SYMPOSIUM DD
Organic and Nanocomposite Optical Materials

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* Invited paper
This tutorial will cover the basics of nanophotonics, focusing on organic and hybrid organic-inorganic nanocomposites and the associated devices and applications. The tutorial will begin with a brief, general overview of photonics and the fundamentals of light-matter interactions. This will be followed with a description of nanoscale engineering, including methods of using light to measure nanoscale properties of materials (e.g., near-field scanning optical microscopy), as well as methods to engineer composites with nanoscale precision to create structures that can manipulate light (e.g., photonic bandgap materials). The underlying physics of these measurement systems, and examples of how one can use light to control the fabrication of nanostructured materials, will be presented.

In addition, the tutorial will include an overview of the important area of hybrid materials, focusing on inorganic nanoparticles embedded within polymeric matrices. A review of the quantum mechanics of nanoparticle emission (quantum-dot emission) will be presented, including specific examples of InP, ZnSe, CdSe, Si, and core-shell structures. The optical properties of these nanoparticles will be discussed in detail. More importantly, optical, electrical, and structural characterization techniques for quantifying and improving the effectiveness of optoelectronic devices based on nanoparticle-polymer composites will be discussed. In addition to materials synthesis and characterization, recent results from literature will be presented that demonstrate the applications of these novel techniques and materials. The tutorial will conclude with a discussion of the current problems and future directions of this exciting research area.

Instructors:
Alexander N. Cartwright
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and have found that the drastic change in sign and the magnitude of γ are expected when the system presents symmetric resonance structures with invertible polarization (SRIP). In previous studies, we have indicated the remarkable variation in γ of H2 model with increasing the bond distance and have suggested the enhancement of γ in the intermediate correlation (intermediate bond breaking) regime. This change is understood to be due to the intermediate bonding electrons are sensitive to the applied field, leading to large fluctuation. Such intermediate bond breaking nature in the intermediate correlation regime is, for example, expected to be realized by the increase in the spin multiplicity in open-shell neutral systems. On the other hand, the investigation of the effect of introducing charge into open-shell systems on γ is important in view of the spin-control of novel open-shell NLO systems since the control of spin states can be induced by external fields like those in open-shell systems in molecular magnetism. Recently, therefore, the effects of spin multiplicity on γ of open-shell neutral and/or charged π-conjugated systems have been investigated using simple open-shell model compounds, and the results have turned out having similar basic molecular structures but containing varying concentrations of the nitro group. For example mononitro-, dinitro-, and trinitrosubstituted azobenzenes are studied. Each of these materials has a similar basic molecular structure but each has a different concentration of the nitro group. It has been suggested that the characteristic emission may be due to a decomposition resulting from exposure of the explosive material to the excitation light. Accordingly, the molecular structures and the optical properties of possible reaction products are also studied. Experiments have also been performed on different phases (solid, liquid, or gas) of the explosive material to determine whether intra- or inter-molecular exchanges influence the characteristic emission. Additionally, the optical properties of explosive materials are investigated using photoluminescence spectroscopy (PL), differential reflectometry (DR), and photoluminescence excitation spectroscopy (PLE). Fourier Transform Infrared spectroscopy (FTIR) and UV-VIS absorption of explosive materials are also investigated.

10:45 AM DD1.5
Excitation Wavelength Dependent Photodynamic Response on Azopolymer Films. Mi-Jeong Kim1,2, Chae-Min Chun3, Tomonobu Nakayama4 and Dong-Yu Kim1;
1Materials Science And Engineering, Gwangju Institute of Science and Technology, Gwangju, South Korea; 2Central Research Center for Young Scientists, National Institute for Materials Science, Tsukuba, Ibaraki, Japan.

Photodynamic property of amorphous azopolymer films was investigated depending on the absorption wavelength of materials and the excitation wavelength of the incident laser beam. Electron donor-acceptor type of photochromic azobenzenes was substituted on the para and meta position of the azobenzenes. All the electron donor groups were amino groups, but different electron-acceptor groups (-CF3, -CN, -CNC, -NO2, and -CN=C) were substituted on the para and meta position of the azobenzenes. Photoinduced linear orientation was measured in terms of birefringence at three different wavelengths (458, 488, 514 nm) using an Ar+ laser. The photoreaction wavelength was in proportion to the absorption intensity at a wavelength of the laser beam. However, the growth rate of birefringence was in inverse proportion to the saturation value of birefringence in the order of -CF3 > -CN > -CNC > -NO2 > -CN=C. This decrease in the growth rate of the photobleaching rate of SRG with a 1 mm grating spacing was investigated by monitoring diffraction efficiency curves and by measuring surface modulation depths from AFM images. When the films were irradiated with the laser interference pattern (wavelength; 458 nm), the slope of the diffraction efficiency curves were proportional to that of the photodecomposed birefringence growth curves. As the wavelength of the Ar+ laser changed to longer region (wavelength; 514 nm), the rate of SRG formation was in the order of -CN > -CNC > -CF3 > -NO2 > -CN=C. The reason for this might be that the trans azobenzenes of the CF3-substituted azopolymer have less absorption coefficient at 514 nm than at 458 nm. Currently, the chiroptical dynamics have been investigated.

11:00 AM DD1.6
Detecting Explosive Materials By Optical Methods. Anna Fuller, Raisinghino Kim, Paul Holloway and Rolf E. Hummel; Materials Science and Engineering, University of Florida, Gainesville, Florida.

Detecting explosive materials is crucial to maintaining security throughout the world. Explosive materials pose an increasing threat to virtually all public places and modes of transportation (e.g., airplanes, trains, etc.). However, current detection methods are expensive, time-consuming, and often inaccurate. A simple, fast, and reliable method for detecting explosive materials is needed. An explosive material detection method using photoluminescence spectroscopy (PL) is proposed. In this work, a characteristic emission with a sharp peak wavelength of 705nm ± 5nm has been detected from explosive materials, such as high explosives, exposed to a suitable light source. The characteristic emission has been confirmed in several explosive materials, including 2, 4, 6 phenylmethylnitramine (Tetryl), Nitroglycerin, Pentamethyldithiaoctanite (PETN), Octahydro 1, 3, 5, 7 tetrazotrihydro 1, 3, 5, 7 tetrazine (RDX), and 2, 4, 6 Dinitrotoluene. These materials have been tested using similar methods and no characteristic emission was detected. Therefore, the emission appears to be exclusive to explosive materials. The characteristic emission from explosive materials has not been previously observed in the literature. In this work it is hypothesized that the sharp emission peak may be due to the presence of functional nitro groups (NO2) and their influence on the electronic structure of the explosive material. The nitro functional group is highly reactive and has the potential to introduce strong electronic effects on the properties of the explosive materials.

11:15 AM DD1.7

In this talk we describe our efforts in the design and synthesis of octupolar nonlinear optical (NLO) materials. Second order NLO effects underpin many of the active functions required in photonics and optoelectronics. Octupolar materials can be obtained from molecules with trigonal, tetrahedral, and cubic distribution of donor and acceptor groups. Octupolar molecules are noncentrosymmetric and exhibit superior optical nonlinearities when compared with related dipolar molecules. We devised a retrosynthetic approach that enables the rational design of trigonal materials in which the molecular octupolar symmetry is preserved in the crystalline solids. This approach is successfully used in two classes of organic compounds: tris(isocyanurates) and tris(triazinyl)azines. The selection of the octopoles is based on a template in which the donor and acceptor groups are situated at the alternate corners of a cube. We devised a hierarchical self-assembly strategy to create a vast number of cubic octupolar materials. This strategy involves the self-assembly of molecules with two donor and two acceptor groups arranged alternately on a square grid, and coordination self-assembly of these molecules into dimers possessing the required cubic distribution of octupolar charges. We are currently exploring this strategy on the dimers of trans-A2D2-porphyrins and trans-A2D2-calixarenes. Structural and nonlinear characterization of several octupolar materials at the molecular and crystal level will be presented.

11:30 AM DD1.8
Experimental and Theoretical Approach to Large Two-Photon Absorption Cross Section in Symmetrically Substituted Diacylenes. S.K. Ohta and Koji Koga; Photronics Research Institute, AIST Kanazi, Ibeda, Osaka, Japan.

Recently two-photon absorption has attracted much attention of researchers from both experimental and theoretical sides due to its potential applicability in the future photonics. Previously, we found that symmetrically substituted diacylenes have relatively large two-photon absorption (TPA) cross sections σ(2) (350-890 GM: 1 GM = 1x10^-60 cm^4 s photon^-1) in the near infrared region [1]. In this study, we have found that one of the diacylenes (MPPBT) exhibits drastic increase in the TPA cross section (up to 2400 GM) at the shorter wavelength region under 650 nm where the incident wavelength is near the one-photon absorption band [2]. The mechanism of the enhancement was discussed based on the four-state model. In order to verify the model, we made molecular orbital calculations using several theoretical models including ab initio and
semi-empirical methods. By using the ab initio method, we can successfully elucidate the role of the higher excited state in the drastic change in optical properties (HOMO-LUMO) of the conjugated and semi-empirical methods. By using the ab initio method, we can successfully elucidate the role of the higher excited state in the drastic change in optical properties of so-called AFX molecules, which will be discussed.

In our ongoing studies to gain insight into the photophysical properties of optical materials, including reverse saturable and two-photon absorbing organic molecules, we recently reported a series of time-dependent density functional theory (TD-DFT) studies of molecular structures and excitation energies, shown to be in a good agreement with experimental data. Further validation and quantitative prediction of the properties for extended porphyrin-based molecular systems will be summarized. In addition, calculations of two-photon absorption cross-sections for substituted stilbenes, and for so-called AFX molecules, will be discussed.

Nonlinear optical properties (NLO) of molecules and atomic clusters have been the subject of intense experimental and theoretical investigation in the recent years due to their potential application in nano-scale photonic and electro-optical devices. Understanding structure-NLO property relationships and modeling new materials utilizing the theoretical tools that have been developed in theoretical studies of this area. Very often the applicability of the predicted results have been limited, however, due to lack of electron correlation, inadequate basis sets, and lack of dispersion effects in the theoretical approach. In this talk, we present an overview of the time-dependent Hartree-Fock (TDHF) method and a recently developed hybrid TDHF and density functional theory (DFT) method to model NLO materials and the properties of molecules and atomic clusters. For large systems it is computationally more practical to use only time-dependent DFT, which also allows us to calculate dynamic polarizabilities in a self-consistent manner. We have developed analytic DFT to allow us to perform first-principles calculations on very large clusters using extended, all-electron Gaussian basis sets. In this talk, we shall present results on polarizabilities of selected organic molecules and nano-scale atomic clusters obtained from our analytic TDFT calculations. The Office of Naval Research, directly and through the Naval Research Laboratory, and the Department of Defense’s High Performance Computing Modernization Program, through the Common High Performance Computing Software Support Initiative (CHSSI) Project MBD-5, supported this work.

Optical responses of conjugated polymers by TD-DFT in real-space and real-time approach. Nobahiko Akinoto and Yasumari Zempo; Sumitomo Chemical, Tsukuba, Japan.

Time dependent density functional theory (TD-DFT) has been widely recognized as a useful method to study the electronic dynamics under the time-dependent external perturbations. As the typical examples of its application, the excited states of atoms and molecules, and the optical responses and the dielectric properties of the systems have been studied and yielded the reasonably accurate results. In this study, we apply this theory to the conjugated polymers and focus on their optical response, which is one of the most important properties in real applications such as polymer light emitting diodes. Since a real polymer is too large to handle, we have performed the calculations of the systems with the different number of repeated units and attempted to extrapolate the response in the polymers. In our calculations, the real-space grid representation is used for the electron wave functions in contrast to a conventional basis set on each atom. We use a uniform grid spacing throughout the space. As the grid spacing is related to the energy resolution, it is needed to be small enough to have desired accuracy. For the electron correlations, the usual local density approximation is employed, and the Troullier-Martins pseudopotentials in the separable form are used. The optical responses of the systems are computed by the real-time approach where we follow the linear responses of the systems under the externally applied perturbation in the real time. This approach gives us not only the clear picture of the time evolution of the physical quantities, but also the responses in the entire range in one calculation. The calculated spectra of several polymers agree with the experiments reasonably well. The spectra are studied as a function of the number of repeating units. In the presentation, we will discuss the calculated spectra and methods, and our future plans. [1] J. Chelikowsky, N. Troullier, K. Wu, and Y. Saad, Phys. Rev. 50, 11355 (1994) [2] K. Yabana and G. P. Bertsch, Phys. Rev. B54, 4488 (1996)

Writing Laser Power Dependence of Second Harmonic Generation in a New Optically Polled Azo-dye/polymer Film. C. H. Wang, Oliver Y.-H. Tai and Yuxiao Wang; Center of Organic Materials for Advanced Technology and Department of Physics, National Sun Yat-sen University, Kaohsuing, Taiwan.

The time and power dependence of the optical poling process of a newazo-chromophore in the PMMA matrix at room temperature has been investigated. Previously published theory does not agree with the writing power dependence. A model is proposed to account for the writing process of the optical poled chromophore/PMMMA system. The model describes the writing laser power dependence of the effective growth rate and the plateau level of the SHG intensity in the all-optical poling process. Theoretical predictions of the growth rate and the plateau SHG intensity are found to be in good agreement with the experiment.


Porphyrins are potentially useful third-order nonlinear optical (NLO) materials due to their highly e-electron conjugated and centrosymmetric structure. In view of their potential applications in optical devices, we have begun a systematic investigation of the fundamental relationship between structure and the linear and NLO properties of porphyrins. We have obtained equilibrium structure of free-base and metal (Pt, Zn, Cu, Co, Fe and Ni) porphyrins with the use of ab initio Hartree-Fock method and a recent ab initio potential energy surface method. The calculated geometrical parameters of the porphyrins show in good agreement with the available experimental and theoretical data. The calculated fundamental electronic transitions of porphyrins ranges between 5.1 to 6.7 eV, with Cu-porphyrin having the smallest value (5.1 eV) and Pt-porphyrin having the largest value (6.7 eV). We have begun the calculations of excited state energy, oscillator strength, and linear and nonlinear polarizabilities of the porphyrins at their optimized geometry. The excited state energy and oscillator strengths are calculated with the use of intermediate neglect of differential overlap (INDO)-configuration interaction method while the (hyper)polarizabilities are calculated by INDO-sum-over-states and time-dependent Hartree-Fock methods. The results for the geometry, excited state energies, and (hyper)polarizabilities of the molecules will be presented at the conference.

Optical Properties of Chalcophories : Bulk to Nanoclusters. Haiying He1, Ranjit Pati1, Shashi Karna2 and Ravi Pandey1; 1Michigan Tech University, Houghton, Michigan, 2U.S. Army Research Lab, Aberdeen Proving Ground, Maryland.

Chalcophories are naturally occurring semiconductor nanocrystals. Recent successes in growing large single crystals of ZnGeP2 and CdGeAs2 have led to renewed efforts to utilize these materials for optoelectronic devices. In this talk, we will present the results of ab initio study of the nanoclusters of ZnGeP2 and CdGeAs2 in an effort to develop a theoretical understanding of the microscopic optical properties of these materials.
For photochemical sciences, Bowling Green State University, Bowling Green, Ohio.

It is well known that porphyrin molecules substituted with ionic groups, like tetra-sulphonatophenyl-porphyrin (TPPS), can self-associate to form aggregates whose structure, dimensions and stability depend on the dye concentration, pH and ionic strength [1]. The aggregates also promote the delocalization of the excitation energy over many molecules, due to the intermolecular interaction between monomers [2]. This interaction results in highly delocalized electronic excitation that should give rise to a nonlinear optical (NLO) response higher than the one expected by the simple sum of the NLO responses of the single porphyrin units forming the aggregate (cooperative effect) [3]. In order to investigate the influence that these cooperative effects have on the two photon absorption (TPA) properties of these aggregates, we present the TPA spectra for a single TPPS molecule in a solution of acidic water/DMSO/urea, where only the protonated monomer is present, and of protonated TPPS in pure acidic water, where aggregation occurs. The TPA cross section at 806 nm are measured using the open aperture Z-scan method, employing a Ti:sapphire amplified laser source delivering 160 fs pulses. The TPA spectral dispersion is recorded with a two-photon section at 4:30 PM DD3.3

4:30 PM DD2.7

Strong enhancement of the two photon absorption cross section of porphyrin aggregates. Camilla Ferrante, Elisabetta Collini and Renato Bozio; Chemistry Department, University of Padova, Padova, Italy.

The use of molecular architecture to design three dimensional rotors for use in molecular devices has been an active area of research. In this presentation will be discussed the use of metal acetylene coordination chemistry to construct novel molecular squares and Paddle Wheel complexes. Also, included is the study of various metal complexes of these novel paddles. Photophysical studies of the photoactive properties of these complexes will be presented.

9:45 AM DD3.4


In this research we are interested in understanding the complete linear photophysical properties of various dyes to better understand the more complicated nonlinear optical properties. Determining structure property relationships of a series of structurally closely related porphyrins is the key in understanding the drivers for the various photophysical properties. Two main classes of materials have been studied and will be presented including the platinum polynyes and various metalated porphyrin systems. Experimental methods for characterization include UV/VIS absorption, steady state and time-resolved emission, femtosecond and picosecond pump-probe spectroscopy, and laser flash photolysis. Briefly we have recently looked at the effect of the platinum metal center on a series of platinum polynyes that differ in the ethylene linker length. From this study we found that the role of the metal is mainly in tuning the kinetic properties whereas the ligands give rise to the various spectral properties. Also in a similar study on a series of benzene and naphthalene annulated porphyrins we found that the central metal does result in small changes of the spectral properties but is also very important for tuning the kinetic properties.

10:30 AM DD3.5

Photochemistry and optical limiting properties of platinum(II) 4'-arylterpyridyl arylacetylide complexes. Wenfang Sun and Fengqi Guo; Chemistry and Molecular Biology, North Dakota State University, Fargo, North Dakota.

