

SYMPOSIUM O

O: Nanostructured Organic Materials

December 1 - 3, 2003

Chairs

Jason Hafner

Dept. of Physics & Astronomy
Rice University
MS 61
6100 Main St.
Houston, TX 77005
713-348-3205

Jeffrey D. Hartgerink

Dept. of Chemistry
Rice University
MS 65
6100 Main St.
Houston, TX 77005
713-348-4142

Eugene R. Zubarev

Dept. of Materials Science & Engineering
Iowa State University
3161 Gilman Hall
Ames, IA 50011
713-348-4142

* Invited paper

SESSION O1:

Chair: Eugene Zubarev
Monday Morning, December 1, 2003
Room 206 (Hynes)

8:30 AM *O1.1

Nano-Structuring of Semiconductive and Conductive Polymers Using Block Copolymer Self-Assembly.

Timothy M Swager, Craig A. Breen, Tao Deng, Hyun A Kang, Thomas Breiner and Edwin L. Thomas; Institute for Soldier Nanotechnologies, MIT, Cambridge, Massachusetts.

We will report a number of new systems that make use of organized block copolymer nanostructures to produce highly organized nanostructures. A new approach based on a conjugated polymer/block copolymer guest/host system for the generation of polarized photoluminescence is reported. Synthetic modification of a poly(p-phenylene-ethynylene) (PPE) conjugated polymer is used for domain-specific incorporation into a cylindrical morphology block copolymer host matrix. Subsequent ordering of the host nanostructure via roll cast processing templates uniaxial alignment of the guest PPE. The ordered films are optically anisotropic displaying both polarized absorption with a dichroic ratio of 3.0 at 440 nm and polarized emission with a polarization ratio of 7.3 at 472 nm. In related systems in which the period of the lattice spacing expanded a photonic band-gap can be created that is coincident with the polymer's emission and we will also report on the consequences to the photophysical behavior. In the area of electroactive polymers we have produced monodisperse block polymers in which one block can be transformed into a highly conducting material. These structures produce nanowires networks that are of interest for sensor applications as well as artificial muscles.

9:00 AM *O1.2

Properties of Organic Molecules on Crystal Surfaces.

Federico Rosei^{1,2}, Yoshitaka Naitoh², Roberto Otero², Peter Thostrup², Erik Laegsgaard², Ivan Stensgaard², Flemming Besenbacher², Ping Jiang³, Andre' Gourdon³ and Christian Joachim³; ¹EMT, INRS, Varennes, Quebec, Canada; ²Physics, University of Aarhus, Aarhus, Denmark; ³CEMES, CNRS, Toulouse, France.

Ordering molecular building blocks into a suitable architecture at nano scale is very appealing for the development of future integrated nanoelectronics [1]. We used two large organic molecules called Single Lander [2] (C90H98) and Violet Lander (C104H108), and investigated their electronic states at room temperature (RT) by Scanning Tunneling Spectroscopy (STS) and its Self-Assembly on Cu(110) by Scanning Tunneling Microscopy (STM). Molecules from the Lander family have a central polyaromatic molecular "wire", terminated by a fluoranthene group, and four Tbp substituents that act as spacer legs. The four legs are imaged as four lobes with three different conformations by STM, two rhomboidal (chiral) shapes that are mirror symmetric to each other and one rectangular shape. To create a suitable template for controlled molecular adsorption, we nanopatterned a clean Cu(110) surface by oxygen chemisorption. When Lander molecules are deposited on this template, they preferentially attach to bare Cu regions, forming 1 D molecular nanostructures. We then took STS spectra from Single Lander and Violet Lander molecules embedded in these nanostructures. Spectra from isolated Lander molecules on Cu(110) terrace reveal two broad peaks observed at -0.5 V and 0.8 V. These are tentatively associated with the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) states of the molecule at RT. References: [1] C. Joachim, J.K. Gimzewski, A. Aviram, Nature 408, 541 (2000). [2] F. Rosei, M. Schunack, Y. Naitoh, P. Jiang, A. Gourdon, E. Laegsgaard, I. Stensgaard, Ch. Joachim, F. Besenbacher, Properties of large organic molecules on metal surfaces, Prog. Surf. Sci. 71, 95 (2002). [2] F. Rosei et al., Organic molecules acting as templates on Metal Surfaces, Science 296, 328 (2002). [4] Y. Naitoh et al., in preparation.

9:30 AM *O1.3

Constructing a Computer from Molecular Components.

James Tour, Chemistry Dept. & CNST, Rice University, Houston, Texas.

James M. Tour Chao Professor of Chemistry Professor of Mechanical Engineering and Materials Science Professor of Computer Science Department of Chemistry and Center for Nanoscale Science and Technology, Rice University P.O. Box 1892, MS 222, Houston, Texas 77251-1892 Email: tour@rice.edu Web: http://www.jmtour.com Research efforts directed toward constructing a molecular computer will be described in the context of recent developments in nanotechnology. Routes will be outlined from the synthesis of the basic building blocks such as wires and alligator clips, to the assembly of the processing functional blocks. Specific achievements include: (1) isolation of single molecules in alkane thiolate self-assembled

monolayers and addressing them with an STM probe, (2) single molecule conductance measurements using a mechanically controllable break junction, (3) 30 nm bundles, approximately 1000 molecules, of precisely tailored molecular structures showing negative differential resistance with peak-to-valley responses far exceeding those for solid state devices, (4) dynamic random access memories (DRAMs) constructed from 1000 molecule units that possess 15 minute information hold times at room temperature, (5) demonstration of single-molecule switching events and (6) initial assemblies and programming of molecular CPUs in a NanoCell configuration that show room temperature electronic memory with days or electronic hold time, and the programming of molecular logic gates.

10:30 AM *O1.4

Water Soluble Molecular Capsules for Drug Delivery.

Jerry L. Atwood, Dept of Chemistry, University of Missouri-Columbia, Columbia, Missouri.

The enclosure of chemical space is one of the essential attributes of a biological system. We have previously shown that macrocycles can serve as building blocks for very large assemblies. In particular, calixarenes and resorcinarenes may be used to enclose space in a manner consistent with the principles of solid geometry attributed to Plato and to Archimedes. 1 is a snub cube made from six resorcin[4]arenes and eight water molecules, and 2 is a great rhombicuboctahedron made from twelve calix[4]arenes. The ability of macrocycles to effect the construction of hydrogen-bonded spherical enclosure assemblies is due to focussed functionality. Aided by the concepts of solid geometry and by an understanding of focussed functionality, we have now prepared a range of new, very large molecular capsules. The use of pyrogallo[4]arenes is particularly noteworthy; 3 is the hexamer of pyrogallo[4]arene. Recently, we have discovered routes to the selective derivatization of the exterior of these hydrogen bonded molecular capsules. Applications of the new capsules for drug delivery are being explored. Nature, 1997, 389, 469. Angew. Chem. Int. Ed. Engl., 1999, 38, 1018. Science, 1999, 285, 1049. Chem. Comm., 2001, 2376.

11:15 AM O1.5

The Self-Assembly of Organic Molecules into Electronically Conducting One-Dimensional Nanostructures.

Benjamin Weaver Messmore¹, James F Hulvat², Eli D Sone¹ and Samuel I Stupp^{2,1,3}; ¹Chemistry, Northwestern University, Evanston, Illinois; ²Materials Science and Engineering, Northwestern University, Evanston, Illinois; ³Feinberg School of Medicine, Northwestern University, Chicago, Illinois.

Oligo(thiophene) based systems are currently being studied as candidates for organic electronic devices because of their stability and high charge carrier mobilities. We report here on the synthesis and characterization of a novel dendron rodcoil molecule with an optically and electronically active oligo(thiophene) rod. The triblock molecule contains a G1 3,5 dihydroxybenzoic ester dendritic segment, an asymmetrically substituted oligo(thiophene) containing rod segment, and a branched alkane coil segment. In poor solvents, these molecules self-assemble into high aspect ratio nanostructures and cause the dilute solutions to gel. The gels are strongly birefringent and show a red shift in absorption that is characteristic of the solid state indicating H aggregation of the aromatic units. Experiments show an increase in conductivity of films cast from the self-assembled state compared to films cast from solutions in good solvents. Preliminary results indicate electrophoretic alignment of nanostructures in an AC field during film casting. These novel materials containing pre-assembled π -stacked nanostructures may offer new opportunities for devices such as OFETs and OLEDs.

11:30 AM *O1.6

Synthetic Duplex Oligomers Defined via Covalent Casting of 1-Dimensional Hydrogen Bonding Motifs. Michael J. Kricheldorf,

Dept of Chem and Biochem, University of Texas at Austin, Austin, Texas.

Abstract: Hydrogen-bonded tapes comprised of monomeric molecular precursors are used to define parameters for the design of related oligomers encoded with predetermined modes of assembly. Application of this covalent casting strategy vis-à-vis the 1-dimensional H-bonding motif expressed by 2-amino-4,6-dichlorotriazine has enabled the design of high-affinity duplex molecular strands. Dimeric, trimeric, and tetrameric duplex oligomers are prepared through an iterative synthetic protocol involving sequential homologation of the oligo(aminotriazine). The mode of assembly and interstrand affinity of homologous oligomers are established in solution by 1H NMR dilution experiments, isothermal titration calorimetry (ITC), vapor pressure osmometry (VPO), cross-hybridization experiments involving the analysis of dye-labeled strands via thin layer chromatography (TLC) and in the solid state by x-ray crystallographic analysis. Binding free energy per unimer ($-\Delta G/n$) increases significantly upon extension

from monomer to dimer to trimer, signifying a strong positive cooperative effect. Nanomolar binding affinity ($K_d = 1.44 \pm 0.50$ nM) was determined for the duplex trimer by ITC in 1,2-dichloroethane at 20° C. Strands that embody photo-isomerizable backbones exhibit switchable on-off hybridization capabilities.

SESSION O2:

Chair: Jeffrey Hartgerink
Monday Afternoon, December 1, 2003
Room 206 (Hynes)

1:30 PM *O2.1

From NanoElectronic to NanoElectroMechanical Systems. Fraser Stoddart, Department of Chemistry and Biochemistry, University of California - Los Angeles, Los Angeles, California.

Molecular compounds, comprised of mechanically interlocked components, can now be obtained efficiently using *template – directed* protocols that rely upon *supramolecular assistance to covalent synthesis*. Since the weak *noncovalent interactions* that orchestrate the synthesis of such compounds—e.g., *catenanes* and *rotaxanes*—containing *mechanical bonds* live on between the components inside the molecules thereafter, they can be *activated* such that their components *move* with respect to each other in either a *linear* fashion (e.g., the ring component along the rod of the dumbbell component of a [2]rotaxane as in a molecular shuttle) or a *rotary* manner (e.g., one ring in a [2]catenane circumrotating through the other ring as in a bistable switch). Thus, [2]rotaxanes can be likened to *linear motors* and [2]catenanes to *rotary motors*. Moreover, these molecules can be activated by switching the *recognition elements* on and off between the components *chemically, electrically, and optically* such that they perform *motions*—e.g., *shuttling* actions or muscle-like *elongations* and *contractions*—reminiscent of the moving parts in *macroscopic machines*. Such *motor – molecules* and *molecular machines* hold considerable promise for the fabrication of *sensors, actuators, amplifiers* and *switches* at the *nanoscale level*. The lecture will highlight how the emergence of the *mechanical bond* in chemistry during the last two decades has brought with it a real prospect of integrating a *bottom – up* approach, based on *self – assembly* and *self – organization* of motor-molecules, with a *top – down* approach, based on micro- and nanofabrication, to (i) construct *molecular electronic devices* to store and process *information* at very high densities using minimal power and (ii) to create *NanoElectroMechanical Systems (NEMS)* in order to harness, manipulate and transfer *energy* on the nanoscale level. It all adds up to an *integrated systems – oriented approach to nanotechnology* that finds its inspiration in the transfer of concepts like *molecular recognition* from the *lifesciences* into *material science*.

2:15 PM O2.2

Nanostructured Organic Materials from Generation Dependent Self-Assembly in Dendrimer-Linear Block Copolymers. Byoung-Ki Cho¹, Anurag Jain¹, Surbhi Mahajan¹, Sol M Gruner² and Ulrich Wiesner¹; ¹Department of Material Science and Engineering, Cornell University, Ithaca, New York; ²Department of Physics, Cornell University, Ithaca, New York.

Dendrimers are regularly branched macromolecules with a globular shape deviating significantly from that of linear coil polymers. Recently, properties of block copolymer systems with a dendrimer and a linear coil block have been explored in solution, bulk and in thin-films. To the best of our knowledge, however, only classical block copolymer bulk phases were observed. Here, we report on the synthesis and study of the bulk self-assembly behavior of a novel dendrimer-linear coil block copolymer system as a function of the dendrimer generation (nG-Coil). Each dendrimer from first generation (1G-Coil) to fourth generation (4G-Coil) can be prepared by a stepwise convergent approach. Employing a combination of differential scanning calorimetry (DSC), small angle x-ray scattering (SAXS) and transmission electron microscopy (TEM) we will show that the particular dendrimer-linear coil architecture chosen for this study gives rise to very interesting phase behavior not observed in conventional linear block copolymers. The results suggest that dendrimer-linear coil block copolymers offer a novel route for the design of nanostructured organic materials with implications in a wide range of areas from microelectronics all the way to nanobiotechnology.

2:30 PM *O2.3

Multiphase Dendritic Macromolecules As Organized Interfacial Nanolayers. Vladimir Tsukruk, Materials Science and Engineering, Iowa State University, Ames, Iowa.

We review our results on design and fabrication of a variety of organized surface and interfacial nanolayers from multiphase dendritic

macromolecules at a silicon oxide surface of silicon wafers. We used chemical grafting from solution and melt as well as Langmuir-Blodgett technique to fabricate monolayers of different grafting densities ranging from individual molecules, separate clusters, and to dense monolayers. We focus on our recent studies of surface microstructures and nanoscale properties of these interfacial nanolayers composed of photochromic monodendrons, functionalized hyperbranched polymers, branched rod-coil molecules, branched discs, and branched hair-pin molecules. An amphiphilic compound containing a benzyl-15-crown-5 focal point, azobenzene spacer, and a dodecyl tail as a peripheral group has been investigated at the air-water interface. High tilt of the alkyl tails from the surface normal was a signature of molecular packing caused by a large mismatch between the cross-sectional areas of the polar heads and the alkyl tail. We synthesized a series of second-generation hyperbranched polyesters with a variable composition of alkyl-terminated groups. We observed that the number of attached alkyl tails was fairly close to the theoretical value, based on the assumption that all targeted hydroxyl groups were available for the reaction despite their different interior/exterior location. Amphiphilic discotic molecules with hydrophilic side branches have been characterized. The discotic molecules based on di-branched oligoether side chains have been observed to self-organize into a well ordered hexagonal columnar structure. We suggest that the hexabenzocoronene cores are packed in a face-on arrangement at the air/water interface and on solid surfaces with surface domains composed of an array of 7:7 molecules. We suggest a crab-like molecular conformation and cluster-segregated monolayers with six-fold symmetry. Rod-coil molecules with propylene oxide branches have been investigated for their ability to form organized monolayers on a solid surface. We observed a complete spectrum of molecular reorganizations at variable surface pressure ranging from separated circular micelles composed of 20-30 molecules to a rectangular lattice of circular micelles with the unit cell of 10.6 x 9.7 nm and further to perfectly ordered lamellar structure with 6.5 nm periodicity. Continuous compression results in folding of water-soluble flexible blocks and their desorption from the air-water interface into the water subphase. As a result, the effective content of the rod blocks at the air-water interface is changing continuously from 20% to 50% initiating molecular reorganizations predicted by the theoretical models.

