

# SYMPOSIUM DD

## Organic and Nanocomposite Optical Materials

November 28 - December 3, 2004

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\* Invited paper

## TUTORIAL

### FT DD: Organic Nanophotonics—Materials and Applications

Sunday November 28, 2004

1:30 PM - 5:00 PM

Room 203 (Hynes)

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

University at Buffalo, State University of New York

Paras N. Prasad

University at Buffalo, State University of New York

SESSION DD1: Nonlinear Optical Properties Materials

Chair: Alexander Cartwright

Monday Morning, November 29, 2004

Room 310 (Hynes)

#### 8:30 AM \*DD1.1

**Linear and Nonlinear Optical Processes in Photonic Crystals and Photonic Crystal Alloys.** Paras Prasad,<sup>1</sup> Chemistry, Physics, Electrical Engineering, University at Buffalo, Buffalo, New York; <sup>2</sup>Institute for Lasers, Photonics and Biophotonics, State University of New York at Buffalo, Buffalo, New York.

There has been much interest in the development of photonic bandgap structures to control the linear and nonlinear optical properties of materials. The ability to enhance the nonlinear response of these materials theoretically predicted and a few have been recently demonstrated experimentally. In this talk, the basics of nanophotonics and the promise of photonic crystals will be reviewed. However, the majority of this talk will focus on some of the recent experimental results from our laboratory. Specifically, the first observation of strong one-step third-harmonic generation in a 1-D photonic crystal medium when the fundamental wavelength coincides with the stop-gap position will be presented. The third harmonic was generated at the low-energy edge of the photonic stop-gap and was observed in reflection as well as in transmission geometry. The observed phenomenon was described by considering phasematching conditions at the edge of the photonic bandgap. Secondly, this talk will include a description of electrically switchable third-harmonic generation in one-dimensional photonic crystals pumped by a near infrared laser beam. In this work, a dramatic enhancement of the third-harmonic signal is observed on the short wavelength side of the photonic crystal stop-band. The enhancement of the third-harmonic generation disappears when an electric field is applied, revealing the electrical switchability of the third-harmonic generation. Thirdly, linear transmittance and reflectance as well as on third harmonic generation in photonic crystal alloys formed by various compositions of polystyrene and polymethylmethacrylate colloidal spheres of same size will be presented. These photonic crystal alloys are structurally ordered, but contain refractive index disorder, and thus provide a random variation of scattering potential. The stop-gap shows a monotonic shift in wavelength as a function of the composition, which

can be fitted by assuming an effective dielectric constant for the colloidal spheres. In each alloy, a dramatic enhancement of third harmonic generation is observed, always on the short wavelength side of the stop-gap. Finally, a general discussion of current limitations and future directions will be provided.

#### 9:00 AM \*DD1.2

**Modeling of Pulse Propagation in Optical Materials.**

Hans Arvid Agren, Royal Institute of Technology, Theoretical Chemistry, Stockholm, Sweden.

In this talk I will describe some recent results from modeling of pulse propagation in optical materials by combining quantum and classical approaches. Such combined modelling allows to estimate the optical transmission from cross sections of multi-photon absorption processes and from considerations of propagation effects, saturation effects and pulse effects. It is shown that in the non-linear regime it is often necessary to account simultaneously for coherent one-step and incoherent step-wise multi-photon absorption, as well as for off-resonant excitations even when resonance conditions prevail. A breakdown of the conventional identification of multi-photon absorption as a one-step process is predicted for the long pulse regime in which incoherent step-wise processes can dominate. It is found that the major role of a solvent environment is to enhance the off-resonant contributions furnished by collisional dephasing. We stress that modelling of non-linear pulse propagation at high intensities of incident fields suffer from shortcomings if the conventional expansion of the non-linear polarization over powers of the electric field strength is employed. In this case not only the saturation effects can be treated poorly but so also the coupling of different multi-photon processes, resulting in neglect of leading terms in the non-linear polarization. The reviewed general methodology transcends the power expansion approach and thus overcomes its limitations. Numerical illustrations are given for some experimentally studied organic and organometallic molecules.

#### 9:30 AM \*DD1.3

**Donor Acceptor Thienothiophenes: Synthesis and Nonlinear Optic Properties.** Sabir H. Mashraqui, Chemistry Department,

Mumbai University, Mumbai, Maharashtra, India.