Square-planar platinum(II) complexes have attracted great interest in recent years due to their intriguing spectroscopic properties. Our group recently discovered that platinum(II) terpyridyl phenylacetylide complexes are promising broadband optical limiting materials. In order to better understand the structure-property relationship, a series of platinum(II) terpyridyl arylacetylide complexes with different 4'-aryl substituents have been synthesized. All of the complexes exhibit room temperature phosphorescence in fluid. The origin of the emitting state varies with the alternation of the 4'-substituent on the terpyridyl ligand and on the acetylide ligand. Examples for the complexes that contain electron-donating substituents on the phenyl ring of the acetylide ligand, the rest of the complexes exhibit a broad, moderately intense band in their transient difference absorption spectra, which may originate from the same excited state as the emitting state or from a state that is in equilibrium with the emitting state. Both the shape of the transient absorption spectra and the lifetime of the transient species are influenced by the nature of the 4'-substituent on the terpyridyl ligand and the aryl substituent on the acetylide ligand. Examples for the complexes that contain electron-withdrawing substituents on the phenyl ring of the acetylide ligand, the rest of the complexes exhibit a broad, moderately intense band in their transient difference absorption spectra, which may originate from the same excited state as the emitting state or from a state that is in equilibrium with the emitting state. Both the shape of the transient absorption spectra and the lifetime of the transient species are influenced by the nature of the 4'-substituent on the terpyridyl ligand and the aryl substituent on the acetylide ligand.

10:45 AM DD3.6


Coordination driven self-assembly of organic and organometallic cycles and cages has witnessed tremendous growth over the past decade. Numerous metal-linkers have been utilized to construct metallosupramolecular assemblies that have not only exhibited interesting structures but also shown promise for applications in catalysis, chemical sensing, and selective inclusion of guest molecules. Despite the importance of chirality in nature, there have been few reports on chiral metallosupramolecular assemblies. We reason that the incorporation of a chiral ligand into a conformationally rigid
metallo-supramolecular system would lead to a well-defined enzyme-like chiral pocket or functionality, which could find application in catalysis and new proof of principle experiments use 1,1'-bi-2-naphthol (BINTOL) as the key building block with the hope of taking advantage of well documented utility of its chirality for enantioselective processes. I would like to report the realization of a variety of metalloccycles of various sizes as well as their applications in chiral sensing, asymmetric catalysis, and light-emitting devices.

11:00 AM DD3.7

Organic poly-yenes and the polymers derived from them are of considerable interest because of their applications in light-emitting diodes, lasers, photovoltaic cells and field-effect transistors [1]. The introduction of heavy transition metal units at regular intervals into the poly-yene chains provides sufficient spin-orbit coupling to allow light emission from the triplet excited state [2], and thus increases the efficiency of the materials compared to the purely organic systems. Recently, we have synthesised a wide range of platinum(II)-containing poly-yene polymers with the general formula trans-[R(dpdp)2-CC-X-CC]- (X = a range of aromatic and heterocromatic linker groups; R = Et, Ph, nBu) and shown that the optical band gap and electronic properties of these materials can be fine tuned by altering the nature of X [3]. We have found that the band gap can be changed by introducing different platinum(II) complexes into the X position, and the energy gap between the excited singlet and triplet states established at ca. 0.7 eV [4]. We have now extended the range of metals to be included in the molecular complexes and polymers to gold and ruthenium, and have investigated the absorption and emission spectra of these and their organic precursors onto metal surfaces [5]. We will report the results of these studies including the formation of polymers of gold poly-yenes where the chains are formed through gold-gold interactions, and where the absorption and emission spectra show differences between solution and solid-state studies. The results of the absorption of these poly-yene polymers and of related metal nanoparticles onto gold surfaces are also described, and the electronic properties of these systems are reported. References [1] J. H. Bridgeley, D. C. Brown, A. R. Marks, R. N. Macley, K. Friend, R. H. Burn, P. L. Holmes, A. B. Nature 1999, 347, 550. [2] Tessler, N., Denton, G. J. and Friend, R. H., Nature 1996, 382, 695. 2. Arnold Tamayo, Xiaofan Ren, Bert Alleyne and Mark E. Thompson, "Materials Science, USC, Los Angeles, California.

11:15 AM DD3.8

Recently, platinum complexes have been applied successfully as phosphorescent emitters in organic light-emitting diodes (OLEDs). OLEDs fabricated with platinum complexes show high emission efficiency, as the strong spin-orbital coupling of platinum allows efficient intersystem crossing, leading to phosphorescent excited states. The emission of monomeric square planar platinum complexes can be tuned to give monochromatic blue, green and red emmission in fluid solution, by changing the cyclometallated ligands. However, in the solid state, the emission is also strongly perturbed by aggregation phenomena that involve either pi-pi excimeric or Pt-Pt dimeric interactions, which leads to broad, red-shifted emission from this intermolecular property. A single dopant white OLED has been fabricated with platinum complex which emit simultaneously from the monomer and excimer/dimer states. The interaction in platinum complexes is useful to achieve efficient intersystem crossing and phosphorescent emission. High efficiency monochromatic blue OLEDs have not been reported for platinum complex emitters, due to dopant aggregation in solid state. Since the photophysical properties of platinum complexes are strongly structure dependent, the control of the geometry allows us to change the emission color. Herein, we demonstrate efficient blue and red OLEDs devices using dinuclear pyrazine bridged platinum complexes as phosphorescent dopants. The metal-metal distance of these dinuclears is strongly dependent on the nature of the bridging pyrazole ligand. Thus, by careful choice of the pyrazole ligands the emission state of these complexes can be changed from a mixed 3LC/MLCT (ligand centered triplet/metal ligand charge transfer) excited state to low-lying MMLCT (metal to metal charge transfer) state. In addition, some other problems related to platinum complexes such as self-quenching, the ancillary ligand effect and irreversible oxidation property will be discussed.

11:30 AM DD3.9
The study on novel organometallic and organic nanocomposited nonlinear optical material. Xu Dong, Quan Ren, Guanghui Zhang, Xingang Wang, Yanling Wang, Tingbin Wang, Rongliang Yang, Y. Ch, Andi Chan and L. Chu, "The State Key Lab of Crystal Materials, Shandong University, Jinan, Shandong, China; 2Department of Optics, Shandong University, Jinan, China; 3Department of Electric Engineering, City University of Hong Kong, Hong Kong, Hong Kong.

Organometallic and organic nanocomposited crystals or films are an important class of optical materials designing and exploring for frequency doubling, electro-optical and all-optical switch, fast response applications, etc. Previous studies with respect to optical material have mainly focused on inorganic oxide or conjugated organic molecular system, while on the contrary, our attention has been paid to organometallic compounds with conductive or semi-conductive properties, which structures not only have coordinating polyhedron in geometry like in inorganic crystals, but also possess conjugated planar structures or radicals like in organic crystals. In this presentation, we report the results of these new nanocrystals and nano-composited films are reported and reviewed. ZnCd(SCN)4 (abbreviated as ZCTC, space group I4 – 1) is a novel organometallic nonlinear optical material. The dielectric and nonlinear optical parameters were measured, c11 = 7.3, c33 = 7.8, d14 = 3.2 pm/V, d33 = 7.6 pm/V. UV transparency occurs at 200 nm; 10.29 mW second harmonic generation (SHG) continuous-wave violet-blue light at 404 nm is obtained by direct frequency doubling of laser diode on 3 mm crystal. The Sellmeier equations of refractive index of the crystal are as follows:

n2 = 2.36064 + 0.02564/ (λ^2 - 0.05141) - 0.02564/ (0.05141 - λ^2)

n2 = 2.88234 + 0.02011/ (λ^2 - 0.01141) - 0.02011/ (0.01141 - λ^2).

Growth mechanisms and surface morphology of organometallic crystals were also discussed. Another examples are organometallic and organic nanocomposited waveguide using for electro-optical or all-optical switch. ET4-4, ET4-4Cu(SCN)2, DBO-TT-DMACB nanocrystals were already prepared. Two and three dimension waveguides in 1.55µm and 1.32 µm were successfully achieved. The electro-optic coefficient, third-order nonlinearity, dielectric properties, absorption properties, nonlinear refractive indices and their dispersion, optical propagation losses were measured. The design idea is to use the organometallic or organic nano-crystal/polymer system to substitute for the molecules/polymer system. Some of ET derivatives or organic conductor and semiconductor have been selected as the building units (guest) of electro-optical or all-optical polymer, because they may commonly possess much higher second and third nonlinear coefficient than that of inorganic or organic materials. The efforts on organometallic and organic semiconductor, particularly with nano-size asymmetrical structure and high mobility is very important for exploring new nonlinear optical materials used in many applications of photo-electronic devices with fast response.

11:45 AM DD3.10
Spin Transfer Effects on Singlet Exciton Formation and Singlet-Triplet Energy Transfer. Bin Hu, Yue Wu, Zongtao Zhang, Sheng Dai and Jian Shen, Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee.

Electroluminescence (EL) in conjugated polymers arises from singlet excitation. But, the recombination injected electrons and holes in these metal-organic and organic semiconductor, particularly with nano-size asymmetrical structure and high mobility is very important for exploring new nonlinear optical materials used in many applications of photo-electronic devices with fast response.
approach of magnetic doping not only presents a new pathway to enhance polymer EL efficiency, but also makes conjugated polymers promising as spintronics materials.

SESSION DD4: Organometallic Optical Materials II  
Tuesday Afternoon, November 30, 2004  
Room 310 (Hynes)

1:30 PM *DD4.1  
Metal Complexes for Monochromatic and White OLEDs.  
Mark Thompson¹, Stephen Forrest², Julie Brown³, Xiaofan Ren⁴,  
Russel Holmes⁵, Arnold Tanay⁵, Jason Brooks⁶, Peter Djuricich⁷,  
Tissa Sajoto⁸, and Biwu Ma⁹  
¹Department of Chemistry, University of Southern California; ²Department of Electrical Engineering, Princeton University; ³Princeton, New Jersey; ⁴Universal Display Corporation, Ewing, New Jersey.

By efficiently utilizing triplet excitons we have demonstrated OLEDs with internal efficiencies near 100%. The phosphorescent dopants in these devices are heavy metal containing compounds (i.e. Pt, Ir compounds). The emission color is readily tuned by ligand design. We have recently demonstrated white light emitting OLEDs, using many of the same emissive materials. These devices emit simultaneously from nonemissive and emitter organic and Pt dopants. The result is an emission spectrum that covers the entire visible spectrum, giving the white light OLEDs good color rendering values and readily stack in the solid state, forming aggregate species. Under the right conditions it is possible to get combined monomer and aggregate emission from a single doped film, leading to a very simple white OLED architecture. We have recently found that it is possible to prepare a biaxial Pt complex that is stable in solution, readily sublimes and gives an emission spectrum matching the aggregate species in our white OLEDs. The photophysics, structure and OLED properties of this biaxial complex will be discussed. We will also discuss our most recent advances in achieving high efficiency blue electrophosphorescence. Both new dopant designs and new device structures, tailored for efficient blue EL, will be discussed.

2:00 PM *DD4.2  
Luminous Metal Alkynes - From Design to Assembly of Molecular Functional Materials and Chemosensors.  
Vivian Wing-Wah Yam, Department of Chemistry, The University of Hong Kong, Hong Kong, China.

Studies of metal alkynyl complexes have attracted growing attention due to the potential applications of organic and metal-containing edgo- and polyynes as molecular wires and junctions, and in molecular optoelectronics and photonics. By making use of the versatile bonding modes of sp-unsaturated C≡C group, recent works in our laboratory have shown that construction of various luminescent metal alkynyl complexes could be accomplished. A number of these complexes have been structurally characterized and shown to display rich luminescence behavior. The luminescence properties have been studied and their emission origins elucidated. Correlations of luminescence behavior with the electronic and structural effects of the metal complexes have also been made. Through rational design and assembly strategies, these metal alkynes may serve as ideal building blocks for the molecular and construction of molecular rods and materials as well as may find potential applications in chemosensing and luminescence signaling.

2:30 PM *DD4.3  
T1 and Tn triplet states in organic and Pt-containing conjugated polymers. Anna Kohler¹, Ning Zhang², David Beljonne³, Mohamed K. Al-Suš⁴ and Muhammad S. Khan⁵  
¹Universidad de La Rioja, Logroño, Spain; ²Chemistry Department, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China; ³Cambridge University, United Kingdom; ⁴Materia Nova, University of Mons, Mons, Belgium; ⁵Department of Chemistry, Sultan Qaboos University, Oman, Oman.

While the singlet excited state in conjugated polymers is well investigated, less is known about the manifold of triplet excited states, even though triplet excited states play a significant role in determining the efficiency of polymer light-emitting diodes. Since emission from the triplet excited state is spin-forbidden in organic polymers, it is usually less accessible to spectroscopic techniques. We have incorporated a heavy Pt-atom in a phenylene-ethynylene polymer backbone to give polymers and monomers of the general structure Pt[Ph2(2,3-C≡C-Ph)]. The spacer R is varied such as to give optical gaps ranging from 1.7 - 3.0 eV. It is possible to detect the triplet state luminescence (phosphorescence) associated with the conjugated system of these polymers since the heavy Pt atom induces a strong spin-orbit coupling. This allows us to access the triplet excited state by cw and time-resolved optical spectroscopy. For the Pt-polymer (and corresponding organic polymers), we find that the T1 and Tn triplet excited states are both separated from the S1 singlet excited state by an energy of + 0.7 eV and - 0.7 eV, respectively. Comparison with analogous monomers shows that the T1 state is highly localized while the Tn state is delocalized. We have also performed quantum chemical calculations to assess how the extent of the T1 and Tn states affects their energetic separation from the S1 state. Using polymers with identical backbones but yet different metal complexes, we have further explored the role of charge transfer in the delocalisation of the excited states and thus the energies of T1 and Tn and the width of the T1-Tn transition signal.

3:30 PM DD4.4  
Novel iridium complexes with polymer cores. Elisabeth Holder¹,² and Urich S. Schubert¹,²  
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New metal-containing and emissive materials find applications in various research fields but are currently not in focus for enzyme mimics and sensor applications. Iridium(III) complexes are highly appealing due to their wide range of emission energies, long lifetimes and high quantum yields. Above all the design of emissive and redox-active d1 transition metal complexes such as those of iridium(III) or ruthenium(II) and the study of their photochemical, photophysical and electrochemical properties has been extended in the last years with respect to their potential applications as phosphorescent light emitters in phosphor doped light-emitting devices. For potential applications such as in device and display technology it is of importance to have phosphorescent emitters that are easily to process, do not aggregate and favorably have high quantum yields and show low yellow shifts for easy device fabrication. This demand can be fulfilled if the emitted light results from metal-to-ligand charge-transfer processes. This way a variation of the respective ligand set may induce a change of the color of the emitted light. Despite these properties the ligands of metal-ligand-complexes can be used to introduce side-chains that can consist of various functionalities such as linear bipyridine [1] and terpyridine [2] systems with polymer tails or star shaped architectures. In this presentation the synthesis of a set of new yellow and orange light-emitting polymer iridium(III) complexes via the so-called bridge-splitting method is described. [3] Therefore the respective dimeric precursor complexes [Ir(ppy)2Cl]2 (ppy = phenylpyridine) and [Ir(CHO)2Cl]2 (ppy-CHO = 4-(2-pyridyl)benzaldehyde) were coordinated to a bipyridine carrying poly(ε-caprolactone) (PCL) tails as well as to terpyridine functionalized poly(ethylene glycol) and to a series of 5 arm star shaped block copolymers bearing terpyridine end-groups. The resulting emissive polymers have been fully characterized revealing the successful coordination of the iridium(III) center to the bipyridine macrocycle and the respective terpyridine functionalized materials. The photophysical and photochemical properties of the iridium(III) containing polymers revealed color-shifts depending on the substituents of the cyclometallating ligands.

3:45 PM DD4.5  
Phosphorescence quantum efficiency and intermolecular interaction of iridium(III) complexes in co-deposited films with organic semiconductor hosts. Yoshiki Kawasaki ¹,²  
¹CREST program, Japan Science and Technology Agency, Japan; ²Department of Photonics Materials Science, Chitose Institute of Science and Technology, 758-65 Bibi, Chitose, Hokkaido, Japan; ³Universal Display Corporation, 375 Phillips Blvd., Ewing, New Jersey.

The efficiency of organic light-emitting diodes (OLEDs) has been dramatically improved by the use of heavy metal phosphorescent emitters. Heavy atom induced spin orbit coupling allows for efficient intersystem crossing from the singlet to the triplet states and therefore can be used to highly efficient OLED devices that are able to utilize both singlet and triplet excited states. Cyclometalated Ir(III) complexes are promising candidates for phosphorescent dopants because they can emit with high efficiency in room temperature from the triplet metal-to-ligand charge-transfer state. An OLED device containing a green emitting Ir(III) complex is reported to have an external electroluminescence (EL) quantum efficiency (ηEL) as high as 10%. Considering losses in efficiency due to light out-coupling from the device, it is believed that cyclometalated Ir(III) complexes may find potential applications in phosphor doped light-emitting devices. In this study, the solid state photoluminescent quantum efficiencies (ηPL) for three Ir(III) complexes used as dopants in OLEDs are reported herein. The green emitting complex, fac-tris(2-pyridyl)iridium(III) (Ir(ppy)), the red emitting bis[2-(2-benzothienyl)pyridinato-N,C4]²⁺
(acetylacetonato)iridium(III) (Btp2Ir(acac)), and FIrpic were respectively 97±2% and 90±2% from T, to So. The spectrum of sensitizer. The distance separating the donor-acceptor pair determines the decay rate (k_{r}) which can be well described by a Förster-type self-quenching interaction. The Förster radii for concentration quenching are estimated to be 1.32 nm for Ir(ppy)_3 in CBP, 0.74 nm for Btp2Ir(acac) in CBP, and 1.14 nm for FIrpic in mCP.

4:00 PM DD4.6

Unusual phosphorescence decay characteristics of Ir(ppy)_3 in a solid matrix. Kenichi Gosh 
1, Yuichiro Kawamura 
2, Jason Brooks 
3, Julie J. Brown 
3, Hirokazu Saab 
1,2, Chihaya Adachi 
1,2.

1Photons Materials Science, Chisette Institute of Science and Technology, Chisette, Hokkaido, Japan; 2Japan Science and Technology Agency, Shibuya, Tokyo, Japan; 3Universal Display Co., Ewing, New Jersey.

Organic phosphors have been used as electro luminescence (EL) materials in organic light emitting diodes (OLEDs) and have attracted considerable attention due to their high EL efficiency. OLEDs using organic dyes as dopants are limited by decreased EL performance due to lower triplet energy and concentration quenching by host materials. These technologies have been improved in the last decade due to the development of higher performance Phosphor layers. Here we present the characteristic temperature dependences of the transient phosphorescence lead us to conclude that the non-radiative transition rate (k_{r}) from the triplet excited state is very small compared with the radiative transition rate (k_{a}) and that the phosphorescence quantum yield is nearly 100% even at room temperature. In addition, we also investigated the temperature dependence of absorbance from the ground state (S_{0}) to the triplet excited state (T_{1}) because k_{r} from T_{1} to S_{0} proportionally to the absorbance from S_{0} to T_{1}. The results showed that the absorbance is temperature independent. These results lead us to conclude that k_{r} from T_{1} to S_{0} is temperature independent.

Based on our experimental results, we discuss a possible decay mechanism to realize the characteristic temperature independence of the transient phosphorescence. By comparing a numerical model with the experimental data, we demonstrate that mutual energy transfer between the sub-levels of triplet states can explain the characteristic temperature dependence.

4:15 PM DD4.7

Lanthaneide Sensitized Quantum Dots with Tunable Fluorescent Lifetimes. Thomas A. Schauder 
1, Thomas Michael Barnard 
1, Chemistry, University of North Carolina at Charlotte, Charlotte, North Carolina.

A series of CdSe/ZnS quantum dots with tunable fluorescence lifetimes have been created using long-lifetime lanthanide complexes as photosensitizers similar to procedures developed by Selvin and coworkers (for instance Proc. Nat. Acad. Sci., USA 91, 10024-10028, (1994)). The lanthanides are tethered to the quantum dots via a thiol terminated ligand of variable length to control the distance separating the II-IV quantum dot and the lanthanide sensitizer. The distance separating the donor-acceptor pair determines the rate of energy transfer from the quantum dot to the lanthanide sensitizer. The rate of energy transfer is proportional to the distance between the quantum dot and the lanthanide sensitizer. The distance between the quantum dot and the lanthanide sensitizer is determined by the thiol ligand length and that of the quantum dot.

The result is a multiexponential fluorescent signal from the quantum dot that includes a tunable long tau contribution from the lanthanide sensitizer. The multiphotonic absorption spectrum of the quantum dot determines the characteristic temperature dependences of the transient fluorescence. In addition, the temperature dependence of absorbance from the ground state (S_0) to the triplet excited state (T_1) because k_r from T_1 to S_0 proportionally to the absorbance from S_0 to T_1. The results showed that the absorbance is temperature independent. These results lead us to conclude that k_r from T_1 to S_0 is temperature independent.

Based on our experimental results, we discuss a possible decay mechanism to realize the characteristic temperature independence of the transient fluorescence. By comparing a numerical model with the experimental data, we demonstrate that mutual energy transfer between the sub-levels of triplet states can explain the characteristic temperature dependence.

8:30 AM DD5.1

Plasmonics: a functional materials approach to photonics "From the bottom up". Naomi J. Halas, ECE, Rice University, Houston, Texas.

Recently there has been a tremendous resurgence of interest in the optical properties of metallic nanostructures. This is primarily due to the fact that their plasmon-derived optical response can be controlled and manipulated in many practical ways by systematic variation of the metal's nanoscale size and shape. In our own work, we have developed a simple core-shell topology for metallo-dielectric nanostructures called a nanoshell, which possesses an optical resonance which is freely tunable across the visible and infrared regions of the spectrum. Nanoshells are a fundamental component of nano-optics, where the relative and absolute size of the nanoparticle's layers control precisely how it interacts with, modifies, focuses or guides the incident optical field. This geometry has been shown to be of tremendous utility in two sensing modalities, surface plasmon resonance and surface-enhanced Raman scattering, where in both cases the response can be controlled and optimized. The interaction between nanoshells and optically active species, such as molecular or ionic fluorophores in optically active embedding media, is dependent upon the spatial extent of the emitting molecule relative to the dimension of the nanoparticle as well as the relative energetics of the plasmon resonance and the excited states of the fluorophore of interest. Systematic modifications of the nanoshell geometry, such as symmetry breaking of the spherical topology or the introduction of surface roughness on the nanoparticle in a controlled manner, introduce modifications in both the near field and far field of the nanoparticle that can affect these processes.

9:00 AM DD5.2

Microscopic near-field optics of metallic nanoparticles. Yongqing Xue and Mark A. Ratner, Chemistry Department and Materials Research Center, Northwestern University, Evanston, Illinois.

The further miniaturization of integrated optical devices requires investigating optical elements with dimensions on the nano-scale. Methods are therefore needed for detecting and guiding light on a scale much smaller than the wavelength of the light. Near-field optics, which exploits evanescent rather than propagating light fields, attracts a lot of attention as a promising way of circumventing the diffraction limit. Since the evanescent fields bound to the nanostructures decay in intensity within a fraction of the light wavelength, they carry information about sample features on a sub-wavelength scale. It is clear that to investigate light-matter interaction in a spatial extension much less than the optical wavelength, one cannot in general have confidence in the macroscopic electrodynamics so far popular in near-field optics and photonic band-structures. Instead a microscopic approach treating rigorously the local-field effect is highly desirable. In this work we present a microscopic theory of near-field optical effect in single and coupled metallic nanoparticles.
electrodynamics, where we treat the nanoparticle optical response quantum-mechanically within the jellium model. We discuss the insights obtained through microscopic and macroscopic light scattering analysis and report on recent experiments. A new type of ligand stabilization, i.e., the use of charged dendrimers, and a new experimental technique, i.e., the use of a tunable laser diode, allow the study of single nanoparticles with a better understanding of the interaction between the nanoparticles and the optical field. Finally, we discuss the potential applications of this approach in the field of nano-optics.

10:15 AM DD5.5

Minimisation of molecular sensors is a rapidly growing field in biomolecular research, where nanoscience will have a major impact. Here we investigate how a molecular sensor based on the spectroscopy of a single gold nanoparticle [1], can be improved by the use of single gold nanoshells. The optical properties of single metal-coated silica nano-dots are expected to improve the optical properties. In the present study, these long-range ordered Au nano-dot arrays with controlled nanometer-sized diameter and spacing were prepared by vacuum evaporation using an anodic porous alumina membrane through-holes of nanometer scale as a mask [1,2]. The optical properties of the long-range ordered metal array fabricated were studied. Anodic porous alumina membranes formed by anodizing aluminum oxide solution have unique properties characterized by their uniformity in diameter and spacing of the holes and straight channel structure over large area [3,4]. This process has an advantage in the preparation of highly ordered nano-dot array because the space and spacing of the dots on the array can be easily controlled by changing the geometrical structure of the anodic porous alumina used as a mask. A peak that was due to the local plasmon resonance for the highly ordered Au nano-dot array could be observed in the visible region. The peak wavelength depended on the heights of the dots and the refractive index of solvent in which the Au nano-dot array was immersed. The development of an optical sensor based on the highly ordered nano-dot array prepared using ideally ordered porous alumina membranes is expected to be easily controlled by changing the geometrical structure of the anodic porous alumina used as a mask [1,2].


9:30 AM DD5.4

Nanometer-sized metal particles have been the focus of extensive studies owing to their greatly simplified nonlinear optical (NLO) response. These amplifications are attributed mainly to large enhancements of surface-induced electric fields at the nanoparticles’ surface plasma resonance (SPR). Adding SPR into “hot-spots” in semiconductor films manifests in extremely large local EM fields and giant enhancements of NLO phenomena. These novel optical features may be accurately controlled by design of nanoparticle geometry. In particular, noble metal nanoshells allow control of EM field distributions and subsequently their SPR. Metal nanoshells consist of thin metal shells, made from dielectrics with Kerr optical nonlinearity, quantum-mechanically within the jellium model. We discuss the optical response of disordered aggregates of metal-coated spherical shells, made from dielectric with Kerr optical nonlinearity, and nanomaterials. In particular, we find a novel homogeneous NPPR position of gold nanoshells shows a higher sensitivity to changes in the environment, (ii) the resonance can be tuned close to the biological window (iii) and the scattering spectra show sharp resonances. In particular, we find a novel homogeneous NPPR position of gold nanoshells shows a higher sensitivity to changes in the environment. The peak wavelength depended on the heights of the dots and the refractive index of solvent in which the Au nano-dot array was immersed. The development of an optical sensor based on the highly ordered Au nano-dot array prepared using ideally ordered porous alumina membranes is expected to be easily controlled by changing the geometrical structure of the anodic porous alumina used as a mask [1,2].


10:30 AM DD5.6

Polymer-metal composites offer the possibility of strongly enhanced nonlinear optical properties, which can be used for ultrasmall photonic devices. In this paper, we investigate numerically, by means of the finite-difference time-domain (FDTD) method, the propagation characteristics of surface plasma polariton modes excited in an optical nanowire consisting of a chain of metallic spheres embedded in dielectric shells made of materials with optical Kerr nonlinearity, namely polymers or semiconductor materials. The radius of the metallic spheres, made from silver, is 50 nm, the center-to-center distance between adjacent spheres in 75 nm, and the thickness of the spherical shells, made from dielectrics with Kerr optical nonlinearity, are 50 nm. Using the FDTD method, the propagation characteristics of surface plasma polariton modes excited in an optical nanowire consisting of a chain of metallic spheres made from silica and gold nanorods, for which the electric field is perpendicular to the axis of the wire and a longitudinal one with \( \lambda_1 = 307.5 \) nm, for which the electric field is along the axis of the nanowire. Furthermore, our simulations show that for an input power \( P_0 = 100 \) MW/cm\(^2\), the wavelength of the transverse surface plasma polariton mode is shifted by \( \Delta \lambda = 45.3 \) nm when the Kerr coefficient is increased from \( n_2 = 10^{-13} \) m/W to \( n_2 = 10^{-11} \) m/W. Conversely, if the electric field is made of a material with large Kerr coefficient \( n_2 = 1.5 \cdot 10^{-11} \) m/W (e.g. GaAs-based semiconductors) the transverse surface plasma polariton mode is shifted by \( \Delta \lambda = 12.9 \) nm when the input power varies between 100 MW/cm\(^2\) and 2.5 GW/cm\(^2\). Finally, the potential use of these nanoshells to enhance the localised plasmon modes. The prospects of observing strong NLO enhancements in ordered arrays of these particles (photoactive crystals) will also be discussed.
design nanoscale active optical devices is discussed.

10:45 AM DD5.5

Although molecular optical or electronic switches promise to deliver fast and accurate solutions to increasing computing demands, these nanoscale devices are limited by our understanding of the physics within current technology and the inherent inability to control and manipulate the molecular optical device structure. We report results on a new plasmonic device that allows us to both characterze and actuate organic molecular switches within metal-molecule-metal junctions. This technique represents a step towards miniaturization and incorporation of optically active materials with nanoscale electronics, as well as deepening our understanding of metal-molecule interactions at the nanometer lengthscale.

11:00 AM DD5.8
Coherent Oscillations of Breathing Modes in Core-Shell Nanoparticles. Arman S. Kirakosyan and Tigran V. Shahboyan; Jackson State University, Jackson, Mississippi.

We study coherent oscillations of radial breathing modes in metal nanoshells with dielectric core. Acoustic vibrational modes in nanoparticles, which are impulsively excited by the rapid heating of the particle lattice that occurs after laser excitation, can be observed using pump-probe spectroscopy as a modulation in time of the surface plasmon (SP) resonance energy position [1,2]. The oscillations originate from oscillations and expansions of a nanoparticle around a new equilibrium, while energy transfer to a surrounding dielectric matrix leads to the damping of oscillations. In solid metal particles, the mode frequencies and decay constants are inversely proportional to the nanoparticle size, although in small particles the laser predominantly excites the lowest (n=0) radial mode. In nanoshells, the presence of two metal surfaces leads to a substantially different energy spectrum of acoustic vibrations. We found that, in contrast to solid particles, two lowest modes of a nanoshell are excited by the pump pulse. These modes correspond to in-phase (n=0) and anti-phase (n=1) contractions of shell-core and shell-matrix interfaces respectively. We calculated the energy spectrum as well as the damping of a nanoshell vibrational modes for stress-free metal boundaries, and found that the size-dependence of in-phase and anti-phase modes are different. In particular, in a wide range of aspect ratios, the frequency of the n=1 mode is inversely proportional to the nanoshell thickness while the lowest mode frequency is nearly independent of it, resulting in significantly longer period of the in-phase mode. We have also shown that the amplitude of the coherent oscillations is much larger in nanoshells as compared to solid particles due to a strong dependence of the SP energy on nanoshell aspect ratio. Supported by NSF under grant DMR-0305557 and NUE-0407108, by NIH under grant 5S06 GM008047-31, and by ARL under grant W911NF-01-0001. 1. N. Del Fatti et al., J. Chem. Phys. 110, 1184 (1999). 2. J. Hodak et al., J. Chem. Phys. 111, 8613 (1999).

11:15 AM DD5.9
Gold Nanorod Nucleation from Colloid Seeds. Hongwei Liao1 and Jason H. Hafner1,2; 1Chemistry Department, Rice University, Houston, Texas; 2Physics and Astronomy, Rice University, Houston, Texas.

Gold nanorods have optical plasmon bands that can be tuned through the visible and near-IR region based on their size and shape. Several approaches for preparing the NRs have been investigated. Seed-mediated growth in the presence of a surfactant is a particularly versatile method. However, the growth of the seeds into nanorods is not entirely understood, but its origin apparently lies in the surfactant altering nanorod growth rates. Growing gold nanorods on surface, rather than in bulk solution, is a unique strategy to study the gold nanorod growth phenomenon. This growth can be monitored by surface analysis method such as Atomic Force Microscopy. In our work, surface growth is employed to investigate nanorod growth mechanisms and kinetics. We introduce a significant simplification by the use of commercially available colloidal seeds deposited by electrostatic attraction. Yields and shape distributions can be determined quantitatively since surface microscopic analysis is carried out without any perturbation of the particle ensemble. We focus on the initial growth of the NRs and design simple strategies to improve reproducibility and simplify interpretations of the growth mechanism. Our results directly demonstrate a minimum seed size for nanorod nucleation and its insensitivity to the surfactant chain length.

11:30 AM DD5.10
Surface Plasmon Excitations and Emission Light due to Molecular Luminescence on Metal Thin Film. Patric Kaneko1,2; Susumu Toyoshima3, Yasuo Ohdara1,2, Kazumori Shimo1,2 and Keizo Kato1,2,3; 1Electrical and Electronic Engineering, Niigata University, Niigata, Japan; 2Center for Transdisciplinary Research, Niigata University, Niigata, Japan; 3Graduate School of Science and Technology, Niigata University, Niigata, Japan.

Emission light due to surface plasmon (SP) excitations has been investigated in Kretschmann configuration of optically active thin films or/and dye thin films by means of direct irradiation of a laser beam from air to the films. Emission light through the prism coincided with the resonant conditions of SP excitations in the configuration. It was thought that SPs on the metal surface were excited by luminescence of dye molecules close to the metal surface, and the SPs propagating along the metal surface were converted to the emission light corresponding to the resonant conditions of SPs in the configuration. Intensity of the spectral maxima of the SP emission light through the prism strongly depended upon emission angles, nanostructures of dye films, combinations of dyes and nano-separation between the dyes and the metal surface. It is thought that the phenomenon of the SP emission is very useful for applications to nanostructured optical devices, conversion between two- (SP) and three- (dimensional) optical waves and connections between near field and far field optics utilizing the SP excitations.

SESSION DD6: Electro-Optic and Electronic Materials
Wednesday Afternoon, December 1, 2004
Room 310 (Hynes)

1:30 PM **DD6.1

The recent advances in organic electro-optics materials (EO) have attracted a great deal of research interest. When incorporated into devices, these materials serve as an effective vehicle for rapid modulation of optical signals using electrical inputs making them attractive for telecommunication and data processing applications. Nonlinear optical (NLO) chromophores are the most successful family of organic EO materials. These chromophores are typically comprised of a delocalized -electron system that connects electron deficient moieties (donors) to electron deficient functionalities (acceptors). Hyperpolarizability (β), is the critical parameter that defines molecular NLO behavior. Optimization of NLO chromophores has proven to be a challenging task because enhancement of β typically results in reduced stability, decreased transparency to telecommunication wavelengths and other unwanted consequences. A family of NLO chromophores has been synthesized containing novel donor systems based on functionalized guanidines. Chromophores utilizing these donor systems display larger hyperpolarizabilities than those incorporating conventional donors, yet possess superior transparency and stability properties. The unusual and highly desirable characteristics of these chromophores make them very promising candidates for EO applications. Systematic study of the molecular hyperpolarizabilities and bulk EO properties of polymers containing these chromophores is being used to guide optimization of these systems.

2:00 PM DD6.2
Highly Ordered Pseudo-Discotic Chromophore Systems for Electro-Optic Materials and Devices. Nishant Praush Bhutambharkar1, Scott Hammond1, Jessica Sinnese1, Olivier Clot1, Harrison L. Rommel1, Antao Chen3, Bruce Robinson1, Alex K.-Y. Jen1, and Larry Dalton1; 1Chemistry, University of Washington, Seattle, Washington; 2Materials Science and Engineering, University of Washington, Seattle, Washington; 3Applied Physics Laboratory, University of Washington, Seattle, Washington.

In order to achieve the desirable quasi-ferroelectric order in organic electro-optic (EO) material systems, a pseudo-discotic chromophore architecture is under investigation. Monte Carlo theoretical calculations suggest head-to-tail inter-chromophore dipole-dipole interactions should drive chromophores having an appropriate aspect ratio to self-assemble into ferroelectric columns similar to those in discotic liquid crystals (DLCs). Therefore, the resulting liquid crystalline properties of these chromophores are being examined by differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction (XRD). Furthermore, the effect of this discotic behavior on the chromophore orientation at the microscopic level and the subsequent macroscopic EO properties of the system are being examined both dynamically by second harmonic generation (SHG) and statically by attenuated total reflection (ATR). As active core layer materials, these chromophores are also being incorporated into waveguide-based photonic devices for potential information.
processing applications.

2:15 PM DD6.3 Synthesis of Dendritic NLO Chromophores for the Improvement of Order in Electro-optics, Jessica Sinness1, Olivier Clo1, Nishant Bhatnagar2, Scott R. Hammond1, Harrison L. Kromm1, Bruce H. Robinson1, Alex K.Y. Jen1 and Larry R. Dalton1 1Chemistry, University of Washington, Seattle, Washington; 2Materials Science and Engineering, University of Washington, Seattle, Washington.