3:30 PM *O2.4

Molecular Imprinting Inside Dendrimers. Steven C. Zimmerman, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Molecular imprinting in polymeric materials is a potentially powerful way to create "synthetic antibodies." These molecular hosts exhibit a guest selectivity that arises from the template used for imprinting. However, the traditional approach to molecularly imprinted polymers (MIPs) has several limitations including slow mass transfer into and out of the polymer, heterogeneous binding sites (nonlinear Scatchard plots), trapped template, and insoluble polymers that are difficult to characterize and manipulate. To overcome some of these problems, much effort has been directed toward making smaller and thinner MIPs, what we have referred to as the "top-down approach." This lecture will focus on a different, "bottom-up" or "monomolecular" strategy in which a single molecular template is imprinted in a single dendrimer. As recently reported, a porphyrin template can be imprinted inside a dendrimer (Nature 2002, 418, 399). Thus, a porphyrin core (template) was linked through ester bonds to 8 Wendland-type dendrons (J. Am. Chem. Soc. 1999, 121, 1389) each containing 8 allyl ether end-groups. The resultant dendrimer with 64 peripheral alkene groups underwent extensive intra-dendrimer ring closing metathesis (RCM) reaction with Grubbs' type 1 catalyst to produce a compact, highly cross-linked dendrimer. The core was removed hydrolytically giving the imprinted dendrimer, which selectively complexes porphyrins containing functionality complementary to the imprint. This proof of principle example shows the basic strategy can work. This talk will focus on our recent efforts to improve the monomolecular imprinting approach by: (1) Creating more rigid imprints by placing cross-linking functionality closer to the core (template). (2) Integrating into the core of the dendrimer reporter chromophores that signal binding. (3) Developing more rapid synthetic approaches (e.g., star polymers) that avoid the lengthy dendrimer synthesis. (4) Developing directed metathesis reactions where cross-linking between dendritic wedges is favored.

4:00 PM O2.5

Derivative Chemistry of Diamondoids. Shenggao Liu, Jeremy E. Dahl and Robert M.K. Carlson; MolecularDiamond Technologies, ChevronTexaco Technology Ventures, Richmond, California.

Diamondoids are cage-shaped hydrocarbons possessing rigid structures consisting of tiny fragments of a diamond crystal lattice with surfaces terminated by hydrogen atoms. Adamantane (C₁₀H₁₆) is the smallest member of this class of compounds and consists of one diamond crystal subunit. Diamantane contains two, triamantane three, and so

on. Recently, we have identified and isolated higher homologous of this class of compounds, higher diamondoids, from petroleum (Science, 299, 96-99, 2003). These include tetramantanes, pentamantanes, hexamantanes, heptamantanes, octamantanes, nonamantanes, a decamantane and an undecamantane which are 1 to 2 nm hydrogen-terminated diamonds containing 4 to 11 face-fused diamond crystal lattice cages. These molecules possess a wide variety of 3-dimensional shapes, including rods, helices, and discs, arising from different ways of face-fusing diamond crystal lattice cages. Structures also include resolvable chiral forms. Diamondoids are readily derivatized allowing customization of shapes and properties, e.g. mechanical, electronic and pharmaceutical. It has been demonstrated that properties of adamantane can be tuned by the attachment of various functional groups, allowing customized applications. Also, the properties of existing materials such as polymers can be significantly enhanced by incorporating adamantane moieties into the polymeric backbones. However, the derivative chemistry of larger diamondoids, especially triamantane and higher diamondoids, has been largely unknown. In this presentation, we focus on diamondoid derivatization chemistry, aiming at understanding the effects of symmetry on basic organic reactions of fundamental importance with a direct link to methods of activating the hydrocarbon cages and to possible immediate applications. The versatile derivative chemistry gives these 3-dimensional, nanometer size diamondoids potential for applications in a wide range of fields, including pharmaceuticals, microelectronics, optics, and specialty chemicals. They are also useful molecular building blocks that may find applications in nanotechnology and new nanostructured functional materials.

4:15 PM O2.6

Nanoscale Morphological Control in Polymer-Inorganic Hybrid Materials derived from Amphiphilic Block Copolymers.

Surbhi Mahajan¹, Sabine Renker², Anurag Jain¹, Byoung-Ki Cho¹, Jochen S Gutmann^{1,2}, Yuanming Zhang¹, Sol M Gruner³, Lewis J Fetters⁴, Geoffrey W Coates⁵ and Ulrich Wiesner¹; ¹Material Science & Engineering, Cornell University, Ithaca, New York; ²Max-Planck-Institute for Polymer Research, Mainz, Germany; ³Department of Physics, Cornell University, Ithaca, New York; ⁴School of Chemical Engineering, Cornell University, Ithaca, New York; ⁵Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York.

Linear AB and ABC triblock copolymers are known to phase separate on the nanometer length scale generating fascinating complex morphologies through self-assembly including bicontinuous cubic structures, cylinders with rings or helices, or the so-called knitting pattern. An area of particular research interest is currently their use as structure directing agents for the synthesis of inorganic silica or metal oxide-type materials. In this way structural control on the nanometer length scale through polymer self-assembly is combined with functional control as obtained from sol-gel derived solid-state materials, thus generating novel material platforms with potential applications in areas ranging from microelectronics to nanobiotechnology. The structure directing effects of AB diblock copolymers like poly(isoprene)-b-poly(ethylene oxide), PI-b-PEO, have indeed already been established. The controlled use of ABC triblock copolymers as structure directing agents for the generation of nanostructured bulk polymer-ceramic hybrid materials still remains a challenge. In order to develop such approaches from AB diblock towards ABC triblock copolymers the C block chosen in the present study is poly(n-hexyl methacrylate), PHMA. To this end, first the synthesis of PEO-b-PHMA diblock copolymers (the BC blocks in our target ABC triblocks) through a combination of anionic polymerization of ethylene oxide and ATRP of n-hexyl methacrylate is presented, and their structure directing ability with respect to an aluminosilicate phase is discussed. The synthetic approach is subsequently extended to poly(ethylene-alt-propylene)-b-poly(ethylene oxide)-b-(n-hexyl methacrylate), PEP-b-PEO-b-PHMA, triblock copolymers and polymer-ceramic hybrid materials derived from them. Characterization of the resulting polymer as well as hybrid mesostructures is performed through a combination of small angle x-ray scattering and transmission electron microscopy. Potential use of these novel materials in sensor as well as separation technologies is discussed.

4:30 PM *O2.7

Strategies for the Geometric Disassembly of Dendrimers.

Dominic V. McGrath, University of Arizona, Tucson, Arizona.

Although strategies for the controlled degradation of polymer systems have found application in both drug delivery and microlithography, examples of degradable dendrimers are scarce. Certainly, degradable subunits could easily be engineered into the dendritic architecture, and a limited number of reports have demonstrated selective fragmentation of dendrimers at the periphery, core, and interior residues of the architecture. These previously reported methods of degradation, whether stoichiometric or catalytic, all require the

interaction of a reagent with each cleavable linkage in the structure. However, we have envisioned a more efficient process whereby an initial stimulus causes a change in the structure that triggers a subsequent cascading destruction of the dendrimer into a number of smaller fragments, i.e., a chemically amplified dendrimer disassembly. This degradation method, or "dendrimer disassembly" process, fragments a dendrimer through a series of cascade cleavage reactions initiated by a single triggering event. In previous reports, we demonstrated linear dendrimer disassembly through a dendritic structure that took advantage of the ubiquitous benzylaryl ether subunit of a standard class of dendrimers. In this contribution we demonstrate the geometric cleavage of similar dendrimers whereby each cleavage event leads to two subsequent fragmentations, or geometric dendrimer disassembly. Implications of the successful implementation of this system will be discussed.

SESSION O3: Poster Session I

Chairs: Jason Hafner, Jeffrey Hartgerink and Eugene Zubarev

Monday Evening, December 1, 2003

8:00 PM

Exhibition Hall D (Hynes)

O3.1

Critical Heating Temperatures for C₆₀ Thin Films In Microfabrication. Ahalapitiya H Jayatissa, Mat. Sci. and Eng., Western Michigan University, Kalamazoo, Michigan.

Several important applications of C₆₀ have been investigated. For instant, C₆₀ has shown higher field effect mobility than many organic electronic materials investigated for thin film transistors. Other proposed applications include photodetectors, solar cells, and nanotechnology. C₆₀ films have been prepared by different techniques such as molecular beam epitaxy, vacuum evaporation and hot wall epitaxy. One of the serious issues in application of C₆₀ films for electronic devices is the degradation of electronic properties by the absorption of oxygen. The I-V characteristics of TFT fabricated by MBE- C₆₀ are degraded within several hours. This phenomenon is ascribed to the increase of electron trapping densities by absorption of oxygen in the channel region of C₆₀. Similar effect can be expected with other optoelectronic devices. One way to reduce this effect is the densification of deposited C₆₀ films by different techniques so that the absorption of oxygen through grain boundary region and interface layers can be minimized. In this study, the structure and electronic properties of C₆₀ films annealed at different temperatures have been characterized. The scope of this study is to investigate the effect of microfabrication conditions on the structure and electronic properties of C₆₀ films. Thin films of C₆₀ fullerene were prepared by vacuum evaporation on a cold substrate. The effect of thermal annealing on C₆₀ films was investigated with Raman, atomic force microscopy and X-ray diffraction. Low temperature annealing resulted in densification of C₆₀ films whereas higher temperature annealing resulted in change of C₆₀ structure to microcrystalline graphite. The C₆₀ films annealed at 100°C have the highest packing density, low surface roughness, high degree of crystallinity and stable ohmic contacts. These results indicated that the electronic properties of C₆₀ can be improved by heating in low temperature range without affecting the heat treatments in the microfabrication.

O3.2

Characterization of C₆₀ and TTF molecules on HOPG and Au(111) surfaces by scanning tunneling microscopy (STM). Jill Atsuko Miwa, Dmitrii F. Perepichka and Federico Rosei; INRS-EMT, Université du Québec, Varennes, Québec, Canada.

The adsorption of organic molecules on surfaces is relevant to the burgeoning field of nanotechnology [1, 2]. Adsorbate ordering is generally controlled by a delicate balance between molecule-molecule and molecule-substrate interactions. Understanding these governing forces will be an important step towards the design and development of novel molecular devices at the nanoscale. Here we present scanning tunneling microscopy (STM) images of buckminster fullerene molecules dispersed on highly oriented pyrolytic graphite (HOPG) in ambient air. These carbon cage molecules can act as low-dimensional molecular conductors or as active units in nanoscale electronic devices [3]. In this work we study the morphology of a full monolayer and its degradation due to oxidation as a function of time. Incidentally, the fullerene is extremely stable and thus more resistant to oxidation. Additionally, we will show highly resolved images of donor-acceptor derivatives of tetrathiafulvalene (TTF) on HOPG and single crystal Au(111). The aim is to determine how these two different substrates affect the adsorption, ordering and patterning of organic molecules. Since these molecules have strong donor and acceptor components, we will explore the possibility of using them as molecular diodes and switches [4]. References: [1] C. Joachim, J.K. Gimzewski and A.

Aviram, "Electronics using hybrid-molecular and mono-molecular devices", *Nature* 408, 541 (2000). [2] F. Rosei, M. Schunack, P. Jiang, A. Gourdon, E. Laegsgaard, I. Stensgaard, C. Joachim, F. Besenbacher, *Science* 296, 328 (2002). [3] P. Moriarty, *Rep. Prog. Phys.* 62, 297-381, (2001). [4] D. F. Perepichka, M. R. Bryce, A.S. Batsanov, E.J.L. McInnes, J.P. Zhao, R. D. Farley, *Chem. Eur. J.*, 8, 20, (2002).

O3.3

A Quantitative Raman Analysis of Carbon Nanotubes Specifically Bound by Peptide Sequences. S G Chou¹, A P Santos^{2,3}, Ge G Samsonidze⁴, C K Y Lau⁵, M S Dresselhaus^{4,2}, Y-M Chiang⁵, A K Swan⁶, B B Goldberg^{7,6} and S M Unlu⁶; ¹Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts; ³Division of Nuclear Fuel and Materials, Centro de Desenvolvimento da Tecnologia Nuclear -CDTN/CNEN, Belo Horizonte, MG, Brazil; ⁴Electrician Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts; ⁵Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ⁶Electrical and Computer Engineering, Boston University, Boston, Massachusetts; ⁷Physics, Boston University, Boston, Massachusetts.

Resonant Raman spectroscopy is performed on carbon nanotube samples that have been specifically bound to peptide sequences identified by the phage library display method. A quantitative analysis is carried out for the nanotube samples associated with different peptide sequences to evaluate the binding selectivity and efficiency, which is being compared to the separation efficiency of the diameter and metallic/semiconducting selective nanotube sorting process achieved by DNA assembly. The MIT authors acknowledge the support from Dupont-MIT Alliances (DMA).

O3.4

Low-temperature CNTs growth. Alexander F. Pal¹, Vladimir V. Dvorkin², Nikolay N. Dzbanovsky² and Nikolay V. Suetin²; ¹Troitsk Institute for Innovation and Fusion Research, Troitsk, Moscow region, Russian Federation; ²Institute of Nuclear Physics, Moscow State University, Moscow, Russian Federation.

CVD provides the possibility of growth of large amounts of identical carbon nanotubes (CNT) on a substrate specially made. It is commonly used technology for fabrication of electronic devices. For several applications it is necessary to grow CNTs upon low melting point substrates, at temperatures about 550 C and lower, to prevent substrate from softening and degradation. It is especially important for glass substrates, because nanomaterials deposited on glass surface could be easily built into present-day glass-to-metal and glass-to-ceramics technology. In microwave (MW) plasma assisted CVD substrate temperatures of 650 C and above are usually used. The main method to decrease the CNT growth temperature is the lowering of gas pressure (Torr). But this leads to significant decrease in the film growth rate. By using CH₄:CO₂ gas mixture it is possible to bind the significant part of H, which is strong nanographite etchant and, thus, one can increase growth rate, but it is not yet enough for CNTs growth at rates of microns/ hour. When pressure is high enough (tens of Torr), decrease the substrate temperatures at CW mode of operation is achieved by emitted MW energy decrease, which results in decreasing plasma volume and essential change of plasmochemistry processes. In order to solve these problems we use pulse mode of plasma excitation. In this case it is possible to eliminate both factors: increasing on-off ratio one can decrease average MW power and, hence, substrate temperature, and keep pulse power constant and, thus, preserve plasmochemistry processes and discharge volume. Our experiments showed that CNT growth at 350 0C substrate temperature can be easily achieved in pulse mode operation (modulation frequency about 1 kHz; on-off time ratio 4; average MW power 200W) and CH₄:CO₂ mixture at pressure about 40-50 Torr. Growth rates reach several microns/hour. The films obtained were studied by TEM and SEM microscopy and X-ray diffractometry.

O3.5

Relative Stabilities of Isomeric Higher Fullerenes C84 and C94: Importance of A Profound Enthalpy/Entropy Interplay. Xiang Zhao¹, Zdenek Slanina² and Hitoshi Goto¹; ¹Dept. of Knowledge-based Information Engineering, Toyohashi University of Technology, Toyohashi, Aichi Prefecture, Japan; ²Dept. of Theoretical Studies, Institute for Molecular Science, Okazaki, Aichi Prefecture, Japan.

Large-scale computations of temperature-dependent relative stabilities for two isomeric fullerene systems C84 and C94 are carried out at semi-empirical and ab initio quantum-chemical levels. C84 is the third most abundant fullerene in the conventional methods of fullerene production next C60 and C70, and has 24 IPR isomers with nine types of point group symmetries. All C84 IPR isomers are fully

optimized at HF/6-31G* levels of theory and harmonic vibration frequencies are calculated by the SAM1 method. Energetics is combined with entropy contributions based on the Gibbs function. Considerable temperature effects on the relative stabilities and behavior of enthalpy- entropy interplay in the system are found. The HF/6-31G* evaluations of the equilibrium isomeric composition of C84 agree very well with the recent experimental data. The similar Gibbs energy treatment is further applied to 134 C94 IPR isomers (with only six kinds of symmetries). If temperature effects are considered accordingly, two distinct structures (Cs, C2) are predicted to be the two thermodynamically most stable species and a good agreement with experimental observation can be achieved. Some general features of two systems will be discussed in details.

O3.6

One Dimensional Alignment of C60 Molecules Prepared on Thermal Treated Substrates. Nobuyuki Iwata, Hiroki Okuyama, Akane Kinjo and Hiroshi Yamamoto; Electronics & Computer Science, Nihon University, Chiba, Japan.

For the future nano-scale devices, the technology which controls the atoms or molecules at desired positions freely in the rather large area easily and/or quickly has been aspired. For the first step we proposed the technique manipulating the functional molecule C60 aligned along the one direction by a bottom-up strategy. The important points to achieve one dimensional (1D) alignment of C60 molecules are the surface shape of the substrate, and the stronger interaction between C60 molecule and metal than that between C60 molecules. We chose MgO(110) and Al₂O₃(0001) as substrates and Au as metal. The structure of annealed MgO(110) surface is mountain chain like due to the cleavage at {100} planes. Annealed Al₂O₃(0001) surfaces exhibit the steps and terraces structures ranging more than 5 μ m. Since the Au metal will be ordered along the mountain chains and/or steps, C60 molecules just on Au metal should remain at rather higher temperature, at which C60 molecules binding by van der Waals interaction re-evaporate, and then 1D alignment of C60 molecules will be achieved. MgO(110) and Al₂O₃(0001) substrates were annealed at 1000 degree C for 12h in air. Deposition process was carried out in MBE system with a background pressure of 1 \times 10⁻⁸ Torr. Au was deposited on the substrates until faint spots caused by Au in the RHEED patterns appeared. C60 molecules were evaporated on Au deposited substrates at less than 200 degree C for 30 min and then annealed at around 300 degree C for 30 min. RHEED patterns were detected during growing and annealing of the film. The film surfaces were evaluated by atomic force microscopy (AFM). As seen in the surface structure of Au//MgO(110), quasi-1D alignment of C60 molecules with about 50 nm \times (500-1000) nm was detected from the AFM image. The height differences of such the alignment between Au//MgO(110) and C60/Au//MgO(110) was 0.8nm, which was approximately consistent with the diameter of C60 molecule. We demonstrated that only one layer of C60 molecules directly deposited on Au metal remained. These results indicated that the significant key for 1D alignment of C60 molecules was how to arrange Au metals as foundation. By choosing suitable substrate temperature and Au flux intensity, Au particles almost was found at the steps, and partially arranged along one direction reflecting the surface structure from the AFM images of Au//Al₂O₃(001).

O3.7

Repeatability and growth mechanism of nanotubes produced by the ferrocene-toluene route. Ian Kinloch¹, Mathias CM Nolte^{1,2}, Christian H Buchel¹, Karl Schulte³, Wolfgang Bauhofer² and Alan H Windle¹; ¹Dept. of Materials Science and Metallurgy, University of Cambridge, Cambridge, Cambs, United Kingdom; ²Materials in Electrical Engineering and Optics, Technical University Hamburg-Harburg, Hamburg, Germany; ³Polymer Composites, Technical University Hamburg-Harburg, Hamburg, Germany.

The pyrolysis of ferrocene-toluene solutions is a practical method for producing aligned carbon nanotube mats of controlled dimensions on a gram scale. A standard experimental procedure incorporating SEM, TEM, Raman spectroscopy and X-ray diffraction has been developed to analyse the nanotubes produced. (NIST has highlighted the need for such a procedure to be established.) In particular, different methods for analysing the alignment and lengths of the nanotubes have been compared. This new analysis procedure has been used to assess the repeatability of five experiments run under identical conditions. Also, by applying the procedure to samples grown under different conditions a deeper understanding of the growth and alignment mechanism of the nanotubes has been obtained.

O3.8

Mechanisms of Carbon Nanotube Attachment To Silicates. Kenneth Tiedge^{1,2} and John Larzelere²; ¹B20, Naval Surface Warfare Center Dahlgren Division, Dahlgren, Virginia; ²B54, Naval Surface Warfare Center Dahlgren Division, Dahlgren, Virginia.

This effort investigated the chemical reactions involving carbon nanotubes and silicates. Carbon nanotubes can be relatively nonreactive along the surface of the tube, and they can have enhanced reactivity at kinks, defects along the surface, and at the ends. The ends can have varying reactive properties depending on whether the end is open or closed. Silicate structures vary widely because of the number of oxides that can be added. These oxides can include aluminum, boron, calcium, potassium, sodium, and titanium. These oxides are also potential sites where carbon nanotubes could be attached to the silicate material. The reactive sites covalent attachments to a silicate were compared to Van Der Waals and/or Coulombic forces alone. Nanotube attachment strength was measured using the Lateral Force Atomic Force Microscope (AFM). Clean, unreacted nanotubes were used as a control to determine Van Der Waals and/or Coulombic forces with the silicate substrate. X-Ray Photoelectron Spectroscopy (XPS) was used to identify chemical reactions at the surface. Ion beam bombardment was used to create defects in the carbon nanotubes. The potential application of the science is to eventually build a dendrimer-like network of glass fiber/carbon nanotubes. The resulting network could be used to increase particulate filtration efficiencies in non-woven High Efficiency Particulate Air (HEPA) filters by orders of magnitude without increasing pressure drops, which is an important energy saving in filtration systems.

O3.9

Alignment of Single-Wall Carbon Nanotubes on Pt Surfaces by Self-assembling Techniques. Belinda Ivette Rosario-Castro, Dafne Lozada and Carlos Raul Cabrera; Chemistry Graduate Program, University of Puerto Rico - Rio Piedras Campus, San Juan, Puerto Rico.

Single-wall carbon nanotubes (SWNTs) are very interesting materials because of their morphology, semiconducting characteristics, and electronic and mechanical properties. Its morphology (high length-to-diameter ratio) and electronic properties suggest potential application for SWNTs as hydrogen storage material for fuel cells and as anodes for lithium ion batteries. The introduction of SWNTs on these types of sources systems will improve their performance, efficiency, and capacity to store energy. SWNTs from commercial sources are usually impure. Impurities typically found in as-prepared SWNTs are metals used as catalysts for their growth, and amorphous carbon. These have to be removed in order to be able to study its properties and obtain the optimal performance on its various applications. A purification method has been applied for the removal of Fe catalysts from CNI SWNTs. This method combines the well-known acid reflux treatment and gas phase oxidation process. The goal of this project is the development of a self-assembled methodology for the preparation of ordered or aligned carbon nanotubes on platinum electrode surfaces. Self-assembled monolayer (SAM) of 4-aminothiophenol was deposited on Pt electrodes, in order to obtain an amino-terminated SAM for the chemical attachment of the carbon nanotubes. This amino SAM was characterized by electrochemical measurements, X-ray photoelectron spectroscopy (XPS), Fourier-transforms infrared (FTIR) spectroscopy, and Raman spectroscopy. Carbon nanotubes were deposited over the amino-terminated SAM by an amide bond formed between SAM amino groups and carboxylic acid groups at the open ends of the carbon nanotubes. This deposition was characterized using Raman spectroscopy and scanning electron microscopy (SEM). The possibility of using high-surface-area nanostructure of SWNTs (nanotechnology) for energy storage may allow for smaller, lighter and more efficient batteries and fuel cell systems.

O3.10

One single electron transistor based on substitutions in C₆₀. Jorge R. Soto, Jordi Austrich, Renela Valladares, Alexander Valladares, Maria Luisa Marquina, Raul Espejel and Alipio Calles; Departamento de Fisica. Facultad de Ciencias., UNAM, Mexico D.F., Mexico.

The first one electron transistor based on C₆₀ was performed by researchers of the Lawrence Berkeley National Laboratory and of the University of California at Berkeley. They deposit a dilute toluene solution of C₆₀ onto a pair of connected gold electrodes fabricated using electron-beam lithography. The entire structure was on SiO₂ insulating layer on top of a silicon wafer that serves as a gate electrode to modulate the electrostatic potential of C₆₀. The device showed a transistor behavior when bias and gate voltage were applied. According to the experiments, the device can give information of the nanomechanical vibrations of the C₆₀ molecule coupled to the gold atoms of the electrodes. In the present work we are simulating substitutions of carbon atoms, by nitrogen, in the C₆₀ molecule in order to study the possible changes in the transistor properties. The electronic and vibrational calculations are made using ab initio methods to compare them with the original transistor made with pure

O3.11

Formation of Conductive Particle Networks in Noryl[®]/Graphite Nanocomposites. Ceyhan Celik, Prabir Patra, Yong Kim and Steve B. Warner; Textile Sciences Department, University of Massachusetts Dartmouth, North Dartmouth, Massachusetts.

Present work focuses on preparation and characterization of electrically conducting Noryl[®] (a modified PPE/PS blend)/expanded graphite composites via a melt blending technique. Different grades of expanded graphite were used with an average sheet thickness of 100 nm as measured under SEM observations. Studies concerning the polymer/graphite nanocomposites showed that electrical conductivity reaches up to 10-2 S/cm with a certain concentration of expanded graphite content. It was found that the conductivity does not increase continuously with increasing filler content but shows a sudden jump to higher conductivity values at a certain filler concentration. This sudden change in conductivity is ascribed to a percolation process within the polymer/filler mixtures. We are reviewing the percolation theory and effective media approach, as they apply to the electrical conductivity of mixtures of conductive and insulating material. We are investigating the parameters that affect the resistivity of the composites, such as particle size and shape, mixing time on filler distribution, filler concentration, composite processing technique, and filler/matrix interactions. Processing of different concentrations of Noryl[®]/EG composites having different average expanded graphite particle diameters, and composites with varying mixing time intervals in a Brabender mixer is under way. Mathematical analysis of our experimental results to corroborate the formation of conductive graphite networks in polymer matrix is in progress.

O3.12

Self-Assembly of Amphiphilic Polyacetylenes on Multi-Walled Carbon Nanotubes. Bon-Cheol Ku¹, Dong Wook Kim³, Ramaswamy Nagarajan¹, Alexandre Blumstein¹, Jayant Kumar² and Lynne A Samuelson^{4,1}; ¹Chemistry, University of Massachusetts, Lowell, Massachusetts; ²Physics, University of Massachusetts, Lowell, Massachusetts; ³Advanced Materials Division, Korea Research Institute of Chemical Technology, Taejeon, South Korea; ⁴US Army RDECOM, Natick Soldier Center, Natick, Massachusetts.

We report a facile and noncovalent functionalization of multi-walled carbon nanotubes (MWCNTs) via self-assembly with amphiphilic polyacetylenes, poly(N-octadecyl-2-ethynylpyridinium bromide) (PEPy-C18). MWCNTs were mixed with PEPy-C18 in methanol (1 mg/mL) and sonicated. AFM on mica showed that after mixing, MWCNTs and PEPy-C18 composites formed that had aggregated nanostructures. Static light scattering and atomic force microscopy (AFM) showed that the C18 side group was aggregated not only in the solution but also on a mica surface. The cmc of C18 was 25 μg/mL (0.057 mM) in methanol and the height of aggregated form of C18 above cmc on the mica surface was approximately 3 nm. The possible applications of such nanocomposites and optimum conditions for functionalization of CNTs with these amphiphilic conjugated polyacetylenes will be reported.

O3.13

Dispersion and Deposition of Individual Single-Walled Carbon Nanotubes for Device Applications.

Phillip A. Williams¹, Buzz Wincheski², Jan M. Smiths³, David Adebimpe⁴ and Marek Zgol⁴; ¹NASA-Langley, National Research Council, Hampton, Virginia; ²NASA Langley Research Center, Hampton, Virginia; ³NASA-Langley, Lockheed Martin Space Operations, Hampton, Virginia; ⁴GMA Industries, Inc., Annapolis, Maryland.

Single-walled carbon nanotubes (SWNTs) hold great promise in a variety of applications due to their desirable mechanical, electronic, and magnetic properties. Most processing techniques to date have resulted in ropes or bundles of SWNTs; however, much experimental and theoretical work has shown that the ultimate success of these novel materials as functional devices relies on placement and characterization of individual nanotubes. The resulting device behavior then can be attributed to the specific nanotube's properties. Here we describe research efforts on exfoliating bundles of SWNTs into individual tubes in a series of organic solvents. We systematically test a combination of solvents and surfactants to obtain reproducible depositions of individual SWNTs. We then fabricate SWNT device test beds through: 1.) the use of photolithography and electron beam lithography to define device templates and contact electrodes to the SWNTs, and 2.) the use of AC electrophoresis for directed placement and alignment of individual tubes. Applications of the SWNTs as nanoprobe for nondestructive evaluation are described, along with measurements of the sensitivity for magnetic field and strain sensing.

03.14

Encapsulation of Single Walled Carbon Nanotubes by Crosslinkable Surfactants. Benjamin Weaver Messmore¹, Michael S Arnold², Mark C Hersam² and Samuel I Stupp^{2,1,3}; ¹Chemistry, Northwestern University, Evanston, Illinois; ²Materials Science and Engineering, Northwestern University, Evanston, Illinois; ³Feinberg School of Medicine, Northwestern University, Chicago, Illinois.

Carbon nanotubes have been of great interest because of their electronic and mechanical properties such as ballistic conduction and high strength. However, they are insoluble in most solvents and therefore lack the necessary processability to use these properties. Nanotubes are not easily solvated and tend to pack into bundles due to van der Waals interactions between tubes, and bundling disrupts their electronic structure. Surfactants have been used to suspend isolated nanotubes in water and those tubes exhibit interesting optical properties as a result of their isolation. In this method of isolation removal of water removes the simple surfactant molecules used so far from the surfaces of nanotubes. We report here a novel class of surfactant molecules for nanotube isolation. The novel structure enables "reversible" covalent capture of surfactant assemblies on the nanotubes. The triblock surfactant contains a tris(hexaethylene glycol) gallic acid hydrophile, three cysteine amino acids, and a cyanobiphenyl hydrophobic core. These tailored amphiphiles have shown the ability to encapsulate reversibly single nanotubes, opening new possibilities for their use in electronics.

03.15

Biologically-Compatible Gd@C₆₀ MRI Contrast Agents. Balaji Sitharaman¹, Robert D. Bolskar² and Lon J. Wilson¹; ¹Chemistry Dept, Rice university, Houston, Texas; ²TDA Research Inc., Wheat Ridge, Colorado.

Gadolinium-containing metallofullerenes are currently being pursued as a new generation of magnetic resonance imaging (MRI) contrast agents. These molecules offer fundamental advantages over commercially-available chelate compounds, the most important being the complete lack of metal-ion dissociation under physiological conditions. Gd@C₆₀ belongs to the most abundantly produced class of endohedral metallofullerenes generated in the carbon arc process. Previously, M@C₆₀ materials in general (including Gd@C₆₀) were thought to be unusable in practical applications due to their insolubility and air sensitivity. However, recent breakthroughs in derivatization, solubilization and stabilization of these species have fully overcome these limitations (Bolskar, R. D. et al., *J. Am. Chem. Soc.*, 2003, 125(18), 5471-5478). Advanced paramagnetic MRI contrast agents can be used to improve angiographic imaging, i.e. the in vivo imaging of the "blood pool". To develop new Gd@C₆₀ compounds for use in MR angiography, typically the compound should show high relaxivity, low osmolality, high chemical stability, and good water solubility at physiological pH. To this end, we have synthesized and characterized new malonoserinolamide metallofullerenes, Gd@C₆₀[C(COSer)₂]_n (Ser=2-amino-1,3-propanediol). The facile synthesis is based on Bingel additions to Gd@C₆₀ at the solid-phase / solution-phase interface of insoluble Gd@C₆₀. Characterization of these new metallofullerene materials will be presented and their MRI properties evaluated. This research is sponsored by the Robert A. Welch Foundation (C-0627) and the NIH (SBIR Grant 5-R44-CA66383 and Grant 1-R01-EB000703).

03.16

Sequential Study Of The Linear Alkylamine Assisted Bulk Separation Of Semiconducting From Metallic Single-Wall Carbon Nanotubes As A Function Of Amine Chain Length. SangNyon Kim, Debjit Chattopadhyay, Mathew Mathai, Zhengtang Luo and Fotios Papadimitrakopoulos; IMS, University of Connecticut, Storrs, Connecticut.

Single wall carbon nanotubes (SWNTs) can be semiconducting (sem-) or metallic (met-), independent of its diameter and depending only on its chiral vectors, making them a unique class of nanostructured material. However, wide applicability of SWNTs has been hindered due to poor control over nanotube diameter and type (met- vs. sem-) during their stochastic growth (generating mixtures of 1:2 in met-sem-SWNTs), that generate SWNTs packed together in bundles. Recently our group demonstrated that, exfoliation of carboxyl-functionalized SWNTs by octadecylamine (ODA) leads to the bulk separation of SWNTs by type, and explained this observation on the basis of enhanced affinity-induced organization of ODA moieties on the sidewalls of sem-SWNTs, leading to the selective sedimentation of met-SWNTs. The goal of this paper is to evaluate the homologous series of commercially available long chain linear aliphatic amines and compare the resulting separation to the ODA-assisted route. This will aid in generating an understanding of the role the hydrocarbon chain length plays in disrupting the hydrophobic interactions between SWNTs and enabling differential

dispersion of met- vs. sem-SWNTs.

03.17

Preparation and Characterization of Thin Polymer Films Reinforced with Carbon Nanotubes. Mikhail Kozlov, Mei Zhang, Amin Saad, Mike Sampson, Richard Margolin, Sergey Li, Alan Dalton, Edgar Munoz, Anvar Zakhidov and Ray Baughman; NanoTech Institute, The University of Texas at Dallas, Richardson, Texas.

We describe methods for making very thin, free-standing films of carbon nanotube polymer composites and characterize the structure and properties of these films. Fine dispersions of single-walled and multi-walled carbon nanotubes in aqueous poly(vinyl alcohol) and poly(vinyl pyrrolidone) solutions were prepared using intense sonication. The prepared dispersions were drop cast on the surface of a coagulating liquid or spin coated on a substrate. Thin, free-standing films were obtained in both cases. Scanning electron microscopy of the films showed a highly uniform nanotube network, which is consistent with observed well-resolved optical spectra, showing sharp peaks at 1450, 1300 and 1200 nm. An observed shift of Raman RBM and G modes was attributed to the polymer/nanotube interaction. Comparative data on the effects of nanotube loading on the mechanical properties of the films are provided and possible applications are discussed.

03.18

Building Single-Walled Carbon Nanotube Architectures on Nano Scale Patterned Substrates. Yung Joon Jung¹, Yoshikazu Homma², Toshio Ogino³, Yoshihiro Kobayashi², Daisuke Takagi⁴, Bingqing Wei¹, Robert Vajtai¹ and Pulickel M Ajayan¹; ¹Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York; ²NTT Basic Research Laboratories, Atsugi, Kanagawa, Japan; ³Division of Electrical and Computer Engineering, Yokohama National University, Yokohama, Japan; ⁴Department of Physics, Meiji University, Higashimita, Japan.

A method for producing self-directed high-density, large area single-walled carbon nanotube networks on nano-scale patterned Si or SiO₂ substrates is presented. Arrays of nano-scale Si or SiO₂ patterned structures were prepared using synchrotron-radiation lithography process and the growth of SWNTs was performed by chemical vapor deposition using methane and iron or cobalt catalysts. After CVD, transition metal particles of a 3-7 nm size, obtained by depositing thin catalyst films (0.5-1 nm), remain as active catalysts for the growth of high-density single-walled carbon nanotubes on the selected catalyst support materials (SiO₂). Highly organized single-walled carbon nanotube architectures with controlled density can be fabricated following the pre-defined nano size substrate patterns. The above results point to the strong possibility of building carbon nanotube-based molecular scale electronic devices.

03.19

Adsorption Studies on Purified Single-wall Nanotubes Demonstrate Potential Gas Storage and Separation Applications. Katherine Gilbert^{1,2}, Anne C. Dillon¹, Philip A. Parilla¹, Jeff L. Alleman¹, Kim M. Jones¹, J. Douglas Way², Robert M. Baldwin², Michael J. Heben¹; ¹National Renewable Energy Laboratory, Golden, CO; ²Chemical Engineering Dept, Colorado School of Mines, Golden, CO.

Carbon single-wall nanotubes (SWNTs) have exciting potential applications for gas storage and separations. However, in order to accurately characterize the gas-nanotube interaction, SWNTs must be free from impurities. Many gas adsorption studies are not performed on highly pure SWNTs making the interpretation of results confusing and difficult to reproduce.

Previously, we reported a simple purification process for laser-synthesized materials (1,2) that may result in > 98 wt% pure SWNTs (3). However, sometimes the laser-synthesis process generates graphite encapsulated catalyst metals that are difficult to eliminate, and the simple purification process does not result in high purity materials. More aggressive acid treatments destroy nanotubes resulting in a low yields.

We have found by oxidizing as-produced nanotubes in carbon dioxide prior to acid treatment, a lower metal content for purified nanotubes is achieved without decreasing the yield. The endothermic oxidation in carbon dioxide at temperatures between 800 and 1100 °C decreases amorphous carbon and the carbon coating surrounding the metal particles in as-produced nanotube samples. This selective oxidation allows for a more effective acid treatment and a lower final metal content. It is then possible to perform gas adsorption studies on highly pure materials. We previously reported hydrogen adsorption on SWNTs at near ambient conditions (4) and now consider adsorption of different gas molecules including methane and carbon dioxide. The adsorption studies have been conducted with both temperature programmed desorption and volumetric techniques. Isoteric heats of adsorption and activation energies for desorption give insight into how

and where the gas molecules are adsorbed. Initial findings indicate striking differences in the gas adsorption affinities of carbon dioxide, methane and hydrogen. Mixed gas adsorption studies are also conducted in order to understand competitive adsorption processes. Our results suggest that purified SWNTs are promising candidates for gas storage and purification applications.

- (1) Guo, T.; Nikolaev, P.; Thess, A.; Colbert, D. T.; Smalley, R. E. *Chem. Phys. Lett.* 1995, 243, 49-54.
- (2) Dillon, A. C.; Parilla, P. A.; Alleman, J. L.; Perkins, J. D.; Heben, M. J. *Chem. Phys. Lett.* 2000, 316, 13-18
- (3) Dillon, A. C.; Gennett, T.; Jones, K. M.; Alleman, J. L.; Parilla, P. A.; Heben, M. J. *Adv. Mat.* 1999, 11, 1354-1358
- (4) Dillon, A. C.; Jones, K. M.; Bekkedahl, T. A.; Kiang, C. H.; Bethune, D. S.; Heben, M. J. *Nature* 1997, 386, 377-379.

SESSION O4:

Chair: Jason Hafner

Tuesday Morning, December 2, 2003
Room 206 (Hynes)

8:30 AM O4.1

Quantitative study of DNA-assisted separation process for Metallic and Semiconducting Single Wall Carbon Nanotubes by resonance Raman spectroscopy. Adelina Pinheiro Santos^{1,10},

Georgii G. Samsonidze², Shin Grace Shou³, Alexander Gruneis⁴, Stephen Cronin⁵, Gene Dresselhaus⁶, Mildred S Dresselhaus^{1,2}, Ming Zheng⁷, Anand Jagota⁷, Bruce A Dinner⁷, G Bibiana Onoa⁷, Ellen D Semke⁷, Anna K Swan⁸, M Selim Unlu⁸ and Bennett Goldberg⁹;
¹Dept of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Dept of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts; ³Dept of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts; ⁴Dept of Physics, Tohoku University, Sendai, Japan; ⁵Harvard University, Cambridge, Massachusetts; ⁶Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts; ⁷Experimental Station, DuPont Central Research and Development, Wilmington, Delaware; ⁸Dept of Electrical and Computer Engineering, Boston University, Boston, Massachusetts; ⁹Dept of Physics, Boston University, Boston, Massachusetts; ¹⁰Division of Nuclear Fuel and Materials, Centro de Desenvolvimento da Tecnologia Nuclear - CDTN/CNEN, Belo Horizonte, MG, Brazil.

Single-stranded DNAs (ss-DNAs) have recently been demonstrated to be powerful bio-macromolecules for processing single wall carbon nanotubes (SWNTs). The ss-DNAs attach to the nanotube body, forming highly-ordered supramolecular self-assembled hybrid structures, which enable the dispersion of individual nanotubes from SWNTs bundles and their separation according to their diameter and electronic properties. In the present work, a detailed resonance Raman study is carried out using multiple laser excitation energies to evaluate the DNA-assisted dispersion and separation process of carbon nanotubes, qualitatively previously reported by M. Zheng and co-workers [1]. The spectral analysis clearly shows that the separation process discriminates between metallic and semiconducting nanotubes, but the process also discriminates between tubes with different diameters. The first eluted fractions are enriched with metallic (M) and small diameter tubes, while the concentration of semiconducting (S) and large diameter tubes is enhanced in the later eluted fractions. A quantitative evaluation of the efficiency of the separation process regarding the S/M and small/large diameter tubes is presented. This evaluation is done by modifying the methodology recently proposed by Samsonidze *et al.* [2] for the octadecylamine-assisted bulk separation process [3], taking into account the diameter distribution for each fraction. The evaluation is corroborated by the analysis of the G⁻ band feature. We also show initial efforts on a spectroscopic study of DNA-wrapped SWNTs at the single molecule level. This work was carried out in part from the Molecular Electronics group at DuPont CR&D. The authors gratefully acknowledge support from the Dupont-MIT Alliance, NSF-DMR 01-16042, and Brazilian Agency CNPq Fellowship (APS). [1] M. Zheng *et al.*, *Nature Mat.* 2, 338 (2003). [2] Ge. G. Samsonidze *et al.*, *Phys. Rev. B* (submitted 6/09/03; accession code BFR907). [3] D. Chattopadhyay *et al.*, *J. Am. Chem. Soc.*, 125, 3370 (2003).

8:45 AM O4.2

Giant Fullerene Recovery and Characterization: A New Fullerene Material. Michael Diener, Robert D Bolskar and J. Michael Alford; TDA Research, Wheat Ridge, Colorado.

The formation of fullerenes in sooting flames is an inexpensive, reliable, high yield process, and was recently up-scaled to create tons of buckyballs per year. Twenty percent (or more) by weight of the as-produced combustion soot can be recovered by extracting the soot with aromatic solvents. However, mass spectrometry data show that

giant fullerenes, apparently abundant in the as-produced combustion soot, are not recovered by solvent extraction. Here we present a simple and inexpensive electron-transfer method that renders the heretofore insoluble giant fullerenes soluble, and allows for their recovery in gram-to-kilogram quantities. As a consequence of the method development, it has been determined that another ca. 20% of the as-produced combustion soot consists of giant fullerenes. The recovered giant fullerenes form a robust, insoluble, polymeric fullerene material, with properties that are distinct from common fullerenes and their mixtures. We will also present preliminary experimental investigations into the chemical and physical properties of mixed giant fullerenes in comparison to the toluene-extractable fullerenes, and review the predominant features of the giant fullerenes' molecular electronic structure.

9:00 AM O4.3

Surfactant-Amine-Assisted Bulk Separation Of Metallic From Semiconducting Carbon Nanotubes.

Fotios Papadimitrakopoulos¹, Debjit Chattopadhyay¹, Izabela Galeska¹, Sang Nyon Kim¹, Mathew Mathai¹, Zhengtang Luo¹, Georgii G Samsonidze², Shin Grace Chou³, Adelina P Santos³, A Selbst², Gene Dresselhaus² and Mildred Dresselhaus²; ¹IMS, University of Connecticut, Storrs, Connecticut; ²Departments of Physics, Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts; ³Departments of Chemistry and Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The bulk separation of metallic from semiconducting single wall carbon nanotubes (SWNTs) presents a unique challenge in nanoscience and nanotechnology. The critical component of any separation methodology hinges on unbundling SWNTs from their naturally occurring rope-like aggregates. This is of pivotal importance, because one has to overpower the collective van der Waals interactions over the length of these nanostructures, estimated to be in the order of 500 eV per micrometer of tube-to-tube contact. Zwitterion-based solubilization, as part of acid-base interactions between the carboxy-functionalities of SWNTs and the amine groups of octadecylamine (ODA) was proved to provide only transient suspension stabilization against nanotube aggregation. On the other hand, semiconducting (sem-) SWNTs was found to form stable charge transfer complexes with ODA, as opposed to its the metallic (met-) counterparts. Our group exploited this fundamental difference in chemical affinities of amines towards SWNTs so as to precipitate the met-SWNTs while keeping sem-fraction in solution. Such profound solubility difference was further coerced through the organizational ability of ODA (a long chain aliphatic amine known to exhibit lamellar structures) to self-assemble onto the atomically uniform nanotube surface along with carefully controlling the concentration and other physicochemical interactions in the SWNT/ODA dispersions. To the best of our knowledge, the ODA-assisted separation process presently represents the state of the art in SWNT separation by type with separation efficiencies for sem-SWNTs being greater than 99 percent. This is further augmented by the enhanced solubility (0.1 - 0.5 mg/ml) of SWNTs in ODA/THF mixtures, along with the ease of regenerating pristine SWNTs following sublimation of the physisorbed ODA moieties at 250 °C. This simple, yet versatile separation methodology can pave the way for enabling SWNTs to attain the required level of purity to positively impact applications such as nanoelectronics, sensors, actuators, composites and energy storage devices, where the use of sem- or met- nanotubes can be tailored as needed. This paper will present an extensive Raman characterization along with supplementary electrical measurements to verify such separation, that has been achieved for both HiPco and laser-ablated SWNTs. In addition it will provide a model, supported by microscopic, calorimetric and X-Ray characterization techniques, to explain the origins for such separation. I D. Chattopadhyay; I. Galeska; F. Papadimitrakopoulos; "A Route for Bulk Separation of Semiconducting from Metallic Single Wall Carbon Nanotubes", *J. Am. Chem. Soc.* 2003, 125, 3370-3375. Financial support from NSF, AFOSR and ARO is greatly appreciated.

9:15 AM O4.4

Structure-based carbon nanotube sorting by ordered DNA assembly: A modern use of a prebiotic process. Ming Zheng¹, A.

Jagota¹, M. S. Strano², P. Barone², S. G. Chou³, B. A. Diner¹, M. S. Dresselhaus³, R. S. Mclean¹, G. B. Onoa¹, Ge. G. Samsonidze³, A. P. Santos³, E. D. Semke¹, M. Usrey² and D. J. Walls¹; ¹DuPont CR&D, Wilmington, Delaware; ²Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Department of Chemical and Urbana, Illinois; ³Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Spontaneous self-assembly of nucleic acid bases occurs on a variety of inorganic surfaces. This phenomenon, considered as an important prebiotic process relevant to the origin of life, has led us to seek a new function for nucleic acids in the manipulation of inorganic

nanomaterials, where interfacial interactions dominate. We have explored this idea in the separation of carbon nanotubes (CNTs) - the single greatest impediment to their technological application. Many attempts at CNT separation have yielded only length sorting. Here we show that a single-stranded DNA ($d(\text{GT})_n$, $n = 10$ to 45) self-assembles into an ordered supramolecular structure around individual CNT, in such a way that the electrostatic properties of the DNA-CNT hybrid depend on tube type, enabling CNT separation by anion-exchange chromatography. Optical absorption and Raman spectroscopy show that the separation is bimodal based on both electronic properties and the diameters of CNTs: early fractions are enriched in the smaller diameters and metallic tubes, whereas late fractions are enriched in the larger diameters and semiconducting tubes. These results clearly demonstrate the utility of ordered nucleic acid structures in inorganic nanomaterial processing.

9:30 AM *O4.5

Controlled Growth of Y-Junction Nanotubes. Apparao M Rao¹, Nick Gothard¹, Chiara Daraio² and Sungho Jin²; ¹Dept. of Physics, Clemson University, Clemson, South Carolina; ²Department of Mechanical & Aerospace Engineering, University of California, San Diego, La Jolla, California.

In-situ CVD synthesis of Y-junction carbon nanotubes will be discussed using a simple process of incorporating Ti-containing catalyst. In this method, initiation or prevention of Y-junction formation on existing carbon nanotubes can be controlled via controlling the composition of Ti concentration in the catalyst particles. It is proposed that the mechanism for the observed Y-junction formation involves the attachment of one or more catalyst particles on the side of growing MWNTs, which subsequently serves as the initiate nucleation of the branching nanotube(s). Cascading Y-junction series as well as quadruple junctions have also been synthesized, which may offer interesting device applications. The simplicity and controllability of such an in-situ Y-junction fabrication technique can be useful for potential nanoelectronics applications as ready-made three-terminal nanoscale transistors, amplifiers, switches and ballistic rectifiers.

10:30 AM *O4.6

Functionalization Of Carbon Nanotubes With Aryldiazonium Salts. Christopher A. Dyke¹, Michael S. Strano², Richard E.

Smalley³ and James M. Tour¹; ¹Department of Chemistry and Mechanical Engineering and Materials Science, and Center for Nanoscale Science and Technology, Rice University, Houston, Texas; ²Department of Chemical and Biomolecular Engineering, University of Illinois, Urbana, Illinois; ³Department of Physics, Rice University, Houston, Texas.

Functionalization of single-walled carbon nanotubes delivers material with increased solubility and better dispersion in host polymers. In using an aryldiazonium salt, which is formed by treating an aniline with a nitrite, it is possible to form functionalized carbon nanotubes with short reaction times without the use of solvent. This approach eliminates the need for a large volume of solvent, which was previously considered essential due to the insolubility of carbon nanotubes. Mechanochemical exfoliation of long bundles of nanotubes occurs merely by deforming the nanotubes with a stir bar, generating reactive sites at the sidewall of liberated nanotubes. Pre-formed aryldiazonium salts also react efficiently with individual SDS-coated SWNTs in water to form aryl functionalized SWNTs. Remarkably, the resulting SWNTs have up to 1 in 9 carbons along their backbones bearing an organic moiety. They remain unbundled throughout their entire lengths, even with these relatively small functional moieties. These materials remain as individuals in organic solvents and have greatly increased solubility. The same methodology that gives functionalized individual nanotubes also produces selectively functionalized material when performed in a controlled fashion, which was conducted in collaboration with the Smalley lab. Here, the metallic carbon nanotubes react to the near exclusion of the semiconducting nanotubes. Selectivity is dictated by the availability of electrons near the Fermi level which serves to stabilize a charge transfer transition state preceding bond formation.

11:00 AM O4.7

One-dimensional lipid bilayers on carbon nanotube templates. Alexander B. Artyukhin², Olga Bakajin¹, Pieter Stroeve² and Aleksandr Noy¹; ¹Department of Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California; ²Department of Chemistry and Materials Science, University of California, Davis, California.

One-dimensional materials have an enormous potential as key components for nanoscale biological sensors. In spite of an obvious need for reconstitution of biomolecules in such devices to enhance their specificity, robust strategies for noncovalent surface modification

of 1-D materials are missing. Lipid bilayers in particular offer a very attractive platform for immobilizing biological molecules. We present a new way of 1-D materials modification based on polyelectrolyte layer-by-layer self-assembly followed by the lipid bilayer formation. We demonstrate our strategy by synthesizing one-dimensional lipid bilayers wrapped around carbon nanotubes. We also show that the lipid molecules maintain their mobility even in these highly-strained structures and present a diffusion model for quantitative description of their behavior.

11:15 AM O4.8

Non-covalent functionalization of carbon nanotubes.

Alvaro Carrillo¹, Jeffrey Swartz¹, Jason Gamba¹, Ravi S. Kane¹, Nirupama Chakrapani², Bingqing Wei² and Pulickel Ajayan²; ¹Chemical Engineering, Rensselaer Polytechnic Institute, Troy, New York; ²Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York.

We describe a strategy for functionalizing carbon nanotubes with multilayered polymeric films. Poly(amphiphiles) adsorb non-covalently onto graphite and carbon nanotube surfaces from aqueous solutions, due to hydrophobic interactions. The covalent attachment of a second polymer layer to this initial adsorbed layer results in the formation of a cross-linked polymer bilayer; additional layers can be deposited by the covalent or electrostatic attachment of polyelectrolytes. The multilayered polymeric films were characterized using contact angle goniometry, IR spectroscopy, and scanning electron microscopy. We used these multilayered polymer films to mediate the attachment of gold nanoparticles to graphite and single-walled nanotube (SWNT) surfaces. This approach provides a convenient method for attaching other nanostructures, biological molecules, or ligands to carbon nanotubes

11:30 AM *O4.9

Tuning the Properties of Carbon Nanotubes by Electron Irradiation and Polyatomic Ion Beam Deposition.

Susan B Sinnott, Materials Science & Engineering, University of Florida, Gainesville, Florida.

Classical molecular dynamics simulations with many-body empirical potentials are used to study the tuning of the properties of carbon nanotubes and nanotube-polymer composites through electron irradiation and polyatomic ion beam deposition. First, crossed single-walled nanotubes of various chiralities are modified through electron irradiation at relatively low energies of 5 eV. Fusing of the nanotubes occurs and the structure and relative stability of the junction are found to depend on the chirality of the nanotubes. The electronic properties of these imperfect junctions are also calculated with tight-binding electronic structure methods and compared to the electronic properties of the more commonly considered ideal nanotube junctions. Next, chemical functionalization of nanotubes is important for controlling their adhesion to polymers in composite materials. Therefore, simulations are used to explore the use of polyatomic ion beam deposition to modify the structure of empty nanotubes and "nanopeapods" of nanotubes filled with buckyballs. The results show that the nanotubes can be chemically functionalized and that cross-links can be produced between adjacent nanotubes in a bundle, between nanotube walls within a multi-walled tube structure, and between the nanotubes and the buckyballs. Lastly, the direct modification of nanotube-polymer composites by ion beam deposition is considered. The simulations show that this approach can produce cross-links between the tubes and polymer chains in situ, but that there are important structural dependencies in the results. This work as a whole illustrates the manner in which the properties of carbon nanotubes can be tuned to meet the requirements of a particular application. The support of the National Science Foundation through grant CHE-0200838 is gratefully acknowledged.

SESSION O5:

Chair: Jason Hafner

Tuesday Afternoon, December 2, 2003

Room 206 (Hynes)

1:30 PM *O5.1

Carbon Nanotubes: From Molecular Electronics to Chemical and Biological Devices. Hongjie Dai, Department of Chemistry, Stanford University, Stanford, California.

This talk will present our latest research in the area of carbon nanotubes. We have been using carbon nanotube as a model system to study interesting nanoscale problems concerning materials synthesis, solid-state physics and devices, and surface science. This presentation will cover our latest results in, (1) Controlled synthesis of nanotube structures on catalytically patterned surfaces. (2) Electrical transport properties of nanotubes, especially semiconducting

nanotubes in field effect transistor structures, including the recent results on high κ gate dielectric integration and ballistic nanotube transistors. And (3) surface chemistry of nanotubes for various chemical and biological applications.

2:15 PM O5.2

Novel Carbon Nanotubes, Nanofibers, and Nanoribbons by Covalent Capture of Confined Liquid Crystals. Christopher Chan¹, Kengqing Jian¹, Gregory Crawford¹, Nancy Yang² and Robert H. Hurt¹; ¹Engineering, Brown University, Providence, Rhode Island; ²Sandia National Laboratories, Livermore, California.

This paper presents three new carbon nanofibers produced by thermal treatment of polyaromatic-based liquid crystals assembled in confined nanospaces. The first material uses thermotropic discotic liquid crystalline precursors assembled in nanochannel alumina to produce "orthogonal" carbon nanofibers whose graphene layers lie uniformly perpendicular to the fiber axis. This arrangement arises from the preferred "edge-on" anchoring state of polyaromatics on alumina coupled with the absence of director elastic strain in this unique orthogonal configuration. Two additional materials use lyotropic liquid crystals formed by water-soluble, polyaromatic-compounds, whose disk-shaped molecules stack into tall rods driven by π -interactions in the core and hydrogen bonding through peripheral hydrophilic groups. The non-covalent assembly of these rods in nanochannel alumina produces, after thermal treatment, unique carbon nanotubes whose graphene layers lie perpendicular to the tube axis. Adjustment of the processing conditions can produce carbon nanoribbons as an alternative to hollow tubes. These materials are quite different from "conventional" carbon nanomaterials and offer complementary properties. Rather than high stiffness and conductivity these inverted forms offer a high surface density of reactive graphene edge sites for functionalization and easy access to interlayer spaces. A variety of other forms can be synthesized by this new principle by systematically changing the template material to one that favors "face-on" molecular orientation, guided by anchoring rules previously determined on flat substrates. We note that by using polyaromatic liquid crystalline phases that already possess the basic kernel of graphitic carbon, this synthesis route combines the two competing approaches of special interest in this session: assembly by soft intermolecular interactions and novel sp²-hybridized carbons forms.

2:30 PM *O5.3

Advances in the Chemistry of Single-Walled Carbon Nanotubes. Robert C Haddon, University of California, Riverside, California.

The problems posed by the synthesis and purification of single-walled carbon nanotubes (SWNTs) has inhibited progress of the field. I will discuss the methods that are available for measurement of SWNT purity and the current status of processes designed to purify carbon nanotubes. In addition we provide a method to clearly distinguish between ionic and covalent chemistry that is unique to SWNTs.

3:30 PM *O5.4

Super Tough Nanotube Composite Fibers for Artificial Muscle and Electronic Textile Applications. Ray H Baughman, Alan B. Dalton, Steve Collins, Edgar Munoz, Joselito M. Razal, Von Howard Ebron, John P. Ferraris, Jonathan N. Coleman and Bog G. Kim; UTD NanoTech Institute and the Chemistry Department, The University of Texas at Dallas, Richardson, Texas.

We describe spinning hundred-meter-long carbon nanotube composite fibers having a higher toughness than spider silk or any natural or synthetic fiber, as well as high tensile strength (1.8 GPa) and modulus (80 GPa). Normalized to density, the strength and modulus is twice that of steel wire. The energy needed to break these fibers is over five times higher than the best spider silk, and at least fifty times the energy to break the same weight steel wire. We make fiber supercapacitors from our spun fibers and weave them into textiles. Long cycle life is demonstrated, as well as gravimetric energy storage density that approaches that of large supercapacitors operated over the same one-volt potential range. These nanotube composite fibers, which are easily woven or sewn into textiles, are quite interesting for artificial muscles and other electronic textile applications -such as distributed sensors, electronic interconnects, electromagnetic shielding, antennas, and batteries. Such applications and the origin of the attractive fiber properties will be discussed.

4:00 PM O5.5

Nematic Alignment of Carbon Nanotubes. Wenhui Song, Ian Kinloch and Alan H Windle; Department of Materials Science & Metallurgy, University of Cambridge, Cambridge, United Kingdom.

Nematic alignment of the aqueous dispersion of carbon nanotubes (CNTs) has been observed. The method of bireflection under polarised light demonstrates multidomain structure both in the

dispersion and in solid films obtained after the removal of the water. The nematic microstructure, as measured in the solid state is also apparent in scanning electron microscopy which can resolve individual tubes. In particular, the observation of structures of disclinations with topological strength ± 0.5 has allowed a direct study of nematic distortions as well as the core structure of the defects. The work also points to the significance of the axial ratio of the tubes, and the segregation of the tube ends.

4:15 PM O5.6

Perpendicularly Aligned Carbon Nanotubes Across Polymer Film For Novel Membrane Structure. Nitin Chopra¹, Vasileios Gavalas², Rodney Andrews³, Leonidas G Bachas² and Bruce Jackson Hinds^{1,2}; ¹Chemical and Materials Engineering, Univ. of Kentucky, Lexington, Kentucky; ²Chemistry, University of Kentucky, Lexington, Kentucky; ³Center for Applied Energy Research, University of Kentucky, Lexington, Kentucky.

Molecular transport through the nm-scale core of carbon tubes has theoretically shown interesting ordering properties and selectivity. However the fabrication of large area membranes utilizing the nm-scale inner cores of aligned graphitic CNTs remains elusive. For several years highly aligned and dense arrays of multi-walled carbon nanotubes (MWCNT) have been synthesized in a ferrocene/xylene CVD process. Although outer wall diameters vary 30+10nm, inner hollow core diameters have much finer control at 4+2.3 nm, thus aligned MWCNTs are a promising candidate for membrane structures. Reported here is a process to readily incorporate polymer in between CNTs without disrupting CNT alignment that is perpendicular to the substrate. The 10um thick composite film is removed from quartz substrate and treated with H₂O plasma to open CNT tips and remove excess surface polymer. The hollow core of CNTs pass from both sides of contiguous polymer film to form an ideal CNT-based membrane structure. This membrane structure confirmed by TEM, SEM, anisotropic electrical conductivity, gas transport and ionic transport studies. N₂ permeance of 2 micromol/(s m² Pa) is observed and is consistent with flux calculated by Knudsen diffusion through nm-scale tubes. Solution transport of Ru(NH₃)₆²⁺ is found to be 10 nanomole/(hr cm²) across membrane the membrane structure from a 5mmol solution. Lengths of nanotubes in membrane structure can be reduced by electrochemical oxidation, allowing higher flux rates. Importantly the plasma oxidation process leaves the CNT tips with COOH groups that are readily functionalizable for bio-selective separations that have broad ranging applications.

4:30 PM *O5.7

Endohedral Metallofullerenes For Medical Imaging. Lon D. Wilson¹, Robert A. Bolskar², Andre E. Merbach³, E. Toth³ and Lothar Helm³; ¹Department of Chemistry & Center for Nanoscale Science & Tech, Rice University, Houston, Texas; ²TDA Research Inc., Wheat Ridge, Colorado; ³Inst de Chimie Moleculaire et Biologique, Ecole Polytechnique Federal de Lausanne, Lausanne, Switzerland.

Resistant to metabolism and non-toxic, water-solubilized forms of carbon nanostructures such as endohedral metallofullerenes possess the potential to deliver medically-interesting metal ions in vivo for diagnostic purposes. For example, ¹⁶⁶Ho@C_n(R)_x species (Ho-166:β, γ-emitter) can serve as radiotracers to explore the fate of carbon nanostructures in mammals, whereas Gd@C_n(R)_x species can perform as superb Magnetic Resonance Imaging (MRI) contrast agents, both *in vitro* and *in vivo*. In such cases, the normal toxicity of the naked M³⁺ lanthanide ion is sequestered by a carbon cage that can be derivatized externally to provide both water solubility and a tissue-targeting capability. Recent developments for synthesizing M@C₆₀ species such as Gd@C₆₀(C(COOH)₂)₁₀ (R. D. Bolskar, et al., *J. Am. Chem. Soc.*, **2003**, 125(18), 5471) can now provide up to gram quantities of these materials for study and evaluation as MRI contrast agents. NMR relaxation rate studies (¹⁷O/H₂O) and complete NMRD profile data will be presented and discussed as they reveal the water proton relaxation mechanism for these highly-unusual MRI contrast agents. This research is sponsored by the Robert A. Welch Foundation (C-0627) and the NIH (SBIR Grant 5-R44-CA66383 and Grant 1-R01-EB000703).

SESSION O6: Poster Session II
Chairs: Jason Hafner, Jeffrey Hartgerink and Eugene Zubarev
Tuesday Evening, December 2, 2003
8:00 PM
Exhibition Hall D (Hynes)

O6.1

Simple and Precision Preparation of Porous Gel for Colorimetric Chemical Sensor by Templating Technique. Yukikazu Takeoka, Chemistry and Biotechnology, Yokohama National

University, Yokohama, Japan.

"Smart" porous gels with different optical behaviors were synthesized by quantitative adjustment of the cross-linker in pre-gel solutions. A periodically ordered interconnecting porous structure could be created in the gels by using a closest-packing silica colloidal crystal as a template. The interconnecting porosity provides fast response to changes in temperature through the reversible swelling and shrinking of the gels, while the periodically ordered mesoscopic structure endows the porous gels with structural color, which can be tuned by simply changing the amount of the cross-linker in the pre-gel solutions. Here we report the accurate design and simple synthesis of a novel porous gel for colorimetrically sensing glucose and specific ion concentration. The systematic preparation of a glucose/ion-sensitive gel producing the desired swelling ratio at a given glucose concentration was accomplished by careful control of the gel recipe. Subsequently, the periodically ordered porous gel using a closest-packing colloidal crystal as a template was prepared by using the same recipe as the bulk gel. The periodically ordered interconnecting porous gel exhibits expected structural color at certain glucose/ion concentration. Hence, a porous gel can be constructed as a colorimetric chemical sensor.

O6.2
Metal-mediated Conduction as Transduction Pathway for Conjugated Polymer-based Sensors. Phoebe Kwan and Timothy M Swager; Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Organic electroactive polymers are promising materials for nanoscale electronic devices. Encapsulation of conducting polymers provides protection against degradation, which can be detrimental to the performance and reliability of the devices. To address this issue, we designed supramolecular complexes that self-assemble into networks of insulated molecular wires upon electropolymerization. Redox active transition metal ions immobilized on the wires serve as critical interconnections for interchain charge hopping. We have found that redox matching of the transition metal ions and the polymer backbone is crucial to the conductivity of the system. The goal of this research is to utilize this metal-mediated conduction phenomenon as the transduction pathway for sensory materials. With each metal ion acting as a receptor, a binding event alters the redox potential of the ion. This affects the ability of the ion to shuttle charges and thereby changing the conductivity. We shall report results from our investigation with conducting polycatenane thin films.

O6.3
Electron-Radiation-Induced Graft of MMA on γ -Al₂O₃ Nanoparticle Surface. xia xiang¹, Xiaotao Zu¹ and bo jiang²;
¹Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu, Sichuan, China; ²Engineering Research Center in Biomedical Materials, Sichuan University, Chengdu, China.

Radiation induces organic monomer to graft onto inorganic particles surface is a novel and promising method to synthesize nanocomposites. It is difficult to synthesize alumina nanocomposites via chemical grafting polymerization because of its strong aggregation during hydrolysis. Electron beam co-irradiation induced graft polymerization had been carried out at a dose of 30 kGy in air at room temperature between methyl methacrylate (MMA) and γ -Al₂O₃ nanoparticles and microparticles (mean size about 20 nm and 64 μ m), respectively. Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectrometer (XPS), optical absorption and photo-luminescence (PL) spectroscopy were used to characterize grafted samples. The results showed that the percentage grafting of nano-Al₂O₃ and micron-Al₂O₃ is 6.4% and 0.9%, respectively. In the FT-IR spectra of irradiation nano samples, there was a new absorption peak appeared at 1725 /cm attributed to carbonyl stretching vibration. But in the spectra of micron-Al₂O₃, the absorption peak at this wavenumber was very weak. X-ray photoelectron spectroscopy (XPS) measurements confirmed the existence of carbonyl. There was no distinct change in optical absorption spectra of two kinds of Al₂O₃. The PL intensity of nano-Al₂O₃ increased after radiation grafting. These results showed that MMA had been successfully grafted on nano-Al₂O₃ surface at the dose of 30 kGy. However, there was little new chemical bond on micron-Al₂O₃ surface. It could be deduced that radiation graft polymerization of γ -Al₂O₃ nanoparticles is easier than that of microparticles.

O6.4
Recognition-Mediated Assembly of Random Copolymers. Raymond Thibault and Vincent Rotello; Chemistry, Univ of Massachusetts, Amherst, Massachusetts.

Applying the methodology of molecular self-assembly to the controlled aggregation of synthetic polymers provides a powerful tool for higher-order assembly in man-made, supramolecular systems. To this end, we have assembled, characterized, and investigated

competing guest interactions with the microscale supramolecular architectures resulting from the recognition-mediated assembly of these systems. Three-point hydrogen bonding elements thymine and diacyldiamidopyridine were covalently attached as pendant sidechains to flexible polystyrene chains and rigid polynorbornene backbones. When these complementary polymers are combined in non-competitive solvents, giant vesicular aggregates form due to specific interstrand three-point hydrogen bonding. As formed, these giant vesicles, or Recognition-Induced Polymersomes (RIPs), provide a unique opportunity to study guest interactions as this vesicular architecture is driven not by phase segregation, rather it is driven by specific hydrogen bonding interactions. Thymine-functionalized gold nanoparticles (Thy-Au) were employed in this capacity. Thy-Au contains the same recognition moiety as well as the desired multifunctionalization required for thermodynamically controlled incorporation. Upon introduction, Thy-Au rapidly incorporates into the RIP wall however, Thy-Au causes a major reorganization of the component RIP polymer strands over time. Lastly, the individual random copolymer strands can also be reversibly and non-covalently crosslinked using preorganized, bifunctional molecules. As before, combination in non-polar media result in micron-scale spherical aggregates. In contrast to the vesicular morphology observed, these aggregates appear to be filled spheres, indicating a microgel morphology.

O6.5
Effect of Silicate Layered Structure on the Crystallization Kinetics for Maleated Polypropylene/Clay Hybrids. Baekjin Kim^{1,2}, Seung-Heon Lee³ and Kookheon Char¹; ¹School of Chemical Engineering, Seoul National University, Seoul, South Korea; ²Textile & Chemical Research Team, Korea Institute of Industrial Technology (KITECH), Chon An, South Korea; ³CRD, LG Chem, Ltd., Daejeon, South Korea.

Although polypropylene (PP) is one of the most widely used polyolefins, it is quite difficult to prepare nanocomposites of PP with clays due to its non-polar characteristics. Recently, it has, however, been reported that polar groups such as maleic anhydride are grafted onto PP to enhance the affinity between clays and PP chains presumably by the hydrogen bonding between the hydrogen in the polar groups and the oxygen in the silicates. Studies on the PP/clay nanocomposites has so far been focused on the nanocomposite structure and its relationship with physical and mechanical properties, but few studies have been geared toward the effect of nanocomposite structure on the crystallization kinetics of PP. In present study, we prepared two series of hybrids of maleic anhydride grafted polypropylene (mPP) with unmodified clay or organically modified clay by melt blending method. Silicate layer structure and crystal structure were first investigated by using wide-angle X-ray scattering (WAXS) and then the dispersed morphology of silicates in both hybrids was confirmed by transmission electron microscopy (TEM). We further investigated the isothermal crystallization kinetics of both mPP/clay hybrids by using differential scanning calorimetry (DSC) and time-resolved WAXS measurements. The effect of silicate dispersion on the mPP crystallization kinetics was quantitatively studied by calculating the crystallization half-times from DSC measurements.

O6.6
Nanostructure of β -Sheet Fibrils Constructed by Peptide Self-assembly. Matthew S Lamm¹, Bulent Ozbas¹, Karthikan Rajagopal², Juliana Kretsinger², Joel P Schneider² and Darrin J Pochan¹; ¹Materials Science and Engineering, University of Delaware, Newark, Delaware; ²Chemistry and Biochemistry, University of Delaware, Newark, Delaware.

A 20-residue peptide consisting of alternating valine and lysine residues flanking a tripeptide turn sequence has been shown to self-assemble via differing pathways into dramatically different materials, depending on the primary structure of the turn sequence. For turn sequences designed to adopt a type II' turn, intramolecular folding of the entire peptide leads to assembly into β -sheet rich hydrogels reversible with pH changes. Alternatively, for turn sequences in which folding is unfavorable at any solution conditions, the peptides adopt an extended β -sheet conformation and irreversibly assemble into fibrillar structures similar to classic β -amyloid or prion fibrils. This research is focused primarily on the structure and assembly mechanism of the β -sheet fibrils. Fibrils exhibit dimensions of 5 to 100nm wide and up to a few micrometers in length. A fibril consists of the lateral assembly of individual β -sheet tapes, with each tape exactly one molecule in width and height providing an exact peptide nanostructure. Electron microscopy, atomic force microscopy, x-ray diffraction, and dynamic light scattering have been used to investigate the crystal structure and self-assembly mechanisms of the fibrils. The single crystalline nature of the fibrils and the ability to easily integrate functionality into the peptides provides opportunities for using the fibrils as templates to exactly control the nanoscale

ordering of inorganic materials as well as for device applications. Initial attempts at inorganic phase growth and nanoparticle assembly on the fibrils will be presented.

O6.7

Coverage dependent evolution of two-dimensional dendrimer/mica domain patterns. Fengting Xu¹, Shane C Street² and John A Barnard^{1,2}; ¹Materials Science and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania; ²Center for Materials for Information Technology, University of Alabama, Tuscaloosa, Alabama.

For a two-dimensional, two-phase system of A and B, with competing short-range attractive and long-range repulsive interactions, the evolution of domain patterns as a function of area fraction should follow the sequence: circular islands of A in a matrix of B (the droplet phase), alternating elongated domains of A and B (the striped phase), and circular islands of B in a matrix of A (the inverted droplet phase). The predicted domain pattern evolution is experimentally verified here for the case of dendrimer molecules on mica, a materials system amenable to control of the competing interactions. This result, along with the coverage dependence of the characteristic domain length scale, is reported for the first time. The domain patterns are fabricated by simple aerosol deposition of dilute solutions of dendrimer molecules in pentanol onto mica followed by slow evaporation. The long range repulsive interaction in this case is electrostatic in origin and is associated with the contact potential between the negatively charged surface of mica submerged in pentanol and the positively charged surface of the dendrimer molecule domains.

O6.8

Growth and Characterization of Synthetic Polypeptide Single Crystals for Inorganic Nanoparticle and Bulk Phase Assembly. Honggang Cui¹, Vahik Krikorian¹, Darrin Pochan¹, Andrew P Nowak² and Timothy J Deming²; ¹Materials Science and Engineering, University of Delaware, Newark, Delaware; ²Materials and Chemistry, University of California, Santa Barbara, Santa Barbara, California.

Single crystals of synthetic peptide have been grown from aqueous solution in different conditions by the addition of salts solutions or nonsolvents. The resultant single crystal morphologies were studied by transmission electron microscopy (TEM), atomic force microscopy (AFM), and field emission scanning electron microscopy (FESEM). Single crystals of poly-L-lysine (PLL) exhibited the forms of regular hexagonal lamellae in both monolayer and multilayer forms with or without a central screw dislocation depending on the growing conditions. The thickness of the resultant crystals can be directly controlled by the PLL molecular weight. The lattice structures of single crystals both in solution and in film were obtained by X-ray scattering and electron diffraction. The application of polypeptide single crystals as templates to control the crystallization of minerals was initially investigated. Calcium carbonate was grown on the PLL lamellae with the inorganic phase exactly mimicking the polypeptide substrate shape. The PLL single crystal lamellae were also used to direct the growth and assembly of cobalt magnetic nanoparticles in an attempt to produce anisotropic magnetic properties. Surface modification of the single crystals involving introduction of new functional group on the self-assembling polypeptides was tried to obtain desired interfacial interaction with inorganic phases.

O6.9

Characterization of Phase Transitions in Long-Chain, Layered Silver Thiolates by DSC-TG, XRD and FTIR. Andrey Levchenko¹, Atul Parikh² and Alexandra Navrotsky¹; ¹Thermochemistry Facility, NEAT ORU, University of California at Davis, Davis, California; ²Applied Science Department, University of California at Davis, Davis, California.

In the past few years there have been a considerable interest in long chain silver thiolates $\text{CH}_3(\text{CH}_2)_n\text{SAg}$ due to their extraordinary ability to combine properties of organic and inorganic materials. In this study, for the first time, recrystallized silver thiolates of various chain lengths with 10 to 18 carbons have been characterized with XRD, evolved gas FTIR, DSC and thermogravimetric analyses. The powder XRD study confirms the recently proposed model of a 3-D layered structure at room temperature for all silver thiolates with an interlayer spacing of approximately twice the length of the alkyl chain. A tilting angle of 14° was calculated from the powder XRD assuming the all-trans conformation of the alkyl chains. To probe thermodynamics of phase transitions, DSC and evolved gas FTIR were employed. Structure changes throughout phase transitions were validated by variable temperature powder XRD. Two transitions are observed by both XRD and DSC, which can be attributed to a reversible transition from the crystalline state to a mesophase, and

subsequently an irreversible transition to amorphous phase. The temperature of the first phase transition to the mesophase is independent of chain length. The enthalpy change, which varies with chain length, is apparently compensated by the entropy change, which is mostly accounted for by disordering of alkyl chains. Both powder XRD and DSC show an irreversible second phase transition at around 210°C which is due to decomposition of alkyl chains. Alkyl chain assembly in silver thiolates is compared to that in 2D monolayers on planar silver and, the use of thiolates as model systems for the study of 2D-SAMs is discussed.

O6.10

Cationic Self-Assembled Monolayers Composed of Thiol-Terminated Gemini Surfactants on Planar and Colloidal Gold Surfaces. Shinobu Yokokawa^{1,2}, Kaoru Tamada^{1,2,3}, Eisuke Ito², Noriyuki Ishii³ and Masahiko Hara^{1,2}; ¹Electronic Chemistry, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan; ²Local Spatio-Temporal Functions Laboratory, RIKEN, Wako, Saitama, Japan; ³Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan.

Two molecules bearing resembling molecular structures, "gemini"-structured didodecyl dithiol (HS-gQA-SH) and didodecyl disulfide (QA-SS-QA), were synthesized to control the distance between charged headgroups. These sulfur compounds can form cationic self-assembled monolayers (SAMs) on planar gold substrates as well as on gold nanoparticles as their capping materials. Assembly of such two-dimensional (2D) and three-dimensional (3D) organic/metal composite materials into well-defined structures can provide a variety of functional materials with applications including sensor devices, catalysis, and nanoelectronics. In case of 2D surface, formation and structure of the SAMs on planar gold were characterized by surface plasmon resonance spectroscopy (SPR), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared-reflection adsorption spectroscopy (FTIR-RAS). In the HS-gQA-SH SAM, the orientation and the distance between QA groups are specified by the covalent bonding with ethylene spacer, while those of the QA-SS-QA SAM are determined by the electric repulsion between charged headgroups, i.e., QA groups in the QA-SS-QA SAM are more randomly located, being more distant than with those in the HS-gQA-SH SAM. We found that L-tartaric acid, a probe molecule with two carboxyl groups having the distance of an ethylene unit, exhibits a strong affinity on the HS-gQA-SH SAM. In contrast, no specific binding was observed on the QA-SS-QA SAM. These results imply the possibility to build up a molecular recognition system on surfaces due to the control of the distance between the charged headgroups with the gemini-structured molecular design. Gold nanoparticles were synthesized by the reduction of hydrogen tetrachloroaurate (III) with sodium borohydride in methanol using HS-gQA-SH and QA-SS-QA as the capping ligands. Formation of gold nanoparticles was confirmed by transmission electron microscopy (TEM), UV-Vis spectroscopy, and IR spectroscopy, where the particles capped by HS-gQA-SH was found to be more spherical with small size distribution compared with those capped by QA-SS-QA. We will monitor specific interactions between cationic groups on spherical gold and tartaric acid in solution as well. The comparison for molecular interactions between 2D and 3D systems will be discussed.

O6.11

Electron deficient conjugated polymers: Highly stable molecular electronic materials. Youngmi Kim¹ and Timothy M Swager¹; ¹Chemistry, MIT, Cambridge, Massachusetts; ²Chemistry, MIT, Cambridge, Massachusetts.

The unique properties of conjugated polymers (CPs) have led researchers to investigate their use for a variety of potential applications. Despite this potential, one of the limitations of this class of polymers has been their sensitivity to air or moisture. Hence, the prerequisites of CPs for all these applications are a high stability to thermal and chemical/photochemical degradation, in addition to high solid state fluorescence efficiency. New electron deficient monomers substituted with bis(trifluoromethyl) groups on phenyl ring were synthesized and incorporated into Poly(p-Phenylene Vinylene)s homopolymers (CF₃-PPVs) and copolymers. Trifluoromethyl groups provide for a strong electronic perturbation of the polymers' electronic structure making them resistant to oxidation and hence extremely durable for various applications. Photobleaching and TGA studies showed that CF₃-PPVs had excellent thermal- and photo-stabilities. These polymers and model compounds are under investigation as n-type materials in molecular electronic devices including LEDs, field-effect transistors, photovoltaic diodes, and laser sensors.

O6.12

Electronic and Optical Properties of Self-Assembling Thiophene Based One-Dimensional Nanostructures. James F. Hulvat¹, Benjamin W. Messmore², Eli D. Sone² and Samuel

I. Stupp^{1,2,3}; ¹Materials Science & Engineering, Northwestern University, Evanston, Illinois; ²Chemistry, Northwestern University, Evanston, Illinois; ³Feinberg School of Medicine, Northwestern University, Evanston, Illinois.

Oligo(thiophene) based molecules are of great interest for organic field-effect transistors (OFETs) due to their stability and high charge carrier mobilities. While the best performance is obtained from vacuum sublimated crystalline films, achieving the low-cost and ease of fabrication anticipated from OFETs necessitates developing solution based processing methods that lead to highly ordered films. Incorporating various substituents on the oligo(thiophene) backbone can improve solubility and enhance ordering of the thiophene segments, leading to higher conductivity and mobility in films prepared from these molecules. We have synthesized a series of novel dendron rod coil (DRC) triblock molecules consisting of a G1 3,5 dihydroxybenzoic ester dendron, an oligo(thiophene) rod and an alkyl tail. In poor solvents, hydrogen bonding and solvophobic interactions drive the self-assembly of these molecules into one-dimensional nanostructures. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) show the presence of highly regular objects on the order of 10 nm in diameter and microns in length. π - π stacking of thiophene oligomers along these one-dimensional structures leads to a strong red-shift in absorption and a decrease in fluorescence upon self-assembly. Films cast from these pre-organized solutions exhibit strong birefringence and significantly higher conductivity than films cast from well solvated molecules. These one-dimensional nanostructures can be aligned in the channel of an OFET by AC electrophoresis during casting of the film. Molecular self-assembly provides a facile, solution-based route to prepare OFETs with highly organized oligo(thiophene) channel layers.

O6.13

A Layered Coordination Solid with Selective Intercalation Properties. Leslie J. May and George K.H. Shimizu; Chemistry, University of Calgary, Calgary, Alberta, Canada.

Coordination networks based on silver organosulfonates show interesting structural features because of the pliant coordination sphere of the metal ion and the coordinative flexibility of the ligating group. The acetonitrile-directed solid state structural conversion of silver 3-pyridinesulfonate is one such example.¹ The "soft" behavior of these coordination solids is also exemplified by the adaptive host behavior of silver triflate (AgOTf).^{2,3} The flexible binding mode of the sulfonate anion allows for the formation of stable intercalate complexes between AgOTf and various guest solvents.³ Here, a 2-D coordination solid capable of selective amine sorption is presented. Silver 4-pyridinesulfonate uptakes aliphatic and aromatic amines to yield layered intercalate complexes $[\text{Ag}(4\text{-pySO}_3)\cdot(\text{RNH}_2)]$, where R = H to C₁₀H₂₁, C₆H₅ and CH₂C₆H₅. Intercalation was not observed for other functional groups such as alcohols, aldehydes, nitriles or benzenes. The structural features and properties of the $[\text{Ag}(4\text{-pySO}_3)\cdot(\text{RNH}_2)]$ intercalates will be presented. 1. S.K. Makinen, N.J. Melcer, M. Parvez, and G.K.H. Shimizu, *Chem. Eur. J.* **7** (2001) p. 5176. 2. A.P. Cote, M.J. Ferguson, K.A. Khan, G.D. Enright, A.D. Kulynych, S.A. Dalrymple, and G.K.H. Shimizu, *Inorg. Chem.* **41** (2002) p. 287. 3. A.P. Cote and G.K.H. Shimizu, *Chem. Eur. J.* accepted for publication.

O6.14

Microwave Synthesis of Sugar-Boron Oxide as Highly Reactive Precursor for Boron Carbide. Manuel Guadalupe Rodriguez², Ubaldo Ortiz-Mendez² and Oxana Kharissova¹; ¹Facultad de Ciencias Fisico Matematicas, UANL, San Nicolas de los Garza, Nuevo Leon, Mexico; ²FIME, UANL, San Nicolas de los Garza, Nuevo Leon, Mexico.

In aim to obtain homogeneous and highly reactive precursors for boron carbide, it was performed a stirred mixture of methanol solution of boric acid with sucrose (calcined or not calcined). In order to form an extremely intimate reactive mixture for the preparation of boron carbide a suitable solvent is employed. This mixture was heated at 80 C, under argon atmosphere, until a substantially dry reactive mixture was formed. The same mixture is dehydrated into a reactor system heated by microwave at intervals of 15 sec, to form a precursor material. Precursors are heated under vacuum (0.0001 torr) in a microwave oven operating at 2450 MHz and power levels up to 1500 W for intervals of 30 min. The precursors and products obtained have been characterized by X-ray diffraction, FTIR analysis, and scanning electron microscopy.

O6.15

Nanoimprinting Mechanics. Barry S. O'Connell, Graham L. Cross and John B. Pethica; Physics, SFI Trinity Nanoscience, Dublin, Ireland.

We report here on rheological aspects of nanoimprint lithography.

Thin films of polymer were printed with spherical stamps patterned by focused ion beam milling. Indentation was performed by a variable temperature nanoindenter under controlled load, displacement and strain conditions. Flow patterns for simple stamping geometries were investigated as a function of stamping program and temperature above and below the glass transition region of the polymer films. Flow conditions were varied by modifying boundary conditions chemically and mechanically. The effect of residual stresses built up during printing on pattern transfer fidelity is discussed. The results are compared to contact mechanic models of the polymer flow.

O6.16

Depletion layer studies at water/Polystyrene interface using neutron reflectivity. Young-Soo Seo and Sushil Satija; NCNR, NIST, Gaithersburg, Maryland.

From neutron reflectivity studies, formation of few nanometer thick depletion layer at the water/hydrophobic substrate interface has been recently reported. Two possible causes of the depletion layer formation were suggested, i.e. organic contamination and vapor layer formation at the interface. In this study we demonstrate that sample preparation has a critical role in the depletion layer formation at water/Polystyrene (PS) interface using neutron reflectivity. In order to verify possible contamination during sampling procedures, we prepared 4 sets of samples i.e., PS or deuterated PS dissolved in toluene or deuterated toluene and controlled sample annealing time. Our experimental results strongly indicate that organic contaminations originated from the sample preparation are attributed to the depletion layer at water/hydrophobic substrate interface.

O6.17

Nanoscale Light Emitting Devices From Ruthenium Complexes. John Andrew DeFranco¹, Yuanjia Zhang¹, Jason Slinker¹, Dan Bernards¹, Ambily Sathna¹, Jason R. Petta², Daniel C. Ralph² and George G. Malliaras¹; ¹Materials Science and Engineering, Cornell University, Ithaca, New York; ²Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York.

Transition metal complexes have recently been used to create light emitting devices of high efficiency. Ruthenium complexes, for example $[\text{Ru}(\text{bpy})_3]^{2+}$, have yielded devices with external quantum efficiencies of more than 5%; among the best single layer devices to date. In previous experiments, a variety of geometries have been investigated for these devices, though typically a thin film sandwich structures is used. In this experiment, electroluminescent material is deposited into a channel of varying width, from 200nm to 30nm, to create a planar device with cross-sectional width around 100nm. This structure is novel for this device class, giving new opportunities to study the mechanisms of charge transport through the material. Our group originally developed the device geometry and fabrication techniques for the purpose of making pentacene transistors with the same critical dimensions. Many characteristics of light emitting are shown to scale with channel spacing including injection barrier, transport characteristics, and recombination profile. Practical aspects of the device are also explored, including external quantum efficiency, turn-on time and operational lifetime. The other key areas in which these devices differ: that they have Pt electrodes (cf. ITO/Au electrodes) and have a controllable gate bias, are analyzed and compared to standard device operation

O6.18

Self-Assembly of Peptides into Controlled Length Super Helices. Jeffery D Hartgerink and William Craig Meddaugh; Chemistry, Rice University, Houston, Texas.

The self-assembly of peptides and proteins into super helical motifs, also known as coiled coils, is a well known, frequently observed occurrence in a variety of both in vivo and in vitro systems. This self-assembly is mediated through two main effects, hydrophobic interactions between typically leucine and isoleucine in the core of the super helix, as well as charge pairing between certain amino acid residues, in this case, lysine and glutamic acid. By utilizing these effects in conjunction with clever design, these coils arrange themselves into a supramolecular polymer, allowing the use of small, easily synthesized precursor peptides to assemble a peptide structure with a length well in excess of that which can be achieved via traditional peptide synthetic chemistry. With this motif, two simple peptides, a positively charged four heptad (28 residue) peptide and a negatively charged three heptad (21 residue) peptide combine to form the only logical structure, a 12 heptad (147 residue) super helix. This technique allows for the construction of peptide based systems in excess of that which can be conveniently synthesized usually conventional synthetic methodologies. It also allows access into a size regime of supramolecular assemblies that has proven difficult to obtain using other methods and may be interesting in various nanotechnology applications.

O6.19

Polydiacetylene Nanocomposite Chemical and Thermal Sensors. Byron McCaughey, Xuan Li, Jiebin Pang, J Eric Hampsey, Donghai Wang and Yunfeng Lu; Chemical Engineering, Tulane University, New Orleans, Louisiana.

Polydiacetylene (PDA) is frequently studied because of its ability to change color due to thermal or chemical stimuli. Layered nanocomposite crystals containing PDA and organic structural components have been self-assembled as a result of steric effects, hydrogen bonding, pi-pi stacking, hydrophobic, and electrostatic interactions. FTIR, XRD, TEM, AFM, and UV-vis demonstrate nanocomposite formation and provide structural information. Introduction of chemical components or increasing temperature caused a chromatic blue-to-red transition and structural rearrangement. The PDA crystal senses chemicals based on equilibrium between organic structural components and new chemicals in solution. Reactants with different structures and functionalities allow detection of a wide array of chemicals. As shown with UV-vis, selected PDA composites reversibility respond to multiple thermal cycles without loss of chromatic response. This reversibility is due to the intramolecular interactions that return PDA side chains to original positions after thermal stress is removed.

O6.20

Design, synthesis, and properties of helical oligothiophenes. Adah Almutairi, Sheraz Butt and Michael Marsella; Chemistry, University of California, Riverside, California.

Chiral pi-conjugated organic systems exhibit unique and interesting optoelectronic properties [1 a) Aoki, T.; Kaneko, T.; Maruyama, N.; Sumi, A.; Takahashi, M.; Sato, T.; Teraguchi, M.; J. Am. Chem. Soc. 2003, 125, 6346-6347 b) Rajca, A.; Safronov, S.; Rajca, S.; Shoemaker, R.; Angew. Chem. Int. Ed. Engl. 1997, 36, 488, c) Marsella, M.J.; Kim, I.T.; J. Am. Chem. Soc., 2000, 122, 974, d) Hu, Q.; Vitharana, D.; Liu, G.; Jain, V.; Wagaman, M.; Zhang, L.; Lee, T.; Pu, L.; Macromolecules. 1996, 29, 1082-1084]. The study of such systems and their properties may ultimately provide organic materials capable of exhibiting novel optical and electronic properties, as well as provide insight toward the rational design of self-assembled materials. Traditionally, chirality in conjugated polymers (CP) has been intrinsic to pendant chiral groups on the CP. An alternative design approach relies not on chirality centers, but chiral axes, planes, or helicity. In CPs, fewer examples of the latter three categories exist (relative to the former) [b) Rajca, A.; Safronov, S.; Rajca, S.; Shoemaker, R.; Angew. Chem. Int. Ed. Engl. 1997, 36, 488]. In the past, we reported the synthesis of a supramolecular double helical polymer using tetra[2,3-thienylene] as a chiral scaffold [c) Marsella, M.J.; Kim, I.T.; J. Am. Chem. Soc., 2000, 122, 974]. Today our focus is still directed towards the synthesis of conjugated polymers with main chain chiral configuration, though with helical hexathiophene oligomers as the chiral scaffold. We have currently established the strong propensity for hexachloro-hexathienylene oligomers to self-assemble into helical motifs in the solid state (racemic crystals). Current efforts focus on establishing homochiral helical assemblies via judicious design of conformational diastereomers. Results to date will be reported.

O6.21

Orientation of Dipolar Molecular Fibers in Electric Fields. James Henry Dickerson^{1,2}, Thuc-Quyen Thai Nguyen^{1,3}, Colin Nuckolls^{1,3}, Louis Brus^{1,3} and Irving Herman^{1,2}; ¹Nanoscale Science and Engineering Center, Columbia University, New York, New York; ²Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York; ³Department of Chemistry, Columbia University, New York, New York.

Recently, there has been significant interest in the fabrication, development, and manipulation of nanoscale conductive materials for use as possible candidates to compete with and to replace eventually silicon-based technology. Given that silicon processing is gradually reaching its physical limits for lithography and, hence, the limits of its speed and scalability, it behooves us to investigate alternative means of producing comparable electrical components. Our contribution to this pursuit is the fabrication, orientation, and characterization of nanoscale, self-assembled organic molecular fibers. Although the synthesis and the subsequent self-assembly of their molecular fibers have been realized, alignment of these nanostructures onto metallic contacts previously had not been observed. We present evidence of the alignment of fibers of hexa-substituted aromatic molecules using a DC electric field. Since each molecule possess a benzene core with three amide bonds, it has an intrinsic electric dipole moment perpendicular to its face. Therefore, an arranged stack of these molecules will possess a substantial net moment. In the presence of an electric field, these dipolar fibers will experience a substantial field interaction that, if appropriately managed, will attract strongly the molecules along the field gradients and, then, will align the fibers along the electric field lines. As well, this class of aromatic molecular fibers should

possess high conductivity along their stacking axes, thereby making them excellent candidates for use as molecular transistors. In support of this, we provide preliminary measurements of their electrical characteristics: current versus time measurements during the alignment process and current versus voltage measurements after the alignment. This work was supported primarily by the Nanoscale Science and Engineering Initiative of the National Science Foundation under NSF Award Number CHE-0117752.

O6.22

Controlled Growth of Ultrathin Molecular Films of the p-phenylene Oligomers on Alkali Halide Substrates. Edward James Kintzel^{1,3}, Detlef M. Smilgies², James G. Skofronick³, Sanford A. Safran⁴ and David H. Van Winkle³; ¹IPNS - Bldg. 360, Argonne National Laboratory, Argonne, Illinois; ²Cornell High Energy Synchrotron Source, Cornell University, Ithaca, New York; ³Physics, Florida State University, Tallahassee, Florida; ⁴Chemistry, Florida State University, Tallahassee, Florida.

The morphology of ultrathin films of para-phenylene oligomer molecules ($p\text{-C}_6\text{H}_5(\text{C}_6\text{H}_4)_{n-2}\text{C}_6\text{H}_5$, or p-nP) grown by vapor-deposition onto cleaved, single-crystal alkali halide (001) substrates has been investigated by x-ray diffraction (XRD) and atomic force microscopy (AFM). The study focused on the orientation adopted by these linear molecules in crystallites composing the films, as a function of the growth parameters: number of phenyl groups in the chain ($n = 4$ to 6); substrate temperature maintained during deposition (25°C to 225°C); and substrate lattice constant (4.64 \AA for NaF to 6.60 \AA for KBr). All films were prepared under high vacuum conditions ($\sim 10^{-8}$ torr) at the same deposition rate ($\sim 0.2 \text{ \AA/s}$). Analysis of the XRD results shows significant trends in the relationship between the growth parameters and the observed crystallite orientations. AFM images contribute independent evidence for a surface microstructure evolution that is consistent with the XRD results. Oriented films of the p-phenylene oligomer molecules can therefore be grown with desired molecular orientations by selection of an appropriate combination of substrate temperature, substrate lattice constant, and molecular chain length.

O6.23

Aspects of the Solid-Solid Electrochemical Interconversion of TCNQ and Semiconducting CuTCNQ (TCNQ = Tetracyanoquinodimethane). Aaron K Neufeld¹, Alan M Bond², Conor Hogan² and Ian Madsen³; ¹Manufacturing and Infrastructure Technology, CSIRO Australia, Highett, Victoria, Australia; ²School of Chemistry, Monash University, Clayton, Victoria, Australia; ³Minerals, CSIRO Australia, Highett, Victoria, Australia.

The origins of extensive solid-solid inter conversions that accompany the electrochemistry of microparticles of TCNQ and semiconducting CuTCNQ (phases I and II) adhered to a glassy carbon electrodes, in contact with $\text{CuSO}_4(\text{aq})$ electrolyte, have been identified. Ex situ forms of electron microscopy, infra-red spectroscopy, X-Ray diffraction, have been used to identify the phase changes that occur during the course of potential cycling or bulk electrolysis experiments. All redox-based transformations require extensive density and morphology changes, and consequently they are accompanied by crystal fragmentation. The net result is that extensive potential cycling ultimately leads to the thermodynamically favored TCNQ/CuTCNQ (phase II) solid-solid interconversion occurring at the nanoparticle rather than micron size level. The overall chemically electrochemical processes is believed to be based on two one electron reactions. Needle-shaped CuTCNQ (phase I) crystals having a density of 1.80 g cm^{-3} are predominately formed in the first stages of potential cycling experiments that commence with micron sized rhombic shaped TCNQ crystals of density 1.36 g cm^{-3} . The rate of subsequent formation of thermodynamically stable CuTCNQ (phase II) which has an intermediate density of 1.66 g cm^{-3} and a crystal shape more like that of TCNQ, is dependant on the number of potential cycles, the scan rate and the initial size of the adhered TCNQ crystals. Evidence obtained by cyclic voltametry and double potential step techniques indicate that the formation of CuTCNQ (phase I and II) involves a rate determining nucleation and growth process, combined with the ingress and reduction of reversible process is described by the reaction of copper ions from the electrolyte. In which CuTCNQ (phase I) is formed initially and then CuTCNQ (phase II) after a large number of potential cycles. The reverse oxidation process involving the transformation of solid CuTCNQ (phases I and II) to TCNQ also involves a nucleation-growth multi-step process and significant crystal size and morphology changes.

SESSION O7:

Chair: Jeffrey Hartgerink
Wednesday Morning, December 3, 2003
Room 206 (Hynes)

8:30 AM *O7.1

Harnessing the Synergies Between Electrostatics and Hydrophobics for the Self-assembly of Complex Nanoscale Architectures.

Hicham Fenniri, ¹National Institute for Nanotechnology, University of Alberta, Edmonton, Alberta, Canada; ²Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada.

Unidimensional nanotubular objects have captivated the minds of the scientific community over the past decade because of their boundless potential in nanoscale science and technology. The strategies developed to achieve the synthesis of these materials spanned the areas of inorganic and organic chemistry and resulted in, for instance, carbon nanotubes, peptide nanotubes, as well as surfactant-derived tubular architectures. This talk focuses on the design, synthesis, and investigation of a new class of adaptive nanotubular architectures resulting from the self-assembly and self-organization of biologically inspired systems. In particular, the synergies between electrostatic and hydrophobic interactions will be discussed to rationalize the driving forces of self-assembly in an aqueous environment. Finally, some of the key advantages of these materials, such as their compatibility with physiological as well as organic media, and their functional versatility will be discussed.

9:00 AM O7.2

Synthesis and Nano-Mechanical Studies of Nanostructured Modular Polymers by Mimicking Titin.

Zhibin Guan, Jason T. Roland, Jane Z. Bai, Sharon X. Ma, Theresa M. McIntire and David A. Brant; Chemistry, University of California, Irvine, California.

Inspiration from natural biopolymers is used in our lab to design macromolecular materials having precise secondary and nanostructures for advanced mechanical properties. Modular domain structures are commonly seen in natural biopolymers such as adhesion proteins and skeletal muscle protein, titin, which assume important mechanical functions in biological systems. The remarkable combined strength and toughness of titin was proposed to derive from its modular structure comprising a linear array of domains, in which each domain is held together by secondary forces. We have synthesized titin-mimicking modular polymers having multiple domain nanostructures by using 2-ureido-4-pyrimidone (UPy) to direct the formation of loops. Following the first, second-generation UPy-containing monomer synthesis, this presentation will discuss about the synthesis and studies of our third-generation UPy-containing monomers and polymers. The mechanical properties of the created polymers are studied both at single-molecule level using atomic force microscopy (AFM) and bulk level using Instron. Single-molecule force-extension experiments using AFM showed similar sawtooth patterns as observed in titin. This suggests the sequential unfolding of loops along polymer chains. Systematic studies are currently underway to understand the fundamental relationship between polymer nanostructures and polymer physical properties.

9:15 AM O7.3

Atomic Force Microscopic Investigations of Genetically-Engineered Polypeptide Molecules for Interconnect Applications.

Narender Rana, Autumn Carlsen, Christopher Kossow, Suparna Mandal, Seiichiro Higashiya, Silvana Ngo, Kenneth Bousman, Robert E Geer, Eric T Eisenbraun, John Welch and Alain E Kaloyeros; School of NanoSciences and NanoEngineering, The University at Albany - SUNY, Albany, New York.

This work reviews the synthesis, characterization, and surface self-assembly of genetically engineered polypeptide molecules for nanoscale molecular interconnect and device applications. These molecules exploit a rigid β -sheet structure to provide a periodic quantum crystalline trellis from which to attach electrically conductive and surface attachment moieties. Chemically modifiable β -turn groups constitute the attachment points for these moieties. This structure employs amino acid sequences based on alanine (Ala) and glycine (Gly) peptides. The fundamental trellis repeat unit is $\{(GlyAla)_3-GlyPhe-(GlyAla)_3-GlyTyr-(GlyAla)_3-GlyGlu-(GlyAla)_3-GlyLys\}$ where anti-parallel strands of this repeat sequence form a β -sheet structure with phenylalanine (Phe) and tyrosine (Tyr) alternating as β -turn groups along one edge of the trellis and glutamic acid (Glu, negative charge) and lysine (Lys, positive charge) alternate as β -turn groups along the other edge of trellis. The termination groups provide specific structural and charge transport functionalities. In particular, phenylalanine constitutes a first-pass test candidate for aromatic groups used to form extended π -conjugation with the potential for ballistic electron transport along the edge of the sheet. A β -sheet structure consisting of 21 such repeats, referred to as YEHK21 has been synthesized. Ex-situ atomic force microscopy (AFM) has been used to study the structure and assembly of these molecules on atomically smooth graphite surfaces. The dimensional analyses of the aggregates have been carried out

utilizing a standard molecular dynamics modeling package, Hyperchem, utilizing Amber force-field calculations to simulate expected β -sheet conformations and compare with observed dimensions of the surface-adsorbed molecular domains obtained via AFM. Preliminary AFM-based molecular imaging data is consistent with the expected β -sheet assembly dimensions of YEHK21. The domain structure determined from TM-AFM phase imaging implies end-to-end stacking. The observation of such molecular order is critical to future applications of these molecules for molecular wire applications and opens the door for material optimization for directional charge transport.

9:30 AM *O7.4

Self-Assembling Peptide Nanotubes.

M. Reza Ghadiri, Chemistry, Scripps Research Institute, La Jolla, California.

Hollow tubular structures of molecular dimensions perform diverse biological functions in Nature. In preparation of such tubular assemblies, biological systems make extensive use of self-assembling and self-organizing strategies. Owing to numerous potential applications in areas such as chemistry, biology, and materials science, considerable effort has recently been devoted to preparation of artificial nanotubular structures. In this lecture I will highlight various design principles employed in our laboratory for the preparation of synthetic peptide nanotubes targeted to biological or materials settings.

10:15 AM O7.5

Atomistic Studies on the thermodynamic stability of hydrogen bond driven selfassembly of supramolecules.

Tahir Cagin, Shiang-Tai Lin, Seong Soon Jang and William A Goddard; Caltech, Pasadena, California.

Self-assembled supramolecules, such as DNA, hemoglobin, Ribosome and dendrimers, are ubiquitously observed in nature and play essential roles in various mechanisms. These complicated and large-scale macromolecular system often consists of many replicas of somewhat simple constitutional subunits, that is, monomers. Interestingly the structures of these giant molecules can be stabilized through noncovalent physical interactions between monomers such as electrostatic, van der Waals, and hydrogen bond interactions. These noncovalent interactions impart reversibility to the self-organization of monomers depending on the various conditions: under a specific condition, a specific self-assembled supramolecular structure can exist stably but not in the others, and whenever that condition is recovered, so does its structure. We have used the vibrational density of state (DoS) derived from classical molecular dynamic simulations to investigate the origin of the generation-dependent stability the hydrogen bond driven self assembly of supramolecular dendritic structures synthesized and characterized by Zimmerman and his coworkers [Zimmerman, et al. Science 1996, 271, 1095]. In this method, the DoS distribution is calculated from the Fourier transform of the velocity autocorrelation function, and the thermodynamic properties are determined by weighting each vibration mode with the harmonic oscillator statistics. Our simulation results support the experimental findings that circular and linear configurations may coexist at lower generations but only circular forms are observed at higher generations. We find that the stability of this self-assembled supramolecular system is dominated by the entropic contribution rather than the enthalpic contribution, through the free energy calculation using the DoS obtained from molecular dynamics simulations. This method provides detailed information on the thermodynamic properties and thermodynamic stability of various motives observed in the supramolecular structures.

10:30 AM *O7.6

Virgil Percec, University of Pennsylvania

(Abstract Not Available)

11:00 AM *O7.7

'Bricks and Mortar' Assembly of Nanoparticles.

Vincent Rotello, University of Massachusetts, Amherst, Massachusetts.

Self-assembly based on selective control of non-covalent interactions provides a powerful tool for the creation of structured molecular-level systems. Application of this methodology to macromolecular systems supplies a potential means for the extension of this structure to the macroscopic level. In recent research, we have developed self-assembly strategies for polymers, nanoparticles, and polymer-nanoparticle composites based on complementary hydrogen bonding functionality. This provides a potentially versatile approach to structural engineering, integrating the 'lock and key' selectivity inherent in molecular recognition with 3-dimensional morphological control provided by self-assembly.

11:30 AM *O7.8

Using Self-Assembly to Create Defined Nanometer Sized Cavities. D. Tyler McQuade, Dept of Chemistry and Chemical Biology, Cornell University, Ithaca, New York.

Both small molecule and macromolecular amphiphiles can self-assemble into a wide array of soluble organized structures, including micellar, reverse micellar (RM), cylindrical micellar, vesicular, and lamellar phases as well as phases that tend to be insoluble, including hexagonal and bicontinuous phases. These organized materials have been used in a wide variety of applications including detergents, paints, drug delivery agents, photonic materials, and scaffolds for creating ordered inorganic materials. Inverse phases such as RMs and inverse hexagonal phases have the unique feature of placing high functional group density toward a core or narrow channel, respectively, and this density can provide unique reactivity. Functional group density around the core and permeability make inverse phases particularly attractive candidates for microreactors. Microreactors can act to sequester incompatible reactions within the same vessel. One limitation of RMs is their capacity to undergo facile phase transitions, thereby limiting the temperature range in which they can be used. Before the range of RM microreactor applications can be realized, a methodology enabling covalent capture that retains the prepolymerized morphology of the RMs must be developed. This presentation will report the first method that allows the capture of a RM without disrupting the prepolymerized dimensions. In addition, approaches to creating functionalized cross-linked RMs will be presented.