectrolytes (PEs) are self-assembled into layers. Modulation of PEM fabrication conditions, such as deposition pH and choice of PEs, allows for PEMs with vastly different properties to be formed.

Cell culturing is a complex process used in biological sciences where cells are grown under controlled conditions. Current cell culture procedures for 'hard to grow' cells, such as neural cells and stem cells, lack a ready-to-use solution that is able to produce consistent results. We present and discuss the fabrication of novel PEMs as substrates for cellular growth. These PEMs have consistently demonstrated the ability to outperform the current 'state-of-the-art' technology by at least 50%.

27-Quantitative Monitoring of Hydrogen Bonding in Aminotriazine Glass-formers

Audrey Laventure, Université de Montréal (Christian Pellerin)

Recent work by Lebel and coworkers has revealed aminotriazine derivatives as a class of small organic molecules that are able to form an amorphous phase even when using cooling rates lower than 0.5 °C/min. Our previous study has shown the influence of the substituent groups and their position on the

glass-forming ability (GFA) of these molecules, the latter being attributed to the poor packing efficiency of the self-assembled aggregates that are held by multiple hydrogen bonds. [1] For instance, the headgroup has a more pronounced impact on the GFA compared to the ancillary groups. However, the role of the groups linking the triazine core to the ancillary groups has not been reported yet. Investigations were thus conducted on derivatives presenting different types of these linker groups, -NH, -NMe and -O, in order to distinguish their capacity of forming hydrogen bonds and the effect of their rotation energy barrier. Chemometrics was used to exploit variable temperature infrared spectroscopy data, allowing us to monitor quantitatively the formation of H-bonds during the vitrification of the compounds. These results once again underline the significant role of hydrogen bonding in frustrating the crystallization upon cooling.

I. A. Laventure, A. Soldera, C. Pellerin, O. Lebel, *New J. Chem.* 2013, 37, 3881.

28-Optimization of a Disk-shaped D-Serine Biosensor for In Vivo Applications

Kitty Chen, McGill University (Janine Mauzeroll)

D-serine, an endogenous co-agonist for the synaptic N-methyl-D-aspartate receptor (NMDAR), is thought to be an influential factor in psychiatric and neurodegenerative diseases such as Alzheimer's, depression, and schizophrenia. In order to investigate its effect on these neurological processes, in vivo quantification of D-serine within the brain is essential. For this purpose, it is possible to use enzymatic amperometric biosensors, whereby the products produced during an enzymatic reaction can be detected electrochemically and correlated back to D-serine concentration. A small scale biosensor showing high sensitivity towards D-serine was recently developed. This biosensor consisted of a 25 μm platinum disk microelectrode backbone with an electropolymerized layer poly-m-phenylenediamine (PPD) and an enzymatic layer of *R. gracilis* D-amino acid oxidase (RgDAAO). Cyclic voltammetry is employed for polymer layer deposition, and chronoamperometry is used to measure oxidative currents. The current aim of the research is to optimize the biosensor assembly to decrease response time and improve reproducibility. Investigation of alternative polymerization procedures demonstrates 5 cycles of electropolymerization as effective in blocking interferences as the previously used 15 cycles, while decreasing the hydrogen peroxide signal to the same extent as 10 cycles. Preliminary biosensors produced by co-immobilization of 4000 U/mL RgDAAO and 300mM m-phenylenediamine have successfully detected oxidative currents for D-serine concentrations in the high micromolar to low millimolar range. An additional enzymatic layer is required to increase the measured oxidative current at lower concentrations. After optimization, the biosensor will be used for detection and localization of D-serine on individual primary astrocytes.

29-Tuning block copolymer film morphologies by light

Josue Grosrenaud, University of Montreal (Christian Pellerin)

Block copolymers in thin films have the ability to self-assemble into well-defined nanostructures depending on several factors, among which is the volume fraction of the blocks. Addition of block-selective small molecules, such as by hydrogen bonding, can change the volume fractions and thereby control the type of surface morphology obtained. We are exploring a new method of dynamic control

of the morphology by irradiating thin films containing photo-active azobenzene molecules during dip-coating. In the initial system under study, the block copolymer, PS-P4VP (28 mol % P4VP), is blended with 4-hydroxy-4'-butyl-azobenzene (BHAB) in various 4VP/BHAB ratios in three different solvents (THF, toluene and chloroform) at a polymer concentration of 10 mg/mL. Results for the THF and toluene solutions reveal a change of morphology between films irradiated at a wavelength that drives trans-cis isomerization of BHAB and films that are non-irradiated during dip-coating. Notably, AFM images show that irradiation changes the morphologies from spherical or spherical/cylindrical to only cylindrical in THF, and from all-spherical to spherical/cylindrical in toluene at specific withdrawal speeds.

Infrared attenuated total reflection measurements indicate that the relative amounts of BHAB taken up in the films, which varies with dip-coating rate and solvent, also increases significantly upon irradiation for THF solutions. Possibly, the change in morphology is caused by this greater BHAB uptake induced by irradiation. However, the same phenomenon is not observed for toluene solutions, where the BHAB uptake is the same irregardless of irradiation. In this case, the morphological change might be related to the change in BHAB conformation from trans to cis, the latter occupying greater volume and thereby inducing a change in block volume fraction. Presumably, both effects take place for THF solutions. Film thickness measurements by ellipsometry correlate with these observations, since the films obtained under irradiation from THF solutions are significantly thicker than non-irradiated films, whereas there is no difference for films obtained from toluene solutions.

30-Effect of inhaled, inorganic particulate on lung surfactant model membranes

Abdullah Khan, Concordia University (Christine E. DeWolf)

As oxygen is inhaled it has to first cross a very thin layered membrane, lung surfactant, before it can enter the bloodstream. This lung surfactant membrane is composed of saturated and unsaturated phospholipids and membrane proteins which serve to reduce surface tension at the air-liquid interface of the alveoli preventing alveolar collapse. To maintain this function through repetitive compression-expansion cycles, the film employs a mechanism of reversible reservoir formation and a high degree of fluidity. The inhalation of nanoparticulate may interfere with the functional properties of pulmonary surfactant including lowering the film collapse, altering viscoelastic properties and modifying lipid reservoir formation. This study aims to determine whether or not nanoparticles interfere with the phase structure, compressibility, and viscoelastic properties when they deposit on the lipid membrane. The lung surfactant films will be modelled using monolayers of lipid mixtures and Survanta (a clinical formulation comprising extracted lipids and proteins). Surface pressure area-isotherms and preliminary results characterizing the rheological properties of the films will be shown.

31-Coaxing unmodified DNA into long-range assembly mediated by a small molecule

Nicole Avakyan, McGill University (Hanadi Sleiman)

DNA assemblies are emerging as promising candidates for nanomaterials and nanostructures. However, assembly design is limited by the natural, A-T G-C alphabet of DNA. Past efforts at expanding the base-pairing alphabet focused on the chemical synthesis of non-canonical bases. Here, we present an alternative to these labor-intensive syntheses. By employing a small molecule (cyanuric acid, CA) with three thymine-like faces, we have revealed a new motif for the assembly of unmodified poly(adenine) (poly(A)) strands. This assembly is solution-based and the resulting fibers were consistent and abundant, as determined by atomic force microscopy (AFM). Circular dichroism (CD) reveals a spectrum distinct from both B-DNA and previously-reported poly(A) duplexes. These unique assemblies are highly sensitive to CA concentration. Above a critical concentration necessary for onset of assembly, increases in [CA] result in corresponding increases in structure stability, as measured by thermal denaturation (TM). The shape of the melting curves is also influenced by the length of the poly(A) strands. For strands shorter than A15, a single melting transition is observed. However, for longer strands, multiphasic transitions appear. Investigations were made into the structure of the fibers, with tethered-strand experiments revealing a preference for parallel orientation of strands. Overall, the use of a small molecule to guide poly(A) assembly presents an alternative to the traditional base-pairing techniques of assembly, and results in easily-accessible nanofibers.

32-Infrared Study of Langmuir-Blodgett Films of a Supramolecular Block Copolymer Complex, PS-P4VP/PDP

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Self-assembly of block copolymers attracts much interest due to their exceptional ability to spontaneously generate highly ordered materials with unique properties. For many applications, such as masks in nanolithography, separation membranes in medical diagnostics, and nanotemplates for nanowire fabrication, manufacturing into thin films is required. Langmuir-Blodgett (LB) is a commonly used technique to produce ultrathin films of block copolymers that self-assemble into morphologies that are quite different from their bulk counterparts. In our work, we are interested in LB films of polystyrene-*b*-poly(4-vinyl pyridine) (PS-P4VP) and their supramolecular complexes with 3-*n*-pentadecylphenol (PDP), particularly in a composition range where the so-called 'dot' morphology is observed.

A previous study from our group[1] has established that the system undergoes a transition from 'hexagonal' to 'square' arrangement of the dots at a surface pressure where a plateau is observed in the Langmuir isotherm. Simultaneously, AFM imaging suggested that the PDP alkyl chains reorient from prone to more vertical relative to the surface. Here, we used attenuated total reflection infrared spectroscopy (ATR-IR) to investigate changes taking place at the transition. We have found that the strength of the H-bond that binds PDP to P4VP differs in these two regimes. With polarized IR measurements, we also found that the hexagonal-to-square transition involves reorientation of the small molecule and pyridine ring relative to the surface and that there is a clear relationship with the changes in the dot spacing observed by AFM. A full model will be proposed to describe the detailed changes in molecular organization that underlie the order-order transition.

1. Peregichka, I. I.; Borozenko, K.; Badia, A.; Bazuin, C. G., *J. Am. Chem. Soc.* 2011, 133, 19702-19705.

33-Towards an understanding of dimensional instability of polymer coatings on wood veneers

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Canadian aerospace companies like Bombardier Aerospace are recognized globally for their innovative contributions to the design and manufacturing of regional and business aircrafts. It is essential that the performance and aesthetics of these products continue to be of superior quality, as compared to the competition. A common problem in the aerospace industry is related to a dimensional instability in the clear coat finish that is applied to the veneer on aircraft cabinetry, which is particularly of concern to business aircraft customers. The defect is referred to as orange peel and appears as an undulation of the coated surface on the scale of a few hundred microns to around 1 mm in depth.

Our goal is to try to understand the mechanisms underlying the formation of this defect. The high-gloss finish currently used by Bombardier is made from a highly polished polyester-based varnish applied in three layers to a previously sealed wood veneer laminate panel. Compositional heterogeneities in the varnish were observed at the air and veneer interfaces, as well as compositional variation with depth using FTIR and Raman spectroscopic techniques. The extent to which this might be related to variable extents of polymerization, irregular solvent evaporation, different wood species, or migration/diffusion of solvents, unreacted monomers, oligomers or wood extracibles into different layers of the coating is being analyzed.

34-Automers for the direct formation of polyazomethines on electrodes - Versatile electroactive layers

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In order to address the stringent reaction conditions for preparing conventional conjugated materials, we opted for easily prepared azomethines. While they are synthetically easier to prepare than conventional materials, they have the added advantage of being air stable. A series of diads consisting of complementary amine and aldehyde were prepared as monomers that could self-condense. The effect of different electronic groups and aromatics on the optical, electrochemical, and spectroelectrochemical properties was investigated. The capacity of these monomers to undergo self-polymerization directly on electrodes was also examined along with their use as electroactive layers capable of undergoing reversible color switching.

35-Multi-metallic Radial Architectures for Magnetic and Photophysical Devices

Elodie Rousset, University of Montreal (Garry S. Hanan)

Dendrimeric architectures allow a fine topological control of functional molecular structures. Dendrimers based on the coordination of metallic centres enable a fine-tuning of the properties by

carefully choosing the monometallic complexes. The aim of this work is to evaluate the advantages of a radial structure compared to the building blocks themselves. Two main fields are concerned for this work:

- Magnetism: by increasing the generation number of spin carriers, the total spin of the molecule increases exponentially. If the assembly presents a high anisotropy, Single Molecule Magnet properties may be observed. In addition, having an isotropic or weakly anisotropic architecture might lead to important magneto-caloric effects.

- Artificial Photosynthesis: A combination of photochromic complexes absorbing at different wavelengths and capable of energy transfer are able to mimic the antenna effect of natural systems. Transferring electrons from the photosensitizer to a catalyst enables water splitting and hydrogen formation. The radial architecture allows all of the actors to be in close proximity on the same molecule thus enabling higher efficiency in energy and electron transfer reactions.