Previous research in polymeric electro-optics has shown dramatic increases in the hyperpolarizability of NLO chromophores. However, this large microscopic activity has not been translated to the macroscopic domain. The polymeric electro-optic (E-O) materials continue to lack the high noncentrosymmetric order of the poled chromophores within the matrix necessary for high E-O response ($\chi^{(3)}$). This deficiency of order represents one major obstacle that must be overcome before device commercialization can be achieved. This lack of order is in part due to the large dipole moments of high $\mu$ chromophores, which causes the chromophores to align in a centrosymmetric fashion through intermolecular electrostatic interactions. However, quantum calculations show that when the aspect ratio between the length and width of the chromophore system is adjusted to be 1.4:1 by adding bulky side groups around the center of the chromophore, it would prevent side on pairing of the chromophores. This would cause a decrease in the large areas of centrosymmetric aggregation and thus allow for easier poling of the system. Here we report the synthesis of a nanoscale NLO architecture in which dendritic moieties have been incorporated around the center of the chromophore in a three-dimensional manner to achieve the 1.4:1 aspect ratio and maximize the macroscopic order of the system.

2:30 PM DD6.4 Molecular Logic Gates with Polymer Nanosheets Assemblies, Jun Matsui1, Masaya Mitsushita1, Atsushi Aoki2 and Tokuji Miyashita3 1Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Miyagi, Japan; 2Graduate School of Engineering, Nagoya Institute of Technology, Nagoya, Aichi, Japan.

Development of organic molecular devices for information processing applications is a major objective in recent materials science. Such devices include wires, switches and logic elements, which can be designed for use in photonic, electronic, and optoelectronic systems. Our group has succeeded to fabricate ultrathin polymer sheet assemblies (polymer nanosheets) using Langmuir-Blodgett technique. We have developed several organic photofunctional devices using the polymer nanosheet assemblies. One of the devices are polymer nanosheets photodiodes, which mimics a photoenergy conversion systems in biomembranes. In this presentation, we like to report optical logic gates using the polymer nanosheets photodiodes. We configure two nanosheets diodes that operate at different wavelengths to produce the logic AND (AND) or EXOR (EXOR). One nanosheet was constructed from phenanthrene containing polymer LB film and electron acceptor polymer LB film, and the other was constructed from anthracene containing polymer LB film and electron donor polymer LB film. First, to produce the AND logic gate, we assembled these films so that each current flows to the same direction. In the polymer nanosheet logic gates, input signals are excitation wavelength of each chromophore and the output is photocurrent, which is attributed to the interlayer charge-transfer between the chromophore layer and the donor or the acceptor layer. The phenanthrene and anthracene chromophore can be selectively excited because they have no overlapping in their absorption spectra. The photocurrents of the array were measured using 3 electrodes electrochemical cell. With the photocurrent response, it was concluded that, in the polymer nanosheet AND logic gate the high and low levels were separated by a factor of 2.7. Furthermore, we construct exclusive OR (EXOR) gate by connecting the two photodiode side so that the direction of each photocurrent flow becomes opposite. For selective photoexcitation of the phenanthrene chromophore in the array, cathodoluminescence was observed. For the two chromophore excited simultaneously, the photocurrents were canceled out because the photocurrent direction was opposite between photodiode 1 and 2, resulted in a very small value. Therefore, the assembly of nanosheets operates as an EXOR logic gate. Notably, these polymer sheet can be assembled on any solid substrate in a tailored manner so that applicable to nano solid-state devices.

2:45 PM DD6.5 High Speed Photo-Detection in Nano Structured Phthalocyanine-Perylene-Phenantroline Structure.

Yutaka Ohmori, Taichiro Morimune and Hironori Kaji; Center for Advanced Science and Innovation, Osaka University, Suita, Osaka, Japan.

Organic-organic and organic-metal nano structure have been investigated to obtain high speed photo response in organic multilayer structures for high speed photodetectors. The organic nano structured systems in biomembranes. Selective photoexcitation of the phenanthrene chromophore in the electron acceptor polymer LB film, and the other was constructed electrochemical cell. With the photo current response, it was concluded that the layer thickness of BPPC and BCP significantly affects the photo response in the device, and the typical layer structure consists of ITO (Indium-Tin-Oxide) anode, CuPc (cupper phthalocyanine) and BPPC (N, N′,N,N′-tert-butyl-N,N′-diphenyl-2,3,5,6-tetrachlorophthalocyanine), BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) and terminated silver electrode. The CuPc and BPPC layers act as carrier generation and recombination layer and the BCP layer as carrier blocking layer. The layer thickness of BPPC and BCP significantly affects the photo response in the device, and the typical layer structure consists of ITO (200 nm), CuPc (20 nm), BPPC (10 nm), BCP (10 nm) and Ag (200nm). Since the photo detector has 100 MHz bandwidth, optical signal of moving picture can be detected using optical transmission with red light emitting diode (620 nm). Photo detectors using cupper fluorinated phthalocyanine has been also examined for photo detection layer. Introducing of nano structured carrier confinement and carrier trapping layers results in high speed response of the photo-detector.
simulations for silver island films are shown to agree with experiment. The plasmonic enhancement has a wide spectral range, and accounts for the observed power enhancement in organic solar cells based on an organic heterojunction of copper phthalocyanine (CuPc) and 3,4,9,10-perylenetetracarboxylic bis-benzimidazole (PTCBI) [1-2].


Numerous experimental studies, mostly based on time-of-flight (TOF) technique, showed that the conductivity mechanism in organic crystals is (trap-transport) band transport. However, recent comparative studies of TOF signals and space charge limited currents (SCLCs) in tetracene crystals revealed a striking difference in carrier mobilities estimated from TOF current transients and from SCLC curves. The analysis of the SCLC curves yielded the mobilities wildly varying within 6 orders of magnitude. Therefore, it is not always clear whether the measured current-voltage (IV) device characteristics are controlled by charge injection or by transport in the bulk. In this work, we suggest a model of dopant-assisted carrier injection across a metal/organics interface and use this model for the analysis of IV curves measured on tetracene and pentacene crystals. The model suggests the occurrence of an energetically disordered layer on the surface of an organic crystal. This might be either an amorphous phase of the starting material or a crystalline layer with high density of defects and/or impurities. Since, at variance with bulk properties, the surface of an organic crystal is poorly controlled and can be strongly modified upon the contact deposition, the model of injection-controlled IV characteristics can explain the striking difference between the TOF mobility and the apparent SCLC mobility measured in tetracene crystals. In order to give more credence to the role of surface states in the dark charge transport, we compare IV characteristics measured on sandwich and coplanar structures. In the latter structure, surface states give a major contribution to the conductivity.

4:30 PM DD6.9 Photo Induced Memory Effect based on Poly(3-hexilthiophene) and Al interface. Keiichi Kaneto, Mitsu Ujimoto and Wataru Takashima.

A photo induced memory cell is constructed on a glass substrate by deposition of 1nm Al on 20 microm channel length of Au electrode array, followed by spin coat with poly(3-hexilthiophene) with the thickness of 25-200 nm. It has been found that the photo induced current of the cell with the depletion layer formed by the interface of poly(3-hexilthiophene)/Al lasts after the shut off the photo illumination. The decay time of the lasting current is consisting of two decay constants of ca. 50 s and a few thousand s. The result indicates a photo induced memory effect. The mechanism of memory effect are not clear at the moment, however, are related to the high impedance of depletion layer, as well as secondary photocurrents. The details will be discussed at the symposium.

SESSION DD7: Organic and Hybrid Light Emitting Devices

Thursday Morning, December 2, 2004
Room 310 (Hynes)

8:00 AM DD7.1 Saturated Color Red, Green and Blue Electroluminescence from Quantum Dot Light Emitting Devices. Seth Coe-Sullivan1, Jonathan S. Steckel2, LeeAnn Kim1, Moungi G. Bawendi2, and Vladimir Bulovic2.

1Department of Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts; 2Department of Chemistry, MIT, Cambridge, Massachusetts.

Quantum dot light emitting device fabrication and optimization is in essence a problem of organic/inorganic nanocomposite material design. Efficient devices require efficient and robust materials, and nanometer precision control over the positioning of the various components that comprise the device. Recent advances in thin film organic/inorganic structure fabrication enabled the creation of QD-LEDs with external quantum efficiencies in excess of 1%. However, dependence on size inherent in this solution based design prevents the production of LEDS with truly monochromatic emission spectra at drive currents necessary for video brightness. The use of wide optical band gap host materials, together with a novel quantum dot deposition technique, now yields QD-LEDs with saturated color emission in the red, green and blue regions of the spectrum. This work will detail the device structure and properties, as well as compare and contrast these new hybrid material fabrication techniques.

8:15 AM DD7.2 Electroluminescence at 1 Micron from a Conjugated Polymer, Magnus Berggren1, Xiaoxiang Chen1, Erik Porzon2, Mats Andersson2 and Robinson Nathaniel1.

1ITN, Linkoping University, Norrkoping, Sweden; 2Chalmers University of Technology, Gothenburg, Sweden.

Low band gap conjugated polymers can be achieved by introducing monomer segments with strong donor-acceptor (D-A) character. Here, we report on a conjugated polymer including D-A segments having a band gap of 1.3 eV. In this material optical absorption peaks at around 800 nm while the electroluminescence spectra peaks at around 1000 nm. In the electrical characteristics of light emitting diodes based on this D-A polymer we find hardly any contact limited current behaviour. Also, electroluminescence is detected already at a forward bias of 1 V. Low band gap polymers are crucial in achieving efficient solar cells, sensors and photo-detectors. Infra-red light emitters are important for the communication technology areas.

8:30 AM DD7.3 Large Area Microcontact Printing Presses for Plastic Electronics. Hee Hyun Lee1, John Rogers1 and Gricelda Blanchet2.

1Materials Science and Engineering, University of Illinois, Urbana, Illinois; 2CRED, Dupont, Wilmington, Delaware.

It was shown that active matrix circuit could be achieved on flexible substrates using micro-contact printing1. However, in order to commercialize high performance flexible display, it is crucial to print large areas cost effectively with good resolution and registration. We prepared 12in x 12in large area PDMS (Polydimethylsiloxane) stamp from positive photore sist. The stamp is then used to print high resolution Au lines onto flexible substrates using standard thermal chemistry at micron resolutions. The exposed positive photoresist held 2micron lines when coated on glass substrate and exposed using glass photomask. In contrast, 5micron lines are obtained on the photore sist when the photore sist is coated on plastic substrate and exposed using a plastic photomask. These stamps, developed for the production of low cost plastic electronic devices show a 10x resolution improvement relative to standard commercial flexographic plates. [1] J.A. Rogers et al, Nature 412, 65 (2001); [2] G. Blanchet et al, Appl. Phys. Lett. 82, 463 (2003).

8:45 AM DD7.4 Achievement of Extremely High Current Density of 120000A/cm2 into Organic Thin Films with High Thermally Conductive Substrates. Hidetoshi Yamamoto1, Hiroki Kajimura1, Wataru Yokoyama1, Hiroyuki Suwa2 and Chihaya Adachi1,2.

1Department of Photonics Materials Science, Chitose Institute of Science and Technology, 738-65 Bibi, Chitose, Hokkaido, Japan; 2CREST program, Japan Science and Technology Agency, 1-32-12 Higashi, Shibuya, Tokyo, Japan.

Recently, we demonstrated amplified spontaneous emission (ASE) from an organic semiconductor laser structure equipped with transparent carrier injection electrodes under optical pumping. The ASE threshold was estimated to be 10 A/cm2, corresponding to a current density of 3000A/cm2 for realization of electrical ASE. However, with the conventional organic light emitting diode (OLED) structure of a-NPD/AIqo, it breaks down at a maximum current density of only Jmax 10A/cm2. In this study, we focused our concern on how much we can inject charge carriers into organic thin films, since it is believed that organic materials, in general, lack durability against high current density due to their organic nature. Here, we employed a single organic layer sandwiched between anode and cathode electrodes for purposes of simplification and examined their durability against high current density. The organic layers were deposited by high vacuum (< 1x10-8 Pa) thermal evaporation onto clean substrates pre-coated with a 110-nm-thick indium-tin-oxide (ITO) layer. After an organic layer was deposited, shadow masks with various diameter-opening sizes were used to define a cathode area consisting of a 100-nm-thick MgAg thin film layer capped with a 10-nm-thick Ag. We examined varied the thickness of the substrate (glass, sapphire and silicon), the organic layers (d = 25, 50, 75 and 100 nm) and the cathode dot-size (S) with various radii, i.e., r = 25, 50, 100, 200 and 500 nm. In this paper, we demonstrate carrier injection and transport of steady-state high current density into organic thin films. The maximum current density reaches Jmax 12222A/cm2, the highest ever reported. Here, we employed a 25-nm-thick Copper phthalocyanine (CuPc) thin film based precissed electrode dot size (S) of S = 2.0x10-5 cm2 (radius: r = 25 μm) with...
a silicon substrate. We observed that the maximum current density depends on the substrates, and the device size and thickness.

Decreasing the device layer thickness significantly changes the current density-voltage (J-V) characteristics, demonstrating that the rate-limiting step of the J-V characteristics changes from the carrier transport process to the carrier injection process. Moreover, we examined the electrode size dependence of the J-V characteristics with the silicon substrate. Although the J-V characteristics with different electrode sizes showed similar behavior in the low current density region (J < 1000mA/cm²), the significant difference of the J-V characteristics was observed in high current density region (J > 1000mA/cm²). These results suggest that the J-V characteristics are controlled by the trap-free space charge limited current (SCLC) [J = \( \frac{9}{8} \mu \text{C}_p \text{V}^2 \text{d}^{-2} \)] in the high current density region, while the J-V characteristics are controlled by the trap charge limited current (TCLC) [J = \( \frac{V}{\mu \text{C}_p \text{d}} \)] in the low current density region.

9:00 AM DD7.5

Blue Luminescence and Electroluminescence from (CdS)ZnS Core-Shell Nanocrystals. Jonathan S. Stockel1, Seth Coo-Sullivan2, John P. Zimmer3, Nathan E. Stott1, Vladimir Bulovic2 and Moungi G. Bawendi1,2

Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts; 1Department of Chemistry, MIT, Cambridge, Massachusetts.

Inorganic semiconductor quantum dots (QDs) enable the fabrication of wavelength tunable, stable and saturated color hybrid organic/inorganic QD-light emitting devices (QD-LEDs). To date, efficient red and green emitting QD-LEDs have been realized with (CdS)ZnS core-shell nanocrystals, but blue QD-LEDs have remained elusive due to lack of blue emitting core-shell material. We report a narrow band width of 50 nm and a maximized perceived power, the ideal wavelength of blue emission for display applications is 470 nm. We also report a procedure for the growth of (CdS)ZnS core-shell QDs suitable for display applications that exhibit blue and narrow luminescence from 460 nm to 480 nm (FWHM < 28 nm), with quantum yields exceeding 95%. The partial quantum efficiency for the equivalent bulk material is 93%. The partial quantum efficiency for the equivalent bulk material is 93%. The partial quantum efficiency for the equivalent bulk material is 93%. The partial quantum efficiency for the equivalent bulk material is 93%. The partial quantum efficiency for the equivalent bulk material is 93%.

9:15 AM DD7.6

New Wide Band Gap Host Materials for Blue Dye-Doped OLEDs. Linda Susan Sapochak, Asanga B. Padmaperuma, Kim F. Ferris and Paul E. Burrows

Materials Science Division, Pacific Northwest National Laboratory, Richland, Washington.

The most efficient organic light-emitting devices (OLEDs) are based on doping organic phosphors into a host matrix where emission results from energy transfer from the host material to the phosphor. We describe the synthesis of a poly(dibenzosilole) blue light emitting polymer which shows considerable resistance to thermal and oxidative degradation. The most efficient blue OLEDs based on this technology has been particularly challenging because the host material must exhibit triplet level (thermal and chemical stability) and preliminary device results will be presented for a series of aryl bridged diphosphine oxide materials. This inorganic coating provides a good passivation of the surface and a significant improvement of the luminescence characteristics. The resulting core-shell nanoparticles are highly luminescent, well-dispersed, thus being suitable for applications in transparent luminescent devices. Surface derivatization has been achieved through the controlled growth of an organic protective layer on silica shell using a functionalized silane precursor. Concentrated solution are obtained, which can be spin-coated on various substrates, leading to perfectly transparent and highly luminescent thin films.

10:30 AM DD7.9

Organic Solvent Molecules Effects on Singlet-Triplet Energy Transfer in pi-Conjugated Materials. Yue Wu and Bing Hu

Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee.

The coexistence of singlet (S) and triplet (T) states has led to two distinctive features: (i) limited 1.3 ratio of S/T excitons and (ii) S-T intersystem crossing in the pi-conjugated polymers under electrical excitation (charge injection). As a consequence, phosphorescence from the allowed T-T transitions becomes an important approach to improve organic electroluminescence efficiency based on the mixture of phosphorescent dye (guest) and fluorescent polymer (host). We note that the Förster energy transfer from S to T requires spin inversion that must be satisfied by strong spin-orbit coupling. In this presentation, we report an effective control of energy transfer in the mixtures of phosphorescent Ir-dye and fluorescent material (fluorescent polymer) by using different organic solvents for spin flip. Time-resolved electroluminescence, photoluminescence, and Raman measurements indicate that an interaction occurs between the residual solvent molecules and the fluorescent polymer chains in the solid thin films. This introduced molecular interaction affects the spin-orbit coupling and thus dramatically influences the S-T energy transfer, presenting a new pathway to improve the organic electroluminescence efficiency.
Phenylene vinylene chromophores are attractive materials for use in optoelectronic applications. In particular, oligomers of phenylene vinylene allow for better control over structural ordering and electronic properties than the corresponding polymers. We have synthesized a series of tri-block molecules consisting of oligo(phenylene vinylene) (OPV) symmetrically end-substituted with a hydrophilic group and flanked by a flexible alkyl chain. These amphiphiles have been characterized by differential scanning calorimetry (DSC), polarized optical microscopy (POM), small- and wide-angle x-ray scattering (SAXS, WAXS), as well as time-resolved fluorescence spectroscopy. We found that these amphiphiles form thermotropic and lyotropic liquid crystals, and their optical properties change as a function of the hydrophilic length due to structural and solubility changes. These amphiphiles self-organize into strongly fluorescent self-supporting gels at appropriate concentrations in water or polar organic solvents. Compared to the unaligned isotropic phase, these highly concentrated systems (30-40 wt%) display enhanced, blue-shifted photoluminescence. This behavior is induced by the two-dimensional layered structure of the liquid crystal, which can inhibit OPV aggregation and reduce exciton migration, a desirable property for optoelectronic devices.

**Influence of Halides on the Luminescence of Oxide/Anthracene/Polymer Nanocomposites.** Dorothee Vinga Szabo, Heike Reutter, Sabine Schlabach and Dieter Vollath, 1 Institute for Materials Research, Karlsruhe, Germany; 2 NanoConsulting, Stutensee, Germany.

Luminescence in oxide/polymer nanocomposites is a well-described phenomenon. The emission wavelength of such materials is overcome by introducing an additional layer of a lumophore between oxide nanoparticles and polymer coating. Due to interactions between ceramic kernel, lumophore interlayer and polymer coating, these materials exhibit interesting luminescence properties, differing from those of the pure lumophore. Furthermore, compared to pure lumophores, these nanocomposites can be dispersed in many different liquids which is an important advantage. The nanocomposites are synthesized by the Karlsruhe Microwave Plasma Process. For this study wide band insulators, such as crystalline ZrO2 and HfO2 are used as ceramic kernels. Chlorides, bromides, iodides, or metalorganic, halide free compounds, were used as precursors for the oxide coating. Due to the halide containing precursors, Zr and Hf can be used as lumophore. The polymer used for coating is PMMA. The influence of halides, stemming either from the precursor or being part of the lumophore, on luminescence of powders and suspensions was studied.


Over the last decade, organic semiconductor thin film transistors have been the focus of many research groups because of potential application of these devices in low-cost integrated circuits. Recently, an organic light-emitting field-effect transistor (OLFET) was discovered. In an OLFET structure, optimum injection of both holes and electrons into the light emitting layer is required for maximum quantum efficiency, whereas the gate contact serves as a controlling electrode. In this work, we investigate the OLFET structure with interdigitated bottom hole injecting Au and electron injecting Ca contacts with a submicrometer channel length. Polycrystalline tetracene has been used as an organic semiconductor. Based on measured current-voltage and light emission characteristics, a model of the OLFET is suggested.
by photomultiplier tube in radiation detection. Nanoparticles containing a highly efficient neutron absorber, Li-6, were synthesized for the purpose of neutron detection. The modification of nanoparticles allows their dispersion at high concentrations in various host matrices, including organic polystyrene-based polymers and inorganic sol-gels. Transparent to translucent solid scintillators made of nanoparticles embedded in host matrices were tested for alpha, neutron, and gamma detection.

1:45 PM DD8.2 Self-assembled oligonucleotide semiconductor conjugated to GaN nanostructures for biophotonic applications. Arup Neogi, Abhijit Sarkar, Purnima Basu Neogi, Harshsheet Liddar, Jianyou Li, Padmalekha Vennum, Terry Golding, Hadis Morkoc and Brian Gorman; 1Physics, University of North Texas, Denton, Texas; 2Michigan Molecular Institute, Midland, Michigan; 3Biology, University of North Texas, Denton, Texas; 4Material Science and Engineering, University of North Texas, Denton, Texas; 5Virginia Commonwealth University, Richmond, Virginia.

We investigate the optical properties of a new class of wide-bandgap semiconductor based biomaterial system. This will be useful for developing biocompatible nanophotonic sensors sensitive to ultraviolet wavelength, as most of the biological agents absorb or emit in this regime. Among biomolecules, DNA has a fundamental role in biological processes. The combination of molecular biology (for engineering DNA with the desired function) and/or self-assembling properties and nanophotonic technology (for device fabrication) thus becomes the tool to realize a new class of nanophotonic elements. Among the conjugated bases forming DNA, the guanine represents a versatile molecule that, depending on the environment, can undergo different self-assembly pathways. Guanine has the lowest oxidation potential among DNA bases, which favors carrier transport. We have synthesized a guanosine derivative, which has a particular sequence of functional groups that, depending on the environment, can lead to different self-assembly processes. Under appropriate conditions, the modified guanosine molecules self-assemble to form a ribbon like structure. Guanine also has a strong dipole moment of the order of 7 D which provides a polarity to each self-assembled guanosine conjugate (SAGC) supramolecular structures. SAGCs were obtained from a solution of deoxyguanosine derivative in chloroform. Ideal self-assembly of SAGCs have been observed in 50-100 nm confined spaces. The self-assembly process resulting in the formation of a biomolecular ribbon. In this process, only at specific concentration of the solution and great care has to be taken in order to control the solid-state assembly of the molecules. The self-assembled deoxyguanosine films behave like wide gap semiconductors, with energy gap in the range of 2-3.5 eV and electron effective mass $m_e > 2 m_0$ (similar to GaN). SAGC were then successfully self-assembled on GaN/AIN QD matrix. Electron transport properties at the interface were investigated using photocurrent spectroscopy. The radiative energy transfer between the GaN quantum dots and SAGC molecule was investigated using photoluminescence spectroscopy. It has been demonstrated that the luminescence from GaN QDs can be resonantly transferred to the SAGC molecules resulting in a significant enhancement in emission from the guanine molecules. The most challenging aspect of conjugating a biological molecule or an analyte to an SAGC structure is to retain its self-assembly characteristics in confined GaN nanostructures. Polyphosphazene is a library of nano-sized hexagonal pits in GaN substrate for the localization of SAGC semiconductor layer. It resembles GaN:SAGC photonic bandgap structures with novel optical properties. This will facilitate the conjugation of a biological molecule to the GaN system with the optical molecule acting as a cross-linker. TFTD simulations is being used to investigate the wave-propagation and subsequently engineer the optical properties of the SAGC conjugated GaN nanostructure.

2:00 PM DD8.3 Supernatant Controlled Synthesis of Monodispersed Zinc Sulfide Spheres and Multimers. Yanning Song and Chekesha M. Lodellite; 1Materials Science and Engineering, Cornell University, Ithaca, New York.

Symmetry reduction is an important approach to the design of novel photonic materials with structures with stable three dimensional band gaps. Only a few methods are available for the synthesis of non-spherical colloids of monodispersed size and well-defined shape. It was previously found that non-spherical zinc sulfide multimers in the size range of 600 nm can be synthesized by photooxidation of precursors induced clustering of preformed monodispersed nanoparticles in acetic aqueous solutions of metal salts and thioacetamide by varying reactant concentration, temperature and time. Here we present a method that enhances control over size and clustering of the multimers. The results show that the primary reaction yield was enhanced in the presence of primary reaction supernatant added. Uniform spheres and multimers ranging in size from 70 nm to 0.2 microns were produced in large quantities. The effects of nitrate and acetate zinc salts on the particle sizes obtained were studied. The particle morphology was investigated by scanning and transmission electron microscopy. Smaller particles exhibited increased surface roughness in the size range from 100 nm to 600 nm can be used as hard refractive index building blocks for photonic crystals with band gaps covering the entire visible spectrum as well as regions of the near-IR and UV. Assembly by convective means using a vertical geometry as well as temperature controlled sedimentation using horizontal geometry was explored.

2:15 PM DD8.4 Selenium/Zeolite Nanocomposites. Andreas Goldbach, Lennox E. Iton and Marie-Louise Saboungi; 1Centre de Recherche sur la Matiere Divisee, Orleans, France; 2Materials Science Division, Argonne National Laboratory, Argonne, Illinois.

Confinement of materials in molecular sieves is a straightforward method to imprint a nanostructured architecture on them. We have carried out extensive studies on nanocomposites of selenium in zeolites, because selenium is an important technical semiconductor, and the interaction between the ionic matrices and the semiconductor provides intriguing possibilities for tuning the band gap of the semiconductor. In particular we studied the effects of zeolitic counter-cations on the structure, electronic properties, and thermodynamic and reactive stabilities of Se encapsulated in zeolites Y and A. The Se structure can be precisely controlled by appropriate selection of the zeolite counter-cation [1], allowing a continuous transition from essentially chain- to solely ring-containing composites. Competition experiments disclosed that the Se inside the nanos is stabilized through bonding to the zeolite cations and also through symmetry reduction is an important approach to the design of novel photonic materials with structures with stable three dimensional band gaps. Among biomolecules, DNA has a fundamental role in biological processes. The combination of molecular biology (for engineering DNA with the desired function) and/or self-assembling properties and nanophotonic technology (for device fabrication) thus becomes the tool to realize a new class of nanophotonic elements. Among the conjugated bases forming DNA, the guanine represents a versatile molecule that, depending on the environment, can undergo different self-assembly pathways. Guanine has the lowest oxidation potential among DNA bases, which favors carrier transport. We have synthesized a guanosine derivative, which has a particular sequence of functional groups that, depending on the environment, can lead to different self-assembly processes. Under appropriate conditions, the modified guanosine molecules self-assemble to form a ribbon like structure. Guanine also has a strong dipole moment of the order of 7 D which provides a polarity to each self-assembled guanosine conjugate (SAGC) supramolecular structures. SAGCs were obtained from a solution of deoxyguanosine derivative in chloroform. Ideal self-assembly of SAGCs have been observed in 50-100 nm confined spaces. The self-assembly process resulting in the formation of a biomolecular ribbon. In this process, only at specific concentration of the solution and great care has to be taken in order to control the solid-state assembly of the molecules. The self-assembled deoxyguanosine films behave like wide gap semiconductors, with energy gap in the range of 2-3.5 eV and electron effective mass $m_e > 2 m_0$ (similar to GaN). SAGC were then successfully self-assembled on GaN/AIN QD matrix. Electron transport properties at the interface were investigated using photocurrent spectroscopy. The radiative energy transfer between the GaN quantum dots and SAGC molecule was investigated using photoluminescence spectroscopy. It has been demonstrated that the luminescence from GaN QDs can be resonantly transferred to the SAGC molecules resulting in a significant enhancement in emission from the guanine molecules. The most challenging aspect of conjugating a biological molecule or an analyte to an SAGC structure is to retain its self-assembly characteristics in confined GaN nanostructures. Polyphosphazene is a library of nano-sized hexagonal pits in GaN substrate for the localization of SAGC semiconductor layer. It resembles GaN:SAGC photonic bandgap structures with novel optical properties. This will facilitate the conjugation of a biological molecule to the GaN system with the optical molecule acting as a cross-linker. TFTD simulations is being used to investigate the wave-propagation and subsequently engineer the optical properties of the SAGC conjugated GaN nanostructure.

2:30 PM DD8.5 Study on the Novel Synthetic Method for Nano-Hybrid Layered Zr-P Derivatives. Tsung-Yen Tai, Fang-Jung Hwu and Ying-Ru Wu; Department of Chemistry & Center for Nanotechnology at CYCU, Chung Yuan Christian University, Chung-Li, Taiwan.

The preparation and characterization of zirconium phosphate/phosphonate derivatives (ZrP) with the functional group of C=C are reported and discussed. The major composition of the inorganic layered materials is zirconium phosphate, which prevents the distortion under high shear strength and provides the higher toughness and stiffness of these types of inorganic-organic hybrid materials. Also, ZrP with C=C functional group, which reaction sites for the monomer or oligomer of polymer, is exposed to the surface of the ZrP layered structure and provides the better compatibility. These new inorganic-organic nano-hybrid materials will create the new applications in organic/organic hybrid nanocomposites in the near future.


Organic nanoparticles consisting of aromatic and dye molecules have attracted increasing attention, as they are expected to be useful as pigments, cosmetics, dyes, and new materials for optical and electronic devices. Despite the difficulty of preparing organic nanoparticles with the size less than 100 nm has been well known. Several approaches have been reported based on vapor deposition and reprecipitation. Recently, we have applied a laser ablation technique to organic nanoparticle preparation.
Microcrystalline powder suspended in a poor solvent is exposed to intense laser pulses, which induces fragmentation of the initial crystals. Combining the facile aqueous processing of the nano-particle system, a transparent colloidal solution was obtained. Precise control of the nano-particle size is achieved through the use of temperature-sensitive surfactants.
effects of the embedded nanoparticles in the matrix, or surface effects between the nanoparticles and the matrix. Pt/TiO$_2$ nanocomposites have been prepared by sputtering and pulsed laser deposition (PLD). In these techniques, it is very difficult to control the size and dispersion of Pt nanoparticles in the TiO$_2$ matrix. In this study, Pt/TiO$_2$ nanocomposite thin films were prepared by PLD/Sputtering combined system using low energy sputtering of TiO$_2$ and pulsed laser deposition of platinum were utilized. Two variations were utilized for the depositions. Sputtering of TiO$_2$ and PLD of Pt were performed sequentially to build the nanocomposite layer by layer or simultaneously to form a homogeneous dispersion. Sequential deposition produced narrow distributions of Pt nanoparticles with sizes between 10-50 nm depending on laser fluence. These films showed negligible visible light absorption and photocurrent as well as pure TiO$_2$ films. Simultaneously deposited Pt/TiO$_2$ films produced much smaller platinum nanoparticles. The films exhibited a pronounced red shift in the optical band gap with increasing Pt content indicating the formation of the surface or impurity states in the TiO$_2$. Upon annealing at 600 °C the films crystallized and a dramatic increase in photocurrent occurred. It is found that the visible photocurrent peaks at an intermediate Pt content. Optical and photoelectrochemical properties were strongly affected by the size and dispersion of Pt nanoparticles in the TiO$_2$ matrix, which can be controlled by process parameters of PLD/sputtering combined system.

4:30 PM DD9.11
Fabrication of Nanocrystals and/or Nanofibers of π-Conjugated Organic Compounds Using the Microwave Irradiation Method. Hitesh Kasai$^{1,2}$, Koichi Baba$^1$, Shuji Okada$^1$, Hitotsubashi Oikawa$^1$, and Hachiro Nakashima$^1$.$^2$. $^1$Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan; $^2$CREST, Japan Science and Technology Agency, Kawaguchi, Japan; $^3$Nanomaterials Laboratory, National Institute for Materials Science, Tsukuba, Japan.

Recently, investigation of nano-technology and science of nanomaterials have been explosively extended all over the world. We have focused on organic nanocrystals in them. Regarding the fabrication of organic nanocrystals, it has been already reported that the reprecipitation method is one of the most effective techniques. However, even using it, it was difficult to prepare the size-controlled nanocrystals of some organic compounds. In this study, we will introduce the fabrication technique using microwave irradiation after the conventional reprecipitation procedure, i.e., the microwave method. As the advantage of this method, nanocrystallization quickly proceeds, and then the nanocrystals with well-controlled size can be obtained. For example, 1,1,4,4-Tetraphenyl-1,3-butadiene nanocrystals with monodispersed size distribution was fabricated by it. In the case of polydiacetylenes, the nanocrystals and/or nanofibers could be obtained by the advanced microwave method, which means nanocrystallization by irradiating microwave under high pressure using the vessel made by quartz glass and Teflon. The size control and characteristics of the nanocrystals and/or nanofibers could also be presented.

SESSION DD9: Poster Session: Organometallic Optical Materials
Thursday Evening, December 2, 2004
8:00 PM
Exhibition Hall D (Hynes)

DD9.1
Enhanced Luminescence and Size Effects of Eu$^{3+}$ Doped Y2O3 and Lu2O3 Nanoparticles and Processed Ceramics. Akira Pradhan, Kai Zhang and G. B. Loutet; Center for Materials research, Norfolk State University, Norfolk, Virginia.

Europium doped Yttrium oxide (Y2O3:Eu$^{3+}$) and Lutetium oxide (Lu2O3:Eu$^{3+}$) nanophosphors were synthesized by wet chemical routes using both precipitation and precipitation techniques. The pellets prepared from the calcined nanocrystalline powders were vacuum-sintered up to 1800 °C leading to very translucent ceramic. We have explicitly illustrated the dynamics of Y2O3:Eu$^{3+}$ nanophosphors with particle size being influenced by the complex structural, revealed by X-rays and Raman scattering. The influence of Eu$^{3+}$ activation on Raman spectra has been illustrated. We have demonstrated the significant enhancement of emission characteristics of the ceramics synthesized from the nanophosphors using the combustion technique by controlling the vacuum sintering conditions. We have illustrated the crystallite size dependence and the influence of Eu$^{3+}$ activation of Lu2O3:Eu$^{3+}$ nanophosphors on Raman scattering. We have also demonstrated the particle size dependence of emission characteristics of nanophosphors and ceramics. The details of the results will be discussed that although the processed ceramics display superior emission characteristics, the nanocrystalline phosphor powders calcined at 1100 °C also display reasonably good emission characteristics, illustrating the possibility of their applications in display technology.

DD9.2
Layered Double Hydroxides as a Matrix for Luminescent Rare Earth Complexes. Andrei Anatolyevich Eliseev$^{1}$, Natalia Gennadiyeva Zhuravleva$^{1}$, Alexey Vluctorovich Lukshin$^{1}$, Ulrich Kynast$^{2}$ and Yuri Dimitrievich Treytakov$^{1}$.$^1$Department of Materials Science, Moscow State University, Moscow, Russian Federation; $^2$Department of Chemical Engineering, FH Muenster, University of Applied Materials Science, Steinfurt, Germany.

Intercalation of rare earth complexes into the interlayer space of layered double hydroxides (LDH) holds the promise to provide red phosphorescent dopants showed the pronounced red shift in the optical band gap with increasing Pt content indicating the formation of the surface or impurity states in the TiO$_2$. Upon annealing at 600 °C the films crystallized and a dramatic increase in photocurrent occurred. It is found that the visible photocurrent peaks at an intermediate Pt content. Optical and photoelectrochemical properties were strongly affected by the size and dispersion of Pt nanoparticles in the TiO$_2$ matrix, which can be controlled by process parameters of PLD/sputtering combined system.

DD9.4
Synthesis and Photophysics of Luminescent Platinum(II) Complexes and Materials. Inna E. Ponomarchuk and Felix N. Castellano; Chemistry & Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio.

This presentation focuses on the design, synthesis, and photophysical characterization of photochemically stable metal-organic chromophores intended to possess systematically variable excited state absorption and emission properties. The unifying theme is to understand how to control the photophysics of metal-organic chromophores with strongly-interacting excited state manifolds which may ultimately result in the observation of new and interesting photophysics. These molecules are comprised of a Pt(II) metal center and a single substituted diimine (LL) or triimine (LLL) ligand, and the remaining coordination site(s) are composed of various arylacetylides, oligo(alkylacetylides), or oligo(arylacetylides). Various polynuclear Pt(II) structures possessing low-lying metal-to-ligand charge transfer (MLCT) excited states are proposed as new luminescent metal-organic materials. Our initial results suggest that proper selection of ligands and/or solvent medium can produce either pure MLCT or triplet $\pi,\pi^*$ excited states in addition to equilibrated or configuration mixed excited states composed of varying degrees of $\pi$MLCT and triplet $\pi,\pi^*$ character. We will demonstrate that this suite of available photophysical behavior can yield a wide range of excited state absorptions, emissions, and associated dynamic. This presentation will overview our recent progress in this area and will discuss the synthetic preparation and structural characterization of the new Pt(II)-containing metal-organic systems as well as their complete static and dynamic photophysical characterization on time scales ranging from femtoseconds to milliseconds.
maximum PL peak around 640nm and excellent luminescence efficiency with 0.65-0.83 compared to Ir(piq)3 as a unit. The device configuration of ITO/HTL/LCB-In-complex(6%)/BCP/Alq3/LIF/Al. The electroluminescence spectrum has a maximum at a wavelength of λmax=588nm. The luminescence efficiencies of the devices were above 1lm/W and maximum brightness were all above 10000 Cd/m2. The Commission Internationale de L’Eclairage coordinates of (x=0.70, y=0.29) are close to meeting video display standards. We demonstrated high-efficiency, high-brightness and saturated red In-complex phosphorescent materials for OLEDs.

**DD10.5 Novel and Efficient electroluminescent organo-iridium phosphorescent OLED materials. Hei-Lung Huang, Kou-Hui Shen, Shu-Tang Yeh, Miao-Cai Jhu, Mei-Rurng Tseng and Jia-Ming Liu; Materials Research Laboratories, Industrial Technology Research Institute, Chutung, Hsinchu, Taiwan.**

Abstract: We investigated and synthesized the different orientation and substituted group of the thieno-pyridine framework organo-iridium complexes. These materials exhibited visible light from yellow to orange color. Fabrication of these emissive phosphorescent dopants with the device configuration of ITO/HTL/CBP-In-complex(4%)/BCP/Alq3/LIF/Al showed the EL emitting from peak 536nm to 588nm. The electroluminescent efficiencies of the devices were from 8 lm/W to 17 lm/W and maximum brightness were all above 6000 cd/m2. We demonstrated high-efficiency, high-brightness and saturated yellow to orange Ir-complex phosphorescent materials for OLEDs.

**DD10.6 High efficiency, high-brightness and saturated yellow to orange phosphorescent complexes: PO-01, PO-02 and PO-03. UV shows the device configuration. There are anode electrode (ITO), hole emitter (CBP), hole blocking layer (BCP), electron transport layer, dopant emitter (PO-01, PO-02, or PO-03), host material, and cathode (Al). Among these three devices, PO-03 has highest brightness compared to PO-01 and PO-02. However, PO-01 exhibits highest electroluminescent efficiency compared to PO-02 and PO-03. The trend of electroluminescent efficiencies is downward with the increase of voltage and current. This is due to the triplet-triplet annihilation at high currents. The electroluminescentefficiencies of these emitters are good enough to apply on the multicolor display.**

**SESSION DD10:** Poster Session: Linear and Nonlinear Optical Properties of Organic and Nanocomposite Materials. Dong-Joon Kang, Jin-Ki Kim and Byeong-Soo Bae; Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, South Korea.


Holography offers a versatile, rapid and volume scalable approach for making large area, multi-dimensional, organic PBGs; however, the small refractive index contrast of organics prevents formation of a complete optical bandgap. The introduction of inorganic nanoparticles to the structure provides a possible solution. Holographic photopolymerization of monomer-nanoparticle suspensions enables one-step fabrication of organic-inorganic photonic band gap (PBG) structures with increased refractive index contrast. The PBGs are formed by segregation of semiconductor nanocrystals during formation of the polymer network. Nanoparticles found amenable to this study include oxides (ZnO, SiO2 and TiO2), nanoparticle ionic liquids and semiconductor quantum dots. A model describing the migration of the nanoparticles into three-dimensional polymer networks, encompassing elements of Kogelnik’s coupled wave theory for volume holograms, mass transport and polymerization kinetics, was utilized to select writing conditions and polymerization rates to obtain optimal morphologies.

**DD10.8 Two-Photon Frequency Upconversion Lasing in Dye-Doped Dual Range Photonic Bandgap Structure. Jongseung Yoon, Wonmok Lee, Edwin L. Thomas, Przemyslaw P. Markowicz and Pascale N. Prasad; 1Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2Institute for Soldier Nanotechnologies, Massachusetts Institute of Technology, Cambridge, Massachusetts; 3Department of Chemistry and Physics, Institute for Laser Science, National Institute of Advanced Industrial Science and Technology, Biophotonics, University of Buffalo, The State University of New York, Buffalo, New York.**

We have developed a novel dye-doped 1D photonic crystal system consisting of alternating layers of titania nanoparticles and dye-doped PMMA for two-photon pumped frequency upconversion lasing. The multilayer stacks were designed to have a dual range photonic bandgap so that not only light of emission from gain material but also light of excitation can be affected by the periodic structure. Spin coating of alternating dielectric stacks enables us good control over the optimization of structure parameters and more flexible incorporation of polar laser dyes. In this investigation, effective gain enhancement and low threshold two photon pumped lasing of the photonic bandgap structure will be discussed.

**DD10.9 Fabrication of Micro-Optical Devices by Holographic Interference of High Photosensitive Inorganic-Organic Hybrid Materials. Dong-Joon Kang, Jin-Ki Kim and Byeong-Soo Bae; Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, South Korea.**

The photosensitive inorganic-organic hybrid materials (HYBRIMER) containing a large quantity of photoactive molecules exhibit the large changes in both refractive index (over 10-2) and volume (over 30%) on UV lamp and laser exposure. Since the photosensitivity is made by photo-migration and photo-locking of photoactive molecules, it can be improved by the simple addition of photoactive molecules, such as dye or metal complex, giving a photointinitator and a photoactive monomer in the HYBRIMER. Thus, the high photosensitive HYBRIMER was optimized with containing a photoinitiator and a photoactive monomer as much as over 90 mole%. Holographic interference of 325 nm He-Cd laser was used for the fabrication of some micro-optical devices on the photosensitive HYBRIMER surface. In this study, different dimensions of gratings patterns were imprinted by changing the number of interference beams in the holography system. Firstly, Fresnel lenses were fabricated by one-beam pinhole diffraction imaging. The shape of the pinhole diffraction fringes exhibits almost same shape as the Fresnel lens. As these changes on the HYBRIMER film can be applied to make a Fresnel lens without using a patterned mask. This technique can overcome the problems associated with the contact method and easily fabricate the Fresnel lenses with better focusing performance. The lens shows a high diffraction efficiency up to about 85%. Secondly, 1-D diffraction gratings were fabricated by two-beam holographic interference method. This technique can simply fabricate the diffraction gratings and easily control the grating periods from submicrometer to tens micrometer. The fabricated diffraction gratings showed the good diffraction performance and their efficiency rely heavily on UV dose. Also, the 2-D array typed gratings can be fabricated using the three-beam holographic interference or three grating diffusion mask. This, it will be demonstrated that the array pattern may be applied to superhydrophobic antireflection coating on glass.

**DD10.10 Colloidal Photonic Crystals with Spatially Varying Refractive-Index Profiles. Jeong-Ho Park, Won San Choi, Hye Young Koo, Seung Hwan Oh and Dong-Yu Kim; Dept. of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, South Korea.**

Photonic crystals (PCs) are materials exhibiting a periodic modulation in the refractive index that has the effect of confining light within specific energy ranges, called as photonic band gaps (PBGs). Fabrication of artificial opals as a PC structure has been extensively investigated due to a cheap and easy alternative to more sophisticated PCs fabricated by lithography and holographic interference. Previously, there have been many demonstrations that various materials can be infiltrated into interconnected nanoscale voids of opals. Based on this fabrication technique, the concept of band gap engineering for photonic crystals is proposed, in which the photonic bandgap properties can be tuned as
desired by controlling parameters such as the refractive index, periodicity, space-filling factor or a defect layer. For example, by infiltration of high-refractive-index materials, PCs with full photonic band gaps in near-infrared (NIR) and visible region can be produced. In this presentation, we discuss a novel photonic crystal in which the background index of colloidal opal crystal is gradually changed from [111] crystallographic axis of the fcc colloidal crystal. This was achieved by infiltrating polymers using the interfacial-gel polymerization with relatively high refractive-index organic dopants or nano sized metal particles. This method results in a novel infiltration of colloidal crystals that has under other spatially varying refractive index distribution. Therefore, this structure has gradually varying stop gap frequencies on the different layer of the crystal. This kind of photonic crystal structures could have various band gap properties based on refractive index. Our method could be one of promising approaches for band gap engineering for a wide or complete photonic band gap. This approach may also be further developed as a defect control method. Detailed optical properties and potentials for other optical applications will be discussed.

**DD10.5 Energy Transfer in Submicron Dielectric Spheres.**
Tsunenobu Onodera 1, Hitoshi Kasai 1,4, Shuji Okada 1,4, Hidetoshi Oikawa 1,4, Hideki Matsune 1,3, Hiroshi Masuhara 1, Hitoshi Kasai 2,3, Hachiro Nakanishi 2,3 and Takashi Sekiguchi 1.

While it is well known that the radiative rate of an excited fluorophore is proportional to the optical density of states O-DOS, the effect of the O-DOS on the rates of energy transfer (resonant dipole-dipole interactions) is less understood. One question being explored is whether tuning the O-DOS can have a significant effect on energy transfer. This requires understanding the distribution of the O-DOS under the wavelength of light, where the Förster mechanism applies. The effect that tuning the O-DOS in sub-micron dielectric spheres has on photoluminescence has not been extensively explored. A series of silica spheres ranging in diameter from less than 100 nm to around 500 nm were generated via a modified sol-gel process (Stober process). Photonetic molecules, such as dyes, of similar size to microspheres, were attached to the spheres through standard silylation chemistry. The fluorescence lifetime and also the fluorescence quenching rate via energy transfer and electron transfer mechanisms were measured as a function of sphere size, quencher concentration, and solvent refractive index. The results of these experiments will be shown.

**DD10.6 Fixation of the Oriented Organic Nanocrystal Dispersion in a Magnetic Field.**
Yuji Kakehi 1,2, Satsumi Shimada 1, Takashi Fukuda 2,3, Tsunenobu Onodera 1, Hitoshi Kusai 1,2, Shigzi Ohada 4, Ishidetsu Oikawa 4, and Hachiro Nakanishi 1,4.

In this work, we demonstrate that the anisotropic orientation of long-chain organic nanocrystals, such as polymeric and inorganic colloidal crystal, can be achieved by the application of magnetic field. The DAST nanocrystals emit blue light in a medium through a process that is not understood. In this study, we report the immobilization of mesophase of DAST using a Faraday magnet, a magnetic field that is applied parallel to the direction of the applied magnetic field. The DAST nanocrystals dispersion in lauryl acrylate as a polymerizable media with benzoin isopropyl ether as a photoinitiator was dropwise added, and then metal nanoparticles were formed on the surface of DAST nanocrystals. Finally, metal nanoshell structure was formed on the surface of polyDAST nanocrystals through the growth of island metal deposition by the treatment with tetrahydroxidinone. Namely, polyDAST serves as surface-mediated reducing agent without generation of new nucleation in this case. Optical properties of the present hybridized polyDAST nanocrystals will be also discussed. Ref. 1: A. E. Neeves et al., J. Opt. Soc. Am. B, 13, 707 (1996). Ref. 2: F. Caruso, Adv. Mater., 13, 11 (2001). Ref. 3: T. Onodera et al., J. Cryst. Growth, 229, 586 (2001).

**DD10.7 Preparation of Polydiacetylene Nanocrystals Covered with Metal Nanoshell.**
Tsunenobu Onodera 1,3, Hitoshi Oikawa 1,3, Hitoshi Kasai 2,3, Hachiro Nakanishi 1,3, and Takashi Sekiguchi 1.

Organic π-conjugated polymers have been attracting considerable interest for the purpose of developing high-speed nonlinear optical (NLO) devices. Polydiacetylene (PDA) would be one of the most promising NLO materials. We report a new NLO-sensitive third-order nonlinearity in comparison with inorganics. Moreover, the magnitude of so-called \( \chi^{(3)}(\omega) \) is still not sufficient. Previously, Neeves et al. [ref. 1] have theoretically demonstrated that \( \chi^{(3)}(\omega) \) for PDA nanocrystals covered with metal nanoshell would be enhanced, because the optical field could be multiplied by the surface plasmon resonance. On the other hand, metal deposition method has been recently developed, using a polymer binder, for chemically surface-modified polystyrene and silica spheres [ref. 2]. In this presentation, the fabrication of PDA nanocrystals covered with metal nanoshell will be reported. In particular, it is important to mildly modify the surface of PDA nanocrystals without damaging π-conjugated main chain of PDA. PDA used was Poly[1,5-Di(N-carbazolyl)-2,4-hexadiyne] (polyDCHD), and polyDCHD nanocrystals as a core was prepared by the precipitation method as follows [ref. 3]: polyDCHD monomer acetone solution (0.2 ml, 5 mM) containing protective agent such as surfactant was injected into vigorously stirred water (10 ml) at 318 K. After retaining at given temperature, the resulting DCHD nanocrystals suspended in water were solid-state polymerized by UV-irradiation (254 nm) using handheld lamp, which provided the dark blue dispersion. Next, aqueous solution of metal salt as a precursor of metal nanoshell was added to the dispersion. Since ionic surfactant molecules were adsorbed on the surface of polyDCHD nanocrystals, metal ions electrostatically trapped at the surrounding of polyDCHD nanocrystals. Further, surfactant solubilization of redispersing of polyDCHD nanocrystals was maintained on the surface of polyDCHD nanocrystals. Finally, metal nanoshell structure was formed on the suspension of polyDCHD nanocrystals through the growth of island metal deposition by the treatment with tetrahydroxidinone. Namely, polyDCHD serves as surface-mediated reducing agent without generation of new nucleation in this case. Optical properties of the present hybridized polyDCHD nanocrystals will be also discussed. Ref. 1: A. E. Neeves et al., J. Opt. Soc. Am. B, 13, 707 (1996). Ref. 2: F. Caruso, Adv. Mater., 13, 11 (2001). Ref. 3: T. Onodera et al., J. Cryst. Growth, 229, 586 (2001).
DD10.9 Fabrication of Rare Earth Ion (Eu$^{3+}$, Tb$^{3+}$)-Doped Polyimide Nanoparticles and Their Unique Luminescence Property. Takayuki Ishizaka$^1$, Hitoshi Kasai$^1$ and Hachiro Nakashita$^1$.

$^1$Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Miyagi, Japan; $^2$CREST, Japan Science and Technology Agency, Kawaguchi, Saitama, Japan.

Optical properties of rare earth ion-doped glass, crystal and rare earth ion complex have been studied extensively for use in optical materials. On the other hand, polymers have good properties, such as transparency, easy processability, low density and low costs. However, common polymers have low stabilities against heat and light as compared to inorganic materials. Polyimide is structural integrity and has stabilities against heat and light, therefore suited to a host for optical materials. The hybridization of polyimide and rare earth ion may give stable optical materials and unique optical properties. In this study, we prepared rare earth ion (Eu$^{3+}$, Tb$^{3+}$)-doped polyimide nanoparticles (30 nm-1 mm) using our original technique of reprecipitation method. At a result, it was found that the hybridized materials have some interesting luminescence properties as below. Luminescence intensity assigned to rare earth ion increased with increase in UV-irradiation time, i.e., UV-irradiation quantity was recorded as luminescence intensity. In contrast, the intensity decreased with elevation of treatment temperature and the luminescence disappeared after a thermal treatment at 200 °C, i.e., the temperature can be detected and recorded. Moreover, after the luminescence vanished, luminescence intensity reversibly increased by UV-irradiation. Luminescence intensity recorded kept for several days at room temperature. The mechanism of the luminescence intensity change will be also reported and discussed.

DD10.10 Synthesis and Spectroellipsometric Characterization of Y$_2$O$_3$-stabilized Zr(II)-Au Nanocomposite Films for Smart Sensor Applications. George Sirinakas$^1$, Lianchao Sun$^2$, Rezina Siddique$^3$, Harry Efstathiou$^3$, Michael A. Carpenter$^4$ and Alain E. Kaloyeros$^5$.

$^1$College of Nanoscale Science and Engineering, University at Albany, Albany, New York; $^2$Sun International Inc, Acton, Massachusetts.

Noble metal nanoparticles exhibit significant potential in all-optical, smart-sensing applications due to their unique optical properties. In particular, gold (Au) nanoparticles exhibit a strong surface plasmon resonance (SPR) band, the spectral position and shape of which depends on the size, shape, and density of the nanoparticles and the physical and chemical properties of surrounding environment.

Embedding the nanoparticles in an ultrathin-stabilized zirconia (YSZ) matrix is believed to expand their range of operation to temperatures above 500 °C. YSZ is a material that has been proven suitable for optical applications due to its high refractive index, low absorption coefficient and high transparency in the visible and infrared regions. Thus, its use as a base platform for nanocomposite thin films is expected to provide significant benefits in the development of harsh environment multifunctional sensors.

In this study, we have synthesized a YSZ-Au composite matrix and demonstrated its suitability for optical and smart-sensing applications. The hybridized materials have some interesting luminescence properties as below. Luminescence intensity assigned to rare earth ion increased with increase in UV-irradiation time, i.e., UV-irradiation quantity was recorded as luminescence intensity. In contrast, the intensity decreased with elevation of treatment temperature and the luminescence disappeared after a thermal treatment at 200 °C, i.e., the temperature can be detected and recorded. Moreover, after the luminescence vanished, luminescence intensity reversibly increased by UV-irradiation. Luminescence intensity recorded kept for several days at room temperature. The mechanism of the luminescence intensity change will be also reported and discussed.


$^1$Department of Chemistry, University of Massachusetts, Lowell, Massachusetts; $^2$Pathology and Laboratory Medicine, Mount Sinai Hospital and University of Toronto, Toronto, Ontario, Canada.

We have demonstrated the use of hydrophobic C60 derivatives in optical, photothermal and photodynamic applications (TOP) via in vitro and in vivo studies with human fibrosarcoma cells. Recent development on two-photon absorption (2PA) excitation process may serve as a potential alternative PDT treatment procedure because of its ability to focus on a confined small treatment area of diseased tissues in a greater depth using a spectral window of 800-1100 nm in mammalian tissue. Synthesis of amphiphilic fullerene-photodynamic conjugates containing polar hydrophilic functional groups, such as carboxylic acid and poly(ethylene glycol), leading to water-soluble fullerene derivatives enhances their possibility in biomedical applications. Accordingly, we synthesized novel A-spi-D-type amphiphilic [60]fullerene-diphenylaminofluorenone-poly(ethylene glycol) conjugates, namely, C60-[D-PAF-PEG]. Compound C60-[D-PAF-PEG] consists of a fullerene cage as the electron acceptor (A) moiety and diphenylaminofluorenone segment as the donor (D) moiety, showing high two-photon absorption (2PA) cross-sections in nanosecond regime. Here, we present molecular self-assembly of the amphiphilic two-photon active fullerene materials at fullerenes in aqueous solution. The conjugates were characterized by dynamic light scattering, turbidity measurements and transmission electron microscopy.


$^1$Chemistry, University of Texas at Dallas, Richardson, Texas; $^2$The Nanotech Institute, University of Texas at Dallas, Richardson, Texas.

Metal nanoparticles are attracting much attention because of their third-order nonlinear optical effect and tunable optical properties. Previous studies include the formation of gold nanoshells on silica or metal oxide fibers. In our research we utilized the gold nanoparticles in the formation of core-shell nanoshells on cross-linked polyethylenimine (PEI) nanofibers in order to prepare conductive and transparent optical fibers. The proprietary polyethylenimine fibers encapsulated with a cylindrical thin gold shell will be presented and discussed. The synthesis involved the immersion of the PEI nanofibers into aqueous solution of chloroauric acid (HAuCl4) and room temperature reduction of HAuCl4 with tetraakis(hydroxymethyl)phosphonium chloride (THPC). By varying the amount of HAuCl4, we observed a change in the gold shell thickness and the nanoshells were characterized by SEM/EDX, TEM and UV-VIS spectroscopy.

DD10.13 Amine-assisted Bottleneck Etching of CdSe Nanocrystals. Rongfu Li$^1$, Jeunghoon Lee$^1$, Baosheng Yang$^2$, David N. Horspool$^3$, Mark Aindow$^4$ and Fotios Papadimitrakopoulos$^1$.


The bottleneck chemical etching of CdSe nanocrystals (NCs) in 3-aminopropyl-1-propanol mixture at 80 degree C is currently reported, as evidenced by spectroscopic and structural characterization data. Interestingly, as a function of etching time, instead of the continuous blue shift expected from a gradual decrease in NC dimensions, a peak position of photoluminescence (PL) is accompanied by maxima in PL quantum yield (34 %) and by minima in the full-width-at-half-maximum (30-40 nm) of the PL emission. It is presently argued that such etching behavior is a result of two competitive processes taking place on the surface of these CdSe NCs: (i) oxidation of the exposed Se-sites to acidic SeO2 entities, that are readily solubilized in the basic APOL/H2O mixture, exposing the underlying Cd-sites that (ii) coordinate with both amines and hydroxyl moieties to temporally impede NC dissolution. This leads to Cd-terminated NC surfaces that minimize the number of exposed Se sites and account for the apparent etching resistance at the plateau regions. High-resolution electron microscopy data are consistent with NCs exhibiting mainly Cd-terminated polar facets by adopting pyramidal morphologies.

DD10.14 Environmentally-induced Photoluminescence Red-shift in Poly(allylamine)/CdSe Nanocrystal Clusters. Jeunghoon Lee$^1$, Rongfu Li$^1$, Baosheng Yang$^2$, Thomas A. Seery$^2$ and Fotios Papadimitrakopoulos$^1$.

$^1$Nanomaterials Optoelectronic Laboratory (NOEL), University of Connecticut, Storrs, Connecticut; $^2$Institute of Materials Science, University of Connecticut, Storrs, Connecticut.

The preparation of water-soluble CdSe nanocrystal/poly(allylamine) (APOL) as a compatibilizing agent is currently reported. Photoluminescence (PL) quantum yields (QY) up to 20% were achieved in water without the need to clad these CdSe nanocrystals (NCs) with higher band gap inorganic layers such as ZnS. These PAA/NC nanoclusters show initial redshift at APOL dispersion. CdSe NCs are introduced to aqueous PAA solution followed by a subsequent blue-shift which is caused by etching of NCs by APOL.
This initial red-shift is believed to be due to the change of dielectric environment around the NCs situated inside the nanoclusters. We have employed effective-mass approximation and perturbation theory to calculate and predict such initial red-shift. These calculations show limited amount of water penetration into the vicinity of CdSe NCs that is consistent with the light scattering measurements. Different co-reprecipitation and colloidal structure of NCs lead to a combination of dynamic and static light scattering, contributes to a varying degree of the PL shifts. The correlation between the compactness of the internal structure of the nanoclusters and the extent of initial red shift will be presented for different PAA/NC ratio and ionic strength.

**DD10.15**

**Fabrication of Hybridized Nanocrystals Composed of \( \sigma \)-Conjugated Polymers Involving Monolayer Nanoparticles.**

Akito Masuhara,1,2, Satoshi Ohashi,1, Hitoshi Kasai,1,2, Yoshikazu Shimohara,1, Shuji Okada,1,2, Hitoshi Oikawa,1,2 and Hischio Nakainaha,1,2,1

1:MRM, Tohoku Univ., Sendai, Japan; 2:CREST, JST, Tokyo, Japan; 3:Polytechnic Institute, Worcester, Massachusetts.

Hybridized materials are expected to show new properties, which cannot be obtained from simple inorganic, organic and metal materials. Especially, peculiar interactions between excitons and plasmons realized by the hybridized systems composed of organic nanocrystals (NCs) and metal nanoparticles (NPs) are of much interest on novel optical properties. In fact, enhancement of nonlinear optical properties, which was theoretically predicted, was reported in the polydiacetylene thin film with gold NPs dispersion. In the present study, we report the fabrication of several hybridized NCs by means of co-reprecipitation and their optical properties and morphology were evaluated using visible absorption spectra as well as electron microscopy. When the hybridized NCs composed of Ag NPs as cores and 1,6-di(N-carbazolyl)-2,4-hexadine (DCHD) as shells were prepared, increasing UV irradiation time, PL peak at 655 nm naturally increased with increasing UV-irradiation time. Simultaneously, the plasmon absorption peak at 405 nm due to Ag NPs decreased and finally disappeared. This plasmon extinction was only observed for the hybrid system, and the plasmon of Ag NCs did not disappear at all in the simple mixture of Ag NP dispersion and poly(DCHD) NC dispersion. Such a plasmon weakening phenomenon was also observed for the hybridized system of Ag NPs and phthalocyaninacetocopper(II). Details of the preparation method, structures and optical properties of hybridized NCs in addition to the mechanism of the plasmon weakening phenomenon will be discussed.

**DD10.16**

**Porphyrin Dimers as Templates for Cubic Octupolar Nonlinear Optical Materials.**

Salimgerey Adilov and Venkat R. Schab-Balcerzak,1 Ewa Schab-Balcerzak2 and Bozena Jarzabek2; 1:Institute of Electrical Optoelectronic Applications. Arlen Valozhyn, Ewa Schab-Balcerzak2 and Bozena Jarzabek2; 2Centre of Polymer Chemistry, Polish Academy of Sciences, Zabrze, Poland.

Polyimide (PI) materials belong to the group of polymers characterized by good mechanical and dielectric properties and wide applications in the electronic industries. Most extensive studies were concentrated on fully aromatic PI because of their high-temperature resistance. However, the processability of fully aromatic PI is difficult and most of them are insoluble in conventional organic solvents, significantly limiting their application. Almost all fully aromatic PI are colored pale yellow to dark brown, causing strong absorption in the visible region. These polymers cannot be used where colorlessness and transparency are required. Using aliphatic monomers as co­

**DD11.1**

**Transparent Copolyimide Films for Micro - and Optoelectronic Applications.**

Arlen Valozhyn, Ewa Schab-Balcerzak2 and Bozena Jarzabek2.

A series of aliphatic-aromatic copolyimides (CPI) have been synthesised by high-temperature copolycondensation of the aliphatic diamines H2N(CH2)nNH2, where n = 4,6,7,9,10,12, 4,4'-methylenebis(2,6-dimethylphenol) or cyclopentantetraacarbonyl dichloride. Various ratios of diamines (aromatic-aliphatic) have been applied for preparation of CPI, soluble in a wide range of organic solvents and showed high thermal stability. In most cases these polymers formed flexible films which presented excellent transparency. On the one hand using aliphatic monomers can cause a decrease of the transparency, decrease the dielectric constant and improvement of solubility but on the other hand the thermal stability of such polymides may be reduced. But the use of the aliphatic monomers can be a good compromise between processability and stability properties. CPI thin films prepared by sol-gel solvo­

**DD11.2**

**Fast-Switching, High-Contrast Electrochromic Thin Films Prepared via Electrostatic Self-Assembly.**

James Coleman,1,2 and Li Shu2; 1:Mechanical Engineering, Texas A&M University, Pasadena, California; 2:Avery Research Center, Avery Dennison Corporation, Pasadena, California.

Using a technique known as glancing angle deposition (GLAD) it is possible to engineer porous micro- and nano-structured thin films. This technique utilizes highly oblique deposition angles (typically >80° with respect to substrate normal) and substrate shadowing to allow fabrication of thin films on a nanometer scale. The GLAD technique has been utilized to fabricate porous chiral nanostructures such as 3D square spiral photonic crystals and helical films exhibiting strong circular birefringence. Helical films are fabricated by holding the deposition angle constant while applying constant substrate rotation relative to the deposition rate. Manipulation of deposition parameters may be used to produce helical films with controlled porosity, handedness and pitch. Due to their chiral structure, helical films have been shown to preferentially transmit circularly polarized light with polarization opposite in nature to the handedness of the film. A left-handed helical film will preferentially transmit right-handed circularly polarized light and visa versa. The results of a study into the mechanism of the plasmon weakening phenomenon will be discussed.
MD Anderson Cancer Center, Houston, Texas.

A variety of electrochromic films have been produced recently using the electrostatic self-assembly (ESA) technique. ESA thin films, typically < 1 μm, are created by alternately exposing a substrate to positively, and negatively-charged molecules or particles in water. Positive and negative deposition steps are continuously repeated until the desired number of bilayers (or cation-anionic pairs) is achieved. Each individual layer may be 1-100 nm thick depending on a variety of factors. The ability to control coating thickness down to the sub-nanometer level, easily insert variable components without altering the process, and operate under ambient conditions are key advantages of this deposition technique. These thin films often have properties that are comparable to, or enhanced, relative to comparable thick films (> 10 μm). Unfortunately, many of the OLEDS in this study have been fabricated using photoconductive inks that suffer from environmental instability and poor contrast ratio (i.e., difference between light and dark states). Higher contrast has been achieved with inorganic oxides, but these films are often too slow to be used due to poor electrical conductivity. In an effort to increase the switching speed of ESA electrochromic films, without sacrificing contrast ratio, a three-component system was prepared. In this case, high-contrast tungstate anions (WO42-) were alternated with poly(4-vinylpyridine-co-styrene) (PVP) and PDDA-stabilized indium tin oxide (ITO) nanoparticles to create a four-layer repeating structure (i.e., PVP and PDDA are alternated and each deposited every fourth layer). In the absence of the PDDA-ITO particles, this system exhibits a contrast ratio > 8 (equivalent to newspaper print) with 60-bilayers, but the time taken to switch states is 25 seconds. Unlike tungstate, ITO has a high intrinsic conductivity (10^4 S/cm) that reduces the required thickness of the organic layer to 2-3 seconds without altering the contrast ratio. It is only with the control afforded by the ESA process that switching speed and contrast ratio can be optimized simultaneously. Furthermore, it would be advantageous for the ESA process to be performed in an effort to deposit the ITO in an effort to deposit from the solution as the tungstate anions, which would reduce the number of layers required to achieve the same properties.

DD11.3 Full Color Polymer Light Emitting Diodes (PLEDs) by a Photolithographic Patterned Method. Mi Kyung Kim, Jeong Ik Lee, Duck Il Kim, Hye Yong Choo, Chi Sun Hwang, Yong Seok Ko Park, Sung Hee Ko Park, Ji Young Oh, Duck Do-Hoon Hwang, and Hyung Jong Lee; ETRI, Daejeon, South Korea.

In recent years, organic light-emitting diode (OLED) have been of great interest for applications as high-quality self-emission displays for portable devices such as mobile telephone display. Multi-color OLEDs have been successfully fabricated by vacuum-deposition of small electroluminescent molecules, but solution processing of conjugated polymers (electroluminescent polymers) would result in a cheaper and simpler manufacturing process. However, polymer LEDs have not yet been commercialized due to the area defined by the sheet resistance of high mobilities of charge carriers, which limits their use in high resolution patterned arrays. The patterning method of conjugated polymers attracting increased interest from several researchers. Their approaches include microcontact printing, screen printing, photolithography, the photopolymerization and the solvent-induced thermal image method and so on. Recently, much attention has especially been focused on the techniques of photopatterning for conjugated polymer by introducing the chemical amplified photolithographic method. This technique uses the application of generating acid upon photoinduced and solubility change between exposed area and unexposed area. We have studied a photolithographic patterning method for polymer light emitting diodes (PLEDs). Blue light emitting polymer based on poly(naphthalene-co-benzimidazole), which can be cured photochemically to yield an insoluble form, have been synthesized using 4-nitrophenyl-4′-methoxyaniline. The relationship between patterning property and several variables such as the exposure dose of UV light, and the baking temperature and time, has been investigated by using optical microscope analysis, UV/visible spectroscopy, and photoluminescence. Using the optimized patterning process, we have successfully fabricated full color PLEDs. Green and red emissions were obtained from the composites of the polymer and dye dopants. In this presentation, the full color PLEDs by photolithography will be discussed in detail.

DD11.4 Thin Film Passivation with a-SiNx Thin Film for Flexible Organic Display. Chi-Sun Hwang, Sang-Hee Ko Park, Ji Young Oh, Yong Seok Yang and Hye Yong Choo; ETRI, Daejeon, South Korea.

Flexible display using organic light-emitting devices (OLEDs) fabricated on plastic substrate attracts much interests as next generation flat panel display devices. Thin film passivation for the OLEDs on the plastic substrate is the key technology for the development of flexible display. a-SiNx thin film is deposited as a passivation layer on the OLEDs devices fabricated on FFS substrate. The water permeability, the light emission characteristics, and life-time of the devices are measured. We optimized the deposition parameter to minimize the damage to the device during deposition temperature and maximize the barrier characteristics of the film. The thickness of 200nm a-SiNx film is deposited to a thin film thickness of 0.18 g/m2 day at (38°C, 96% RH). Moreover, the barrier characteristics are improved much through the post-treatment using H2 plasma. We found that the deterioration of the barrier characteristics of the film is originated from the degradation generated during deposition process. Additional thin film to decouple the pin-hole greatly improve the barrier characteristics. With double layer of 200nm a-SiNx film and 300nm AlO film, the WVTR decrease as low as 0.07 g/m2 day. The lifetime of the OLEDs is increased by two times with a-SiNx films as compared with a-SiOx thin film. The research for the removal of the plasma damage on the OLEDs is under progress. The improvement of barrier characteristics using multi-layer with another inorganic layer or organic layer will be presented.

DD11.5 Enhancement of Electron Injection in Organic Light-Emitting Diodes using an CsCl Layer between Organic and Cathode. K.H. Cho, J.Y. Yi, J.M. Koo, K. Han, M.K. Noh and K. Jeong; Department of Physics, Yonsei University, Seoul, South Korea.

Typically the insertion of a thin lithium fluoride (LiF) interlayer between the tri-(8-hydroxyquinoline) aluminum (Alq3) layer and a metal cathode has shown the most drastic performance improvement of both drive voltage and power efficiency of OLEDs. Recently, cesium chloride (CsCl) has been used to produce the efficient OLED. Instead of lithium fluoride, we fabricated OLEDs with a CsCl interlayer between the Alq3 layer and a Li cathode. We found out cesium chloride interlayer result in improved device performance. We investigated the electronic structure of Al/Cesium chloride/Alq3 by x-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS). By inserting cesium chloride, tunneling effect in Al cathode to Alq3 electron transport layer is more effective. Cesium chloride deposition on Alq3 is possible to make the highest occupied molecular orbital (HOMO) level and the lowest unoccupied molecular orbital (LUMO) level in Alq3.’ Tunneling effect and energy level shift with cesium chloride interlayer are two major reasons of enhancement of electron injection in OLED.

DD11.6 Application of Columnar Liquid Crystals in OLEDs and Their Characterization. Seyed Tadayyon, Holger Eichhorn, Bryan Bornais and Peter R. Norton; 1 The University of Western Ontario, London, Ontario, Canada; 2Windsor University, Windsor, Ontario, Canada.

Columnar liquid crystalline and columnar crystalline phases in which disc-shaped aromatic moieties are stacked closely and in parallel have been of great interest in organic light-emitting diodes (OLEDs) due to their unique electronic and optical properties. This work presents a novel approach to the fabrication of the disc-shaped molecules used for OLED fabrication. The disc-shaped molecules organize spontaneously in one-dimensional stacks within the fluid state, and the stacks form a two-dimensional lattice. Such self-organization is known to influence electronic properties and light-emission spectrums of the OLEDs. The combination of flexible film originated from the pin-hole generated during deposition process. Positive and negative depositions are continuously repeated until the film thickness of 60-bilayers, but the time taken to switch states is 25 seconds. Unlike tungstate, ITO has a high intrinsic conductivity (10^4 S/cm) that reduces the required thickness of the organic layer to several seconds without altering the contrast ratio. It is only with the control afforded by the ESA process that switching speed and contrast ratio can be optimized simultaneously. Furthermore, it would be advantageous for the ESA process to be performed in an effort to deposit the ITO in an effort to deposit from the solution as the tungstate anions, which would reduce the number of layers required to achieve the same properties. The ability to control coating thickness down to the sub-nanometer level, easily insert variable components without altering the process, and operate under ambient conditions are key advantages of this deposition technique. These thin films often have properties that are comparable to, or enhanced, relative to comparable thick films (> 10 μm). Typically the insertion of a thin lithium fluoride (LiF) interlayer between the tri-(8-hydroxyquiniline) aluminum (Alq3) layer and a metal cathode has shown the most drastic performance improvement of both drive voltage and power efficiency of OLEDs. Recently, cesium chloride (CsCl) has been used to produce the efficient OLED. Instead of lithium fluoride, we fabricated OLEDs with a CsCl interlayer between the Alq3 layer and a Li cathode. We found out cesium chloride interlayer result in improved device performance. We investigated the electronic structure of Al/Cesium chloride/Alq3 by x-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS). By inserting cesium chloride, tunneling effect in Al cathode to Alq3 electron transport layer is more effective. Cesium chloride deposition on Alq3 is possible to make the highest occupied molecular orbital (HOMO) level and the lowest unoccupied molecular orbital (LUMO) level in Alq3. Tunneling effect and energy level shift with cesium chloride interlayer are two major reasons of enhancement of electron injection in OLED.
inorganic metal-containing moieties and macromolecules lead to novel systems with new and exciting photo- and electrochemical properties as well as interesting architectures. The high inorganic transition metal ions, terpyridine ligands are of particular interest for introducing metal binding sites into polymers. [1] In particular the modification of terpyridine ligands with polymer blocks in the 4'-position enables the construction of linear photo- and electroactive systems. Furthermore, by using ligands such as functionalized 2-phenylpyridines in the coordination sphere of iridium(III) complexes additional to the terpyridine moiety, unsymmetrical substituted substituted systems with varied functionality and electronic properties are possible. A large variety of applications of isolated low molecular mass iridium(III) systems are already described, ranging from polymer chemistry to biochemistry. In this contribution we present the synthesis of a novel polymeric terpyridine macromolecule that can be used as a mixed ligand iridium(III) complex. Coupling of hexylamine functionalized terpyridine to a hydrofunctionalized poly(ethylene glycol) yielded a PEG-functionalized macromolecule. After a bridge-splitting reaction of the orthometallated dimer [Irppy-CHO]2Cl2 (where (ppy-CHO) is 4-(2-phenyl)benzaldehyde) and coordination to the tpy-PEG macroligand a novel polymeric monothiophene-iridium(III) complex revealing beneficial processing features was obtained. The complex revealed yellow emission after excitation at 365 nm. The emission spectra display maxima at 535 and 570 nm in CH2Cl2 solutions whereas on thin films on glass substrates the maxima were observed to be 10 nm red-shifted. Two oxidation potentials were observed of 1.45 and 1.64 V (Ag/Ag+ reference electrode). The mixed ligand iridium(III) complex functionalized with one polymeric poly(ethylene glycol) terpyridine and one 4-(2-phenyl)benzaldehyde ligands gives freedom to introduce further macrocyclic chains ranging from functionalized polymers to biomaterials. [1] U. S. Schubert, C. Eschbaumer, Angew. Chem. Int. Ed. 2002, 41, 2892.

DD11.8 Supramolecular Star Shaped Block Copolymers: Novel Light-Emitting Materials Bearing Iridium(III) Complexes. Michael A. R. Meier1,2, Elisabeth Holder1,2, Veronica Martinez2, and Ulrich S. Schubert1,2,1 Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology (TU/e), 5600 MB Eindhoven, Netherlands; 2Dutch Polymer Institute (DPI), 5600 AX Eindhoven, Netherlands.

Star shaped polymeric architectures offer interesting properties such as lower crystallinity or lower melt viscosity if compared to corresponding linear systems. Furthermore, the higher end-group functionality of star shaped macromolecules compared to linear polymers of the same molecular weight offers the possibility of controlled attachment of functional groups such as transition metal complexes to the polymer at an higher extent. It was already shown in the past that the combination of inorganic metal-containing moieties and macromolecules can lead to systems with interesting photo- and electrochemical properties: [1] In that sense terpyridine ligands are of particular interest since they can form stable complexes with a large variety of inorganic, organic, and coordination metal complexes. Star shaped iridium(III) complexes represent an interesting system with tunable light-emitting and electroactive properties. In this contribution we describe the synthesis and characterization of a series of 5 arm star shaped block copolymers bearing terpyridine end-groups. These polymers offer a core shell architecture and can act as unimolecular micelles. The terpyridine end groups were subsequently utilized to form mixed linear and cyclic crown ether-like complexes of these polymeric unimolecular micelles. Coupling of pentylamine functionalized terpyridine to the hydrofunctionalized arms of the star shaped block copolymers (via CDI activation) yielded 5 arm star polymers with terpyridine end groups. After a bridge-splitting reaction of the orthometallated dimer [Irppy-CHO]2Cl2 (where (ppy-CHO) is 4-(2-phenyl)benzaldehyde) and coordination to the tpy-PEG macroligand a novel polymeric monothiophene-iridium(III) complex revealing beneficial processing features was obtained. The complex revealed yellow emission after excitation at 365 nm. The emission spectra display maxima at 535 and 570 nm in CH2Cl2 solutions whereas on thin films on glass substrates the maxima were observed to be 10 nm red-shifted. Two oxidation potentials were observed of 1.45 and 1.64 V (Ag/Ag+ reference electrode). The mixed ligand iridium(III) complex functionalized with one polymeric poly(ethylene glycol) terpyridine and one 4-(2-phenyl)benzaldehyde ligands gives freedom to introduce further macrocyclic chains ranging from functionalized polymers to biomaterials. [1] U. S. Schubert, C. Eschbaumer, Angew. Chem. Int. Ed. 2002, 41, 2892.

DD11.9 Doping Effects on the Optical Properties of Semiconductor Nanoclusters. Billie Lynn Abrams1,2, Jess Patrick Wilcoxon1,2, Steven George Thoma1 and James M. Kraus3,1 Sandia National Labs, Albuquerque, New Mexico; 2Dept of Chemistry, University of Washington, Seattle, Washington.

The surface properties of nanoclusters (< 2-3nm in size) play a critical role in controlling their luminescent characteristics. By changing the type of species present on the surfaces of nanoclusters such as CdS or CdSe, the photoluminescent (PL) emission, photoluminescent excitation (PLE) and absorption onset can be tuned to different wavelengths and intensities. Using this concept, the optical properties of CdS and CdSe nanoclusters (1.8-3nm in size) were altered and controlled by depositing (or doping) Mn2+ ions and Zn2+ ions. The PL of CdS nanoclusters was tuned from blue (300nm) to orange (600nm). When Zn2+ was added after addition of Mn2+, there was much larger red-shift in the PL (585nm to 575nm). Deposition of ZnS added by heat (PEG surfactants is required for efficient energy transfer from the CdS core to the transparent Mn/ZnS islands on the cluster surface. The concept of using dopant ions deposited onto the nanocluster surface as activator sites for the tuning of PL can be extended to other semiconductor nanocluster/dopant systems. One such system of interest is Si or Ge with Sn and Sb as dopants. Preliminary work on these systems will be discussed.

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DD11.10 Investigation on the Degradation Mechanism in Organic Light Emitting Diodes using Scanning Photoelectron Microscopy. Soo Young Kim1, Ki-Boom Kim1, Yoon-Heung Tak2 and Jong-Lan Lee3,1 Pohang University of Science and Technology, Pohang, South Korea; 2LG Electronics Inc., Kumi, South Korea.

Since Tang and Van Slyke have developed multilayer organic light emitting diodes (OLEDs), intense research has been focused on its potential applications in display technology. However, for practical application, the reliability of the OLEDs still needs further improvement. One of the degradation mechanisms in OLEDs is the formation of dark spot. Although the appearance of dark spots can be detected by operating OLEDs in ambient air, the origin of the dark spot formation is still far from being complete. In order to investigate on the origin of the dark spot, the experiments were performed using the scanning photoemission microscopy (SPM). Because SPM is operated in two modes, photoelectron spectroscopy from a microspot and imaging, it is considered that SPM is the powerful tool in studying the origin of the dark spot. The device structure is glass/ indium tin oxide (ITO, 1500 Å)/ 4,4'-bis[N-(1-naphtyl)-N-phenyl-amino]biphenyl (a-NPD, 500 Å)/ tris(8-hydroxyquinoline) aluminum (Alq3, 600 Å)/ LiF (40 Å)/ Al (1000 Å). As the device operation time lengthened, the performance of OLEDs degraded. Optical microscopy data show that dark spots formed in both the surface of ITO and Al. SPM data show that the composition of dark spot is diverse. In 3d peak appeared and the contents of C is increased at dark spot in the surface of Al. This result shows that In and C out-diffused from ITO and organic material. Therefore, it is considered that the origin of dark spot is out-diffusion of In and C. We conclude that using the diffusion barrier in the organic material/electrode interface minimize the probability in the formation of dark spot.
An efficient flexible top-emitting device (FTFLED) was fabricated on an aluminum-laminated polyester (Al-PET) substrate. A spin-coated light-emitting polymer layer was sandwiched between a silver anode and a multilayered structure\[5\]. Using the FDTD method, we have found that the PBG surfaces (0.2-0.4 nm RMS roughness) while maintaining a high level of control over the infiltration coating thickness, enabling formation of an efficient flexible top-emitting device with good electrical and optical characteristics. The overall structure is on the order of 40-60 nm in thickness, the mechanism of the index change, and absorption from the dyed layers. To gain further insight into the nonlinear refraction response of the dyed material under high excitation (e.g. ground-state depletion, excited-state absorption and reflection), an ultrafast femtosecond white-light continuum (WLC) method femtosecond white-light continuum (WLC) transient absorption and reflection experiments are performed to determine the characteristics of the PbPc(CP)4 photonic bandgap material. This is readily verified in the spectral range 450-720 nm. The wavelength dependent results in the nanosecond range, where the excited-state absorption cross-section is approximately equal to that of the ground-state absorption cross-section. The induced reflectivity and spectral width of a photonic bandgap depends on the index difference between layers, uniformity of the layers, and the location of the index change, and absorption from the dyed layers. To gain further insight into the nonlinear refraction mechanism femtosecond white-light continuum (WLC) transient absorption and reflection experiments are performed to determine the characteristics of the PbPc(CP)4 photonic bandgap material. For these measurements, the output of a Ti:sapphire regenerative amplifier (771 nm, 130 fs FWHM, Clark MXR CPA-2001) was used to excite the sample, and also to produce a WLC in sapphire to probe the sample at various time delays from -100 picoseconds to 2.4 nanoseconds after excitation. The results from these experiments have demonstrated the synthesis of monodisperse spherical colloids of amorphous selenium (a-Se) in large quantities.
Nanofabrication of Organic and Inorganic/Organic Structures for Nanophotonics. Alexander N. Cartwright1, William David Kirby1, Michael Pan4, Vincent Hisao2, Ram Thapa1, Derrick Lucey1 and Paras Prasad2; 1Electrical Engineering, University at Buffalo (S.U.N.Y.), Buffalo, New York; 2Chemistry, University at Buffalo (S U N Y ), Buffalo, New York

Hybrid nanophotonic materials consisting of nanoparticles or nanostructures distributed within a polymeric matrix are presented. These hybrid materials allow us to combine the flexibility and ease of fabrication of organic materials with the stability and versatility of inorganic technology. This talk will present recent work on the incorporation of optically active semiconductor nanoparticles within organic device structures. Specifically, we will present a variety of efficient luminescent semiconductor nanoparticles synthesized by rapid and efficient methods. These include Si, InP, and II-VI nanoparticles, as well as a variety of core-shell structures. The structural and optical characteristics of these nanomaterials are described and the feasibility of utilizing these inorganic nanoparticles as the light-emitting species within a conductive organic device structure is discussed. Using the use of holographic interferometry to fabricate photonic bandgap structures comprised of ordered nanoscale inorganics embedded in polymer hosts will be presented. In this work, the use of optical interference-based patterning of a photosensitizer containing these nanoparticles is demonstrated as a method to pattern highly ordered one-dimensional photonic bandgap structures. We demonstrate that these techniques can be used to periodically align gold or silica nanoparticles within an organic host, resulting in diffractive elements with diffraction efficiencies approaching 100%. Silica particles containing embedded dyes have also been used to form comparable structures which can be easily characterized optically. Future applications of these structures will be discussed.

10:30 AM DD12.7 Internal Light Emitters in Silicon Photonic Crystals by Local Infiltration of IR-Emitting HgTe Quantum Dots

Polymercomposites. Stefan Riehler1, Renald Hillebrand3, Margit Zacharias1, Ralf B. Wehrspohn2, Stefan Schweizer1, Ulrich Gosele1, Martin Steinhardt1, Andrey L. Rogach3, Nikolai Gaponik4, Alexander Eychemuller1 and Joachim Wendorff3; 1Max-Planck-Institute Halle, Halle, Germany; 2Department of Physics, University of Paderborn, Paderborn, Germany; 3Department of Physics, University of Munich, Munich, Germany; 4Institute of Physical Chemistry, University of Hamburg, Hamburg, Germany; 72 Institute of Physical Chemistry and Center of Materials Science, University of Marburg, Marburg, Germany.

Internal light emission in 2D silicon photonic crystal and 2D silicon coupled cavities has been achieved. We developed a novel process based on the covalent bonding of 2D silicon photonic crystal. This allowed us to infiltrate the pores with polymer/quantum dot mixtures. The light emission of the HgTe quantum dots was modified by the density of states of the 2D photonic crystal. In particular, a change in the emission properties was observed when locally infiltrating individual pores of large cavities. Each dip in the emission characteristics could be attributed by numerical simulations to a cavity resonance. SNOM-measurements confirm the strong confinement of light inside the cavities. The polymer-mediated infiltration method is not limited to HgTe quantum dots and can be applied to any colloidal quantum dots emitter.


Certain periodic dielectric structures can prohibit the propagation of light. These artificial, so called photonic crystals are impacting how researchers can interact with electromagnetic fields and dielectric media from radio to optical wavelengths. Because of their great technological potential, the search for an easy to make photonic crystal with a large gap is still a major field of study. A complete photonic band gap is a frequency range for which electromagnetic waves within the structure are forbidden irrespective of their propagation direction. This physical property has opened the possibility of many novel optical applications such as the inhibition of spontaneous emission, the enhancement of semiconductor lasers, and the integration and miniaturization of optical components. We demonstrate that the top twenty distinguishable photonic crystal structures are all based on the diamond morphology. The architectures are graphically displayed in order to appreciate the similarities that make the structures retain the basic diamond gap. We show that considerable structural modifications still allow the retaining of the large gap. We will also discuss the photonic band gap properties from their 2D opaline lattices.

9:45 AM DD12.6 Nanofabrication of Organic and Inorganic/Organic Structures for Nanophotonics. Alexander N. Cartwright1, William David Kirby1, Michael Pan4, Vincent Hisao2, Ram Thapa1, Derrick Lucey1 and Paras Prasad2; 1Electrical Engineering, University at Buffalo (S.U.N.Y.), Buffalo, New York; 2Chemistry, University at Buffalo (S U N Y ), Buffalo, New York

Two-dimensional magneto-photonic crystal circulators. Zhiwei Wang1 and Shuhui Pan2; 1 Applied Physics, Stanford University, Stanford, California; 2Electrical Engineering, Stanford University, Stanford, California.

During the past decade, defect engineering in photonic crystals has successfully miniaturized many optical devices, such as optical filters and lasers, to a sub-wavelength scale. Previous research has also demonstrated enhanced’s rotational photonic crystal resonators to allow further miniaturization and monolithic in-plane integration with current integrated optical devices. The nonreciprocal magneto-resonators are constructed by alternating the magnetization directions of the ferromagnetic domains in the cavities side-coupled to photonic crystal waveguides. We show angle-tuning of the photonic crystal cavity resonance, and the strength of magnetic hybridization of cavity modes are determined by the overlap integral between the domain magnetization vector and the modal cross product. Using 3D integrated magneto-photonic crystals, we can create a perfect absorption structure that forms a bandgap for the propagation of magnetic fields. We tune the magnetic splitting and the decay constants of the rotating modes to create a three-port optical circulator with a 3dB extinction ratio. Future applications of these structures will be discussed.
emission of broadly emitting laser dye molecules thermally evaporated onto the structured surface of the substrate is studied. The effects of varying the air volume fraction and of the order of rotational symmetry on the light emission from these three families of visible spectrum 2D photonic quasicrystals are described. Finally, we make recommendations for the efficient use of PQCs in practical applications.

11:30 AM DD12.11
Optical Properties of polystyrene opals infiltrated with cyanine dyes in the form of J-Aggregates. Franco Marabelli1, Davide Conoretto2, Daniele Bajoni1 and Matteo Galli1; 1CNR-INFM and University of Pavia, Pavia, Italy; 2CNR-INFM and University of Genova, Genova, Italy.

Among photonic crystals, artificial opals are widely investigated as three-dimensional systems. Infiltration with active materials make them very interesting both from fundamental and device-oriented points of views. The J-aggregation phenomenon of cyanine dyes makes these commercially available molecules interesting candidates because their narrow absorption and emission lines lie in a convenient spectral region for the tuning of the optical properties within a cavity created by the opal structure. Polystyrene artificial opals with different sphere diameters (222 - 426 nm, refractive index 1.59) are grown by evaporation of monodisperse sphere suspensions in a humidity-controlled atmosphere. The morphology of the surface has been characterized by atomic force and scanning electron microscopies. In addition, a careful micro-optical characterization of these samples has been performed and the photonic band structure of the opals was derived from variable-angle micro-reflectance measurements, and favorably compared with that theoretically calculated. J-aggregate, characterized by a sharp and intense "red-shifted" absorption (compared to the monomer), are formed upon adding the polyvinyl sulfate (PVS) to the dye aqueous solutions. Several different conditions have been tested either for the concentration of the solution to obtain the best aggregate properties, either for the infiltration process of the opals in order to improve its homogeneity. Optical characterization of the produced samples evidenced the shift of the photonic gap structure due to the change in the dielectric contrast and now experiments are in progress to match the optical properties of opals and J-aggregates, in order to study the new confined optical states and the whole changes in the optical response.

11:45 AM DD12.12
The Effect of Dielectric Interfacial Roughness on the Normal Reflectivity of 1D Photonic Crystals. Karlene Rosner Maskaly1,2, Garry R. Maskaly1,2, W. Craig Carter1 and James L. Maxwell2; 1Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2Materials Science and Technology, Los Alamos National Laboratory, Los Alamos, New Mexico.

Dielectric reflectors that are periodic in one dimension, also known as 1D photonic crystals, have become extremely useful tools in the optics industry due to the presence of wavelength-tunable photonic band gaps. However, little is known about the practical effects of manufacturing defects, such as interface roughness, on this technologically useful property of 1D photonic crystals. We have employed a Finite Difference Time Domain (FDTD) code to explore this problem and gain further insight into the effect of interface roughness on the reflectivity of quarter-wave tuned 1D photonic crystals in the center of the band gap at normal incidence. This provides an estimate of the magnitude of the effect of roughness for even the most robust incidence conditions. We have also studied the alteration of the bandgap at normal incidence due to interfacial roughness. The presence of the roughness appears to red-shift the bandgap, with the severity of the shift increasing with larger roughness scales. We propose a mechanism that partially explains this phenomenon and other trends that are observed. Finally, we will discuss further calculations that have been done at off-normal incident angles.