The field of nonlinear optics (NLO) continues to attract world-wide interest for potential applications in the domain of opto-electronics and photonics. The realization in 1980's that organic materials might be a better choice for NLO applications ignited much of efforts in this field, thereby resulting in the synthesis of a number of organic chromophores, many exhibiting large molecular hyperpolarisabilities. Although considerable progress has been made in understanding the factors responsible for high molecular nonlinearities, there is still an element of trail and error in development of electro-optic materials. None the less, a large body of theoretical and experimental results shows that significant nonlinear responses such as SHG generally could arise by combination of strong donor and acceptor positioned at the opposite ends of a suitable conjugation bridge. Among the many heteroaromatic NLO phores, donor-acceptor thiophenes in particular have shown promising nonlinear optic properties. We find that thieno[2,3-b] thiophene ring, a  $10\pi$  analog of naphthalene has not yet been exploited as a donor component in the development of NLO systems. In analogy to the thiophene, it was hoped for that thienothiophene with its lower resonance energy and high  $\pi$ -donor characteristic might allow us to create polarized push-pull structures with potential for high nonlinear optic properties. Accordingly, we have utilized thienothiophene core to synthesize a number of push-pull thienothiophenes. All the available positions on thienothiophene core have been functionalized with different bridges and acceptors by rational synthetic protocols. For many of the donor-acceptor thienothiophenes, we have experimentally determined first hyperpolarisability  $\beta$  and thermal stability to evaluate their potential in the NLO fields.

#### 10:15 AM \*DD1.4

**Theoretical study on the molecular-based nonlinear optical systems including open-shell and/or charged species.**

Masayoshi Nakano<sup>1</sup>, Tomoshige Nitta<sup>1</sup> and Kizashi Yamaguchi<sup>2</sup>;

<sup>1</sup>Department of Materials Engineering Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-8531, Japan;

<sup>2</sup>Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan.

Most of the organic nonlinear optical (NLO) systems studied so far are limited to the closed-shell and neutral systems though several studies have highlighted the potential of open-shell and/or charged systems and some of them have suggested the possibility of the attractive multi-functional materials, e.g., exhibiting both of magnetic and optical properties. We have investigated the second hyperpolarizabilities ( $\gamma$ ) of condensed-ring and/or alternant conjugated systems such as pentalene, pentafulvalene and s-indacene,

and have found that the drastic change in sign and the magnitude of  $\gamma$  are expected when the system presents symmetric resonance structures with invertible polarization (SRIP). In previous studies, we have indicated the remarkable variation in  $\gamma$  of H2 model with increasing the bond distance and have suggested the enhancement of  $\gamma$  in the intermediate correlation (intermediate bond breaking) regime. This feature is understood by the fact that 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  $\gamma$  is important in view of the spin-control of novel open-shell NLO systems since the control of spin state is often achieved by introducing the charges into systems in molecular magnetism. Recently, therefore, the effects of spin multiplicity on  $\gamma$  of open-shell neutral and/or charged  $\pi$ -conjugated systems have been investigated using simple open-shell model compounds, and the magnitude of  $\gamma$  has turned out to sensitively depend on the spin and charged states. Such attractive dependence of  $\gamma$  is turned out to be connected with the variation in bonding nature associated with the change of spin and charged states. In this study, we also propose novel open-shell singlet NLO systems, whose NLO property has the possibility of being controlled by the diradical character. The dependence of  $\gamma$  on the diradical character is investigated using diradical model compounds, p-quinodimethane (PQM) models with different both-end carbon-carbon (C-C) bond lengths, by several ab initio molecular orbital and density functional theory methods. The result at the UCCSD(T) with 6-31G\* diffuse p ( $\zeta=0.0523$ ) basis set, shows that the longitudinal static  $\gamma$  takes a maximum for the PQM with an intermediate diradical character ( $y\approx 0.5$ ). This feature suggests that the  $\gamma$  values of diradical systems in the intermediate and somewhat strong correlation regimes are significantly enhanced as compared to those in the weak correlation regime. On the basis of these results, we discuss the possibility of a new class of NLO systems, i.e., open-shell NLO systems.

#### 10:45 AM DD1.5

##### Excitation Wavelength Dependent Photodynamic Response on Azopolymer Films. Mi-Jeong Kim<sup>1,2</sup>, Chae-Min Chun<sup>1</sup>,

Tomonobu Nakayama<sup>2</sup> and Dong-Yu Kim<sup>1</sup>; <sup>1</sup>Materials Science And Engineering, Gwangju Institute of Science and Technology, Gwangju, South Korea; <sup>2</sup>International 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 selected. All the electron donor groups were amino groups, but different electron-acceptor groups (-CF<sub>3</sub>, -CN, -CNC<sub>l</sub>, -NO<sub>2</sub>, and -(CN)<sub>2</sub>) 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<sup>+</sup> laser. The saturation value of birefringence 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 -CF<sub>3</sub> > -CN > -CNC<sub>l</sub> > -NO<sub>2</sub> > -(CN)<sub>2</sub>. Using the same polymeric materials, the photofabrication rate of SRG with a 1 mm grating spacing were 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 photoinduced birefringence growth curves. As the wavelength of the Ar<sup>+</sup> laser changed to longer region (wavelength: 514 nm), the rate of SRG formation was in the order of -CN > -CNC<sub>l</sub> > -CF<sub>3</sub> > -NO<sub>2</sub> > -(CN)<sub>2</sub>. The reason for this might be that the trans azobenzenes of the CF<sub>3</sub>-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, Kwanghoon 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, train, 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 particular, a characteristic emission with a sharp peak wavelength of 705nm  $\pm$  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, Trinitrotoluene (TNT), Trinitro 2, 4, 6 phenylmethylnitramine (Tetryl), Nitroglycerin, Pentaerythritol tetranitrate (PETN), Octohydro 1, 3, 5, 7 tetranitro 1, 3, 5, 7 tetrazocine (HMX), Hexahydro 1, 3, 5 trinitro 1, 3, 5 triazine (RDX), and 2, 6 Dinitrotoluene. In contrast, volatile, yet non-explosive 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 reported previously in the literature. In this work it is hypothesized that the sharp emission peak may be due to the presence of functional nitro groups (NO<sub>2</sub>) and their influence on the electronic structure of the explosive material. The nitro functional group can be found in all of the explosive materials tested. The hypothesis is tested using molecular structure studies, decomposition studies, and phase measurements. The nitro group and its influence on the molecular structure of explosive materials is investigated. This is accomplished by studying materials having similar basic molecular structures but containing varying concentrations of the nitro group. For example mononitro-, dinitro-, and trinitrotoluene 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.

#### 11:15 AM DD1.7

##### Crystal Engineering of Organic and Metal-Organic Octupolar Nonlinear Optical Materials. Venkat R. Thalladi, Department of Chemistry and Biochemistry, Worcester Polytechnic Institute, Worcester, Massachusetts.

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: trialkyl isocyanurates and triaryloxytriazines. The most efficient of the octupoles 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 octupoles. This strategy involves modular covalent synthesis 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-A<sub>2</sub>D<sub>2</sub>-porphyrins and trans-A<sub>2</sub>D<sub>2</sub>-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 Diacetylenes. Koji Ohta and Kenji Kamada;

Photonics Research Institute, AIST Kansai, Ikeda, 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 diacetylenes have relatively large two-photon absorption (TPA) cross sections  $\sigma^{(2)}$  (350-850 GM: 1 GM =  $1 \times 10^{-50}$  cm<sup>4</sup> s molecule<sup>-1</sup> photon<sup>-1</sup>) in the near infrared region [1]. This  $\sigma^{(2)}$  value is larger than those of the compounds with similar molecular size linked with a double bond as the central unit. Moreover, we have found that one of the diacetylenes (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 enhancement of the  $\sigma^{(2)}$  value in shorter wavelength region only within the CIS (configuration interaction with single excitations) model. Based on the density analysis using the INDO/S-CISD (configuration interaction with single and double excitations) method, we present a novel structure-property relationship for TPA in term of the charge state at the both ends of the molecules [3]. [1] Y. Iwase, K. Kondo, K. Kamada, K. Ohta, J. Mater. Chem. 13, 1575 (2003). [2] K. Kamada, K. Ohta, Y. Iwase, K. Kondo, Chem. Phys. Lett. 372, 386 (2003). [3] R. Kishi, M. Nakano, S. Yamada, K. Kamada, K. Ohta, T. Nitta, K. Yamaguchi, Chem. Phys. Lett., in press (2004).

SESSION DD2: Nonlinear Optical Materials  
Monday Afternoon, November 29, 2004  
Room 310 (Hynes)

#### 1:30 PM \*DD2.1

**Photophysical Properties of Nonlinear Optical Materials: Time-Dependent Density Functional Theory Studies.** Kiet A. Nguyen, Paul N. Day and Ruth Pachter; Materials & Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio.

In our ongoing studies to gain insight into the photophysical properties of nonlinear optical materials, including reverse saturable and two-photon absorbing organic molecules, we recently reported a series of time-dependent density functional theory 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.

#### 2:00 PM \*DD2.2

**Time-Dependent Analytic Density Functional Theory to Predict Nonlinear Optical Properties of Molecules and Atomic Clusters.** Brett I. Dunlap<sup>1</sup>, Rajendra R. Zope<sup>2</sup> and Shashi P. Karna<sup>3</sup>; <sup>1</sup>Code 6189, Naval Research Laboratory, Washington, District of Columbia; <sup>2</sup>Department of Chemistry, George Washington University, Washington, District of Columbia; <sup>3</sup>Weapons and Materials Directorate AMSRD-ARL-WM-BD, Army Research Laboratory, Aberdeen Proving Ground, Maryland.

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 those relationships have been the focus of theoretical studies in this area. Very often the applicability of the predicted results have been limited, however, due to lack of electron correlation, inadequate basis sets, and/or 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 their applications to predict NLO 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 TDDFT 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.

#### 2:30 PM DD2.3

**Optical responses of conjugated polymers by TDDFT in real-space and real-time approach.** Nobuhiko Akino and Yasunari Zempo; Sumitomo Chemical, Tsukuba, Japan.

Time dependent density functional theory (TDDFT) has been widely recognized as a useful method to study the electron 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[1] 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 forms 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[2]. This approach gives us not only the clear picture of the time evolution of the physical quantities, but also the responses in the entire energy 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. F. Bertsch, Phys. Rev. B54, 4484 (1996)

#### 2:45 PM DD2.4

**Writing Laser Power Dependence of Second Harmonic Generation in a New Optically Poled 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, Kaohsiung, Taiwan.

The time and power dependence of the optical poling process of a new azo-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 poling of the chromophore/PMMA 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.

#### 3:30 PM \*DD2.5

**Structure - Nonlinear Optical Property Relationship of Porphyrins.** Govind Mallick and Shashi P. Karna; Weapons and Materials Research Directorate, Army Research Laboratory, Aberdeen Proving Ground, Maryland.

Porphyrins are potentially useful third-order nonlinear optical (NLO) materials due to their highly  $\pi$ -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 *abinitio* Hartree-Fock method and an effective core potential basis set. The calculated geometrical parameters of the porphyrins show in good agreement with the available experimental and theoretical data. The calculated  $\Delta E$  (HOMO-LUMO) of the 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 molecules 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.

#### 4:00 PM \*DD2.6

**Optical Properties of Chalcopyrites : Bulk to Nanoclusters.**

Haiying He<sup>1</sup>, Ranjit Pati<sup>1</sup>, Shashi Karna<sup>2</sup> and Ravi Pandey<sup>1</sup>;

<sup>1</sup>Michigan Tech University, Houghton, Michigan; <sup>2</sup>U.S. Army Research Lab, Aberdeen Proving Ground, Maryland.

Chalcopyrite nonlinear optical semiconductors are presently enjoying a major renaissance. Recent successes in growing large single crystals of ZnGeP<sub>2</sub> and CdGeAs<sub>2</sub> have led to renewed efforts to utilize these materials for optoelectronic devices. In this talk, a general review of chalcopyrites, and of their applications in laser systems that exploit second-harmonic generation or optical parametric oscillation will be given. We will also present the results of *abinitio* study of the nanoclusters of ZnGeP<sub>2</sub> and CdGeAs<sub>2</sub> in an effort to develop a theoretical understanding of the microscopic optical properties of these materials.

#### 4:30 PM DD2.7

**Strong enhancement of the two photon absorption cross section of porphyrin J-Aggregates in water.** Camilla Ferrante, Elisabetta Collini and Renato Bozio; Chemistry Department, University of Padova, Padova, Italy.

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 aggregation process promotes 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 J 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 pump-probe experiment, in which the fundamental at 806 nm is used as the pump, and the probe is the white light continuum (650-1000 nm). The TPA values measured for the monomer in solution are compared with data from the literature [4]. Upon aggregation a strong enhancement of the TPA response in the whole spectral range investigated is observed. These experimental findings are discussed in the frame of the TPA absorption theory. 1. O. Ohno, Y. Kaizu, H. Kobayashi, *J.Chem. Phys.*, 1993, 99, 4128; N.C. Maiti, S. Mazumdar, N. Periasamy, *J. Phys. Chem. B*, 1998, 102, 1528. 2. J. Knoester, F.C. Spano, in *J-Aggregates*, ed. T. Kobayashi, World Scientific, Singapore, 1996. 3. F.C. Spano, J. Knoester, in *Advances in Magnetic and Optical Resonance*, vol. 18, ed. W.S. Warren, Academic Press, New York, 1994. 4. M. Drobizhev, A. Karotki, M. Kruk, A. Rebane, *Chem. Phys. Lett.*, 2002, 355, 175; M. Kruk, A. Karotki, M. Drobizhev, V. Kuzmitsky, V. Gael, A. Rebane, *J. of Luminescence*, 2003, 105, 45.

SESSION DD3: Organometallic Optical Materials I  
Tuesday Morning, November 30, 2004  
Room 310 (Hynes)

#### 8:30 AM \*DD3.1

**Linear and Non-Linear Optical Properties of Platinum Acetylde Materials.** Kirk Schanze, Chemistry Department, University of Florida, Gