

CUNY NANO DAY

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Poster Abstracts

1. Dimeric synthetic receptor for carbohydrate recognition

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By targeting the pyranosides that are prevalent on the glycocalyx, synthetic carbohydrate receptors could serve as agents for disease detection, drug delivery, or even therapeutics¹. Currently, synthetic lectins are rarely used for these applications because they primarily bind only all equatorial glucosides that are absent from the glycocalyx. To address this challenge, we have previously reported a highly flexible synthetic carbohydrate receptor that achieved mannoside-specific binding by relying upon multivalent and cooperative binding modes². The major drawback of this previous receptor, however, is that binding has been demonstrated only in chloroform. Herein we have developed a new pyranoside receptor, **1**, (Figure 1) that relies upon H-bonding, C-H \cdots π interactions, and conformational flexibility to achieve high binding affinity with C1-methoxy pyranosides. Like natural glycan binding proteins, this receptor binds pyranosides by accessing multivalent interactions, and studies suggest a new approach towards the biomimetic design of synthetic carbohydrate receptors, where conformational flexibility and promiscuity are considered beneficial. Binding

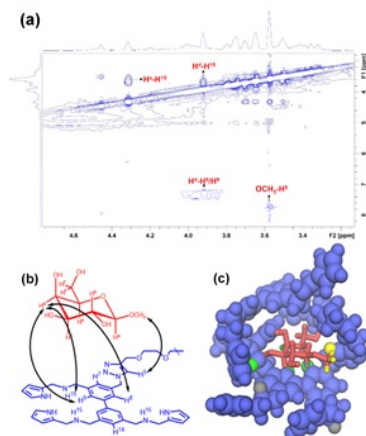


Figure 1. a) Partial NOESY spectrum (800 MHz, mixing time: 500 ms) of **1** (0.2 mM) with 1 equiv. MeO- β -Gal (250 mM) in D₂O/H₂O (v/v = 5/95) at 283 K. b) NOESY contacts observed for the complex between MeO- β -Gal and **1** (800 MHz, 298 K, D₂O, 500 ms mixing time). c) A computational model of the complex, consistent with the NOESY data. MeO- β -Gal is colored red, and **1** is blue. NOESY contacts are color coded, and distances are from the computational model: H¹⁵-H¹ (5.542 Å, 6.965 Å) [Grey]; H²-OCH₃ (2.516 Å) [Yellow]; H³-H¹ (3.056 Å), H³-H¹ (3.708 Å), H¹⁵-H² (3.722 Å), [Green].

studies via NMR titration of the complex will reveal its affinity which will have implications to medicine and increasing our understanding of biological recognition.

2. Strong coupling of molecular excitons to localized surface plasmons and lattice modes of 2D plasmonic nanoparticle arrays

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Thin film solar cells are an attractive alternative to conventional crystalline Si cells due to their relatively light weight and lower cost of production. However, only a fraction of sunlight will be absorbed by most photovoltaic materials at micron and submicron thicknesses unless cell geometry and additional materials and structures are used to trap the incident light. To address this need, researchers have employed plasmonic nanoparticles to enhance the efficiencies of thin film solar cells by increasing the percentage of incident light absorbed, an effect that is mediated by the localized surface plasmon resonances (LSPRs) of the particles. In addition to LSPRs, periodic two dimensional arrays of nanoparticles also support delocalized, propagating plasmonic-photonic hybrid modes known as surface lattice resonances (SLRs). Recent research has demonstrated that, like LSPRs, SLRs can interact strongly with the excitons of organic dyes and photovoltaic materials. The primary goal of this work is to produce SLR-supporting 2D plasmonic nanoparticle arrays onto which exciton-generating supramolecular dye aggregates will be adsorbed, ideally allowing the SLRs and the organic excitons to strongly couple. This ternary (plasmonic-photonic-excitonic) coupling could serve to enhance the efficiency of thin-film solar cells not only by enhancing the absorptivity of organic thin film solar cells, but also by opening up a delocalized mode with excitonic character whose presence increases the effective diffusion lengths of the excitons, thereby facilitating the transport of the excitons to surfaces or contacts at which the charge carriers may be separated and collected.

3. II-VI/III-V Heterovalent Interfaces and Novel Applications

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In the MBE lab at CCNY we have been focusing on the growth of world class II-VI semiconductors for various applications including high efficiency photovoltaics, novel spintronic materials, light emitting devices and detectors that span a wide range of the visible and IR spectrum. III-V substrates are used to achieve high quality II-VI materials. These substrates are prepared in a dedicated III-V chamber prior to II-VI growth. Samples are shuttled to the II-VI chamber via an ultra-high vacuum track, never exposing the surface to atmosphere. The preparation of the heterovalent interface is of paramount importance and requires a sequence of carefully designed steps. Being able to take advantage of heterovalent structures for their use in devices provides opportunities that cannot be achieved with isovalent ones. However, interdiffusion, charge imbalance, interlayer formation and electric dipoles are all critical factors that can affect the heterostructure properties. We are exploring the growth of new heterostructures by studying these effects and controlling this interface formation for future devices and novel physics.

4. Bi₂Se₃ Van der Waals Virtual Substrates for II-VI Heterostructures

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We report on the growth and characterization of optical quality multiple quantum well structures of ZnxCd1-xSe / ZnxCdyMg1-x-ySe on an ultra-thin Bi₂Se₃/CdTe virtual substrate on c-plane Al₂O₃(sapphire). Excellent quality highly oriented films grown along the (111) direction were achieved as evidenced by reflection high energy electron diffraction and x-ray diffraction studies. We also observed room temperature and 77K photoluminescence emission with peak energies at 77K of 2.407eV and linewidths of 56meV comparable to those achieved on structures grown on InP. Exfoliation of the structures is also possible due to the Van der Waals bonding of Bi₂Se₃. Exfoliated (substrate free) films exhibit photoluminescence emission nearly identical to that of the supported film. Additionally, contactless electroreflectance measurements show good agreement with simulations of the multiple quantum well structure as well as evidence of excited state levels. These results open new avenues of research for substrate independent epitaxy and the possibility of ultra-thin electronics.

5. Elucidating The Crystal Growth Mechanism of

Indomethacin and Nifedipine

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The delivery of poorly water-soluble drugs is a crucial problem for the pharmaceutical industry. Approximately 80% of current drug candidates in the R&D pipeline have low water solubility and risk to fail due to solubility problems. Several drug delivery systems have been developed in the last decades to increase the solubility and/or the dissolution rate of poorly soluble drugs. These systems aim to create a temporary state of supersaturation in the GI tract to enhance the drug absorption. Supersaturated solutions, however, are inherently unstable, and they tend to crystallize over time to reach the equilibrium solubility. Therefore, to successfully enhance the intestinal absorption of poorly-soluble drugs, a drug delivery system must not only generate a state of supersaturation in the GI tract, but also maintain it for an extended period of time. Polymeric precipitation inhibitors (PPIs) can delay crystallization from supersaturated solutions and extend the time that the drug molecules spend in solution. However, their mechanism of action remains poorly understood and the selection of polymeric inhibitors is mostly based on empirical criteria.

The proposed project aims to gain a better insight of the mechanisms by which polymers inhibit the crystal growth of pharmaceutical drugs from solution. The first step towards this goal is to understand, at the molecular level, the crystal growth mechanisms of poorly soluble drugs. In this work, single crystals of Indomethacin (IMC), an anti-inflammatory drug, and Nifedipine (NIF), a calcium-channel blocker, were obtained from solution and were characterized by using Differential Scanning Calorimetry (DSC) and RAMAN microscopy. X-Ray Single Crystal Diffraction was used to determine the unit cell and to assign the Miller indices of the crystal faces. This analysis combined with the X-ray structures of crystals was used to determine the fastest growing face and the main intermolecular interactions involved in the crystal growth. Preliminary atomic force microscopy (AFM) images of IMC crystal surface in under-saturated solution showed that the crystal dissolved forming pits that resemble the macroscopic crystals. Future studies will aim to measure by AFM the kinetics of dissolution and growth of the crystals obtained in this work. The results will provide quantitative and qualitative information regarding the polymer-crystal surface interactions and will help to elucidate some of the mechanisms by which polymers stabilize supersaturated solutions of poorly-soluble drugs.

6. Surface Enhanced Raman Scattering on Photoetched GaN Nanowires

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In this work, we examine surface enhanced Raman Scattering (SERS) on photoetched gallium nitride (GaN) nanowires using of 4-mercaptopyridine (4-MPy) as probe molecule. Nanowires were formed by photoetching GaN grown via metal-organic chemical vapor deposition (MOCVD) using potassium peroxydisulphate and potassium hydroxide

solution (K₂S₂O₈—KOH) under UV exposure. The process resulted in uniform bundles of nanowires with remarkable homogeneity in distribution across the surface. In the SERS spectrum, large enhancements to the a₁, b₁, and b₂ modes are seen using an excitation wavelength of 488nm (2.54 eV). An enhancement factor (EF) of 2.3 × 10⁶ is observed, comparable to the one obtained with silver nanoparticles. We propose that is due to: 1) proximity of the excitation wavelength to the energy required to incite transitions between the valence band (VB) of GaN and lowest unoccupied molecular orbital (LUMO) of 4-MPY; 2) sizeable contributions from small feedgap "hotspots" that create strong electromagnetic field enhancement between wire tips.

7. Supramolecular Light Harvesting Thin Films

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Organic materials are increasingly explored as active components in electronic, energy harvesting, and sensing applications. In these systems new optoelectronic properties emerge from the interactions of electron donor and acceptor polymers.¹ However, the inability to control the donor-acceptor interface limits key figures of merit, such as charge separation and collection efficiency. An alternate approach to addressing this challenge involves assembling small molecular donor and acceptor compounds into precisely ordered superstructures via specific noncovalent bonding.² To this end, we have created a library composed of diketopyrrolopyrrole (DPP) donors and perylene bisdiimide (PDI) acceptors that assemble into hierarchical superstructures that undergo photoinduced charge separation following supramolecular organization. From the ability to chemically modify molecular components and donor-acceptor pairings, we have established systematically the relationship between donor-acceptor molecular structure, frontier molecular orbitals, morphology, and emergent photophysics. Understanding of these supramolecular systems allows for their direct integration into electronic devices, such as solar cells, transistors, and sensors.

8. Nanopatterning of Biomaterials by Thermochemical Nanolithography

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The adhesive and topographical features ranging from nano-meters to micrometers on the extracellular matrix (ECM) serve the significant role of interacting with various individual cell and profoundly impact their complex multicellular behaviors. Therefore, controlling the surface chemistry and nano- or micro-sized topography on ECM is of great importance in cell biology and tissue engineering. In this work, amine patterns on biopolymer surface was achieved by local thermochemical reaction induced by a commercial

scanning probe lithography-based technique—NanoFrazor. Amine pattern with density gradient was visualized by using Confocal Fluorescent Microscope. Current results suggested that the density of exposed amine group will peak at certain patterning temperature. To improve the binding specificity of fluorescence dyes and biochemicals, a block containing sulfobetaine groups was added to the biopolymer backbone as anti-fouling agent. In the future, the polymer films with sulfobetaine groups will be patterned and binding specificity will be compared by using fluorescence dyes and enzymes.

9. Epitaxial Al/InAs Josephson Junctions

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10. Nanoscopic Investigations of Self-Assembled Supramolecular Light Harvesting Nanotubes and Semiconductor Quantum Dots

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Self-assembled quasi one-dimensional (quasi-1D) nanostructures of π -conjugated molecules exhibit unique optoelectronic properties, including sharp exciton transitions, large oscillator strengths, and high exciton mobility and photoconductivity, and inorganic semiconductor nanocrystals similarly exhibit distinct non-linear optical properties. Thus, the integration of these organic and inorganic nanomaterials offers the possibility of developing new photonic and optoelectronic devices. However, to control such complex material systems it is essential to understand how their various parts interact, and whether these interactions result in coherently shared excited states or in diffusive energy transport between them. Here, we utilize near-field scanning optical microscopy (NSOM) to investigate (1) an artificial model system: well-defined, thoroughly characterized quasi-1D light-harvesting nanotubes (LHNTs) self-assembled from cyanine dye molecules, and (2) cadmium selenide colloidal quantum dots (CdSe QDs). The nanostructures were isolated from solution and immobilized on a solid substrate without altering their supramolecular structures, then simultaneous topographical and optical images were obtained for individual LHNTs and for single CdSe QDs. These results lay the groundwork for future NSOM investigations of nanoscale excitation energy transfer in supramolecular aggregates and of resonance coupling in hybrid organic/inorganic nanostructures.

11. Room-temperature quantum emitter arrays in hexagonal boron nitride

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Defects in hBN have recently been shown to be a narrow linewidth, room temperature single photon emitters (SPE) [1]. While the exact nature of the defect is still unclear, the narrow linewidth, room temperature operation and spectral tunability make these emitters highly attractive for quantum technologies. Despite these advantages, difficulties in precise control over defect formation both spectrally and spatially [2–5] makes integration into nano-photonic optical devices a non-trivial technological hurdle. Here, we address these challenges by demonstrating nanoscale spatial control of emitter formation in hBN. The hBN exhibits preferential quantum emission highly localized to the pillar locations. In addition, we find the zero phonon lines (ZPLs) spectrally clustered within ~290 meV centered at 580 nm. These findings pave the way for device integration of defect states in hBN in quantum optical systems and offers a means to realize robust on-demand deterministic room temperature quantum emitters.

12. MMP-9 responsive peptide nanocarriers for targeted delivery of metallodrugs

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Drugs such as, cis- platin, oxaliplatin, and carboplatin have limitations including poor solubility, quick clearance, lack of selectivity, and limited therapeutic activity. These limitations can be addressed by peptide nanotechnology, which offer unique design space for developing safer and more effective medicines. Here we report on the development of peptide nanocarriers that target matrix metalloproteinase-9 (MMP-9) and use highly active unconventional metallodrugs as the payloads. The up-regulation and the roles of MMPs have been associated with cancer invasion and metastasis. Therefore, MMP-9 is a suitable cancer specific bio-target and the enzyme action can be exploited to produce a desirable response in the peptide nanocarriers: 1) formation of fibers that stay localized near the cancer cells and 2) site specific release of payloads. Scheme 1 shows the structures of two metallodrugs synthesized by the Contel group that were cytotoxic in vitro and displayed impressive tumor reduction in vivo in MDA-MB-231 and Caki-1 cells and xenografts. We will present on the characterization of novel peptide amphiphiles with tunable MMP-9 cleavage kinetics and desired self-assembly properties, as well as preliminary studies on the entrapment of the metallodrugs. Using unconventional metallodrugs that are highly active against MMP-9 overexpressing cell lines as payloads in the MMP-9 targeting peptide nanocarriers will provide a minimally invasive method to kill cancer cells that are resistant to current chemotherapy.

13. 4D Chemical Nanolithography

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Controlling the organization of biomaterials on surfaces with nanometer resolution is of paramount importance for fundamental biological, physical, and medical

studies, and for the development of optical and electronic devices.¹ State of the art technologies for constructing materials composed of delicate organic and biologically active matter are based primarily upon ink-jet printing, pin-printing, which cannot achieve features below 10 microns, whereas conventional photolithography is expensive and destructive. By marrying massively parallel scanning-probe based nanolithography, specifically polymer-pen lithography (PPL) and beam-pen lithography (BPL), with the new surface organic chemistry, we have developed approaches for preparing glycan arrays,² functionalizing graphene,³ and creating brush polymer arrays.⁴ Recently, combining massively parallel scanning probe nanolithography, microfluidics, and brush polymer chemistry, we have achieved 4D organic micromanufacturing, where the four dimensions are the 3 Cartesian coordinates (x,y,z) and the fourth is the chemical composition of each spot in an array (Figure 1).⁵ This novel materials manufacturing approach could pave the way towards materials with the chemical and topological complexity common to biological interfaces.

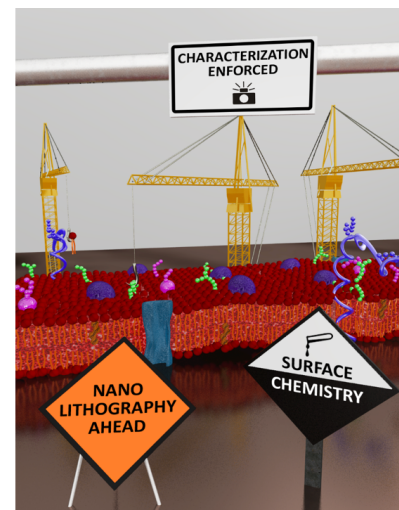


Figure 1 The Road to Hyperspace Nanofabrication. To accomplish such 4D nanofabrication, it will be necessary to advance nanolithography surface chemistry and 3D characterization.

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14. USING SPORES OF BACILLUS TO CREATE EVAPORATION-DRIVEN ENGINES

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Evaporation is the dominant form of energy transfer in Earth's climate. Here we report evaporation-driven engines that can power common tasks like locomotion and electricity generation. These engines start and run autonomously when placed at air-water interfaces, and operate as long as the air is not saturated. To create these engines, we developed hygroscopy driven artificial muscles (HYDRAs) that exhibit moisture-driven high actuation strain and energy density. We designed device architectures for HYDRA engines that generate sustained linear oscillatory motion (piston-like) and rotary motion (turbine-like) in the presence of evaporation. Using these engines, we demonstrate an electricity generator

that rests on water while harvesting its evaporation to power a light source, and a miniature car (weighing 0.1 kg) that moves forward as the water in the car evaporates.

15. AFM characterization of Al/InAs for studying topological superconductivity

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16. Epitaxial Growth of Al (111) on Si (111) substrates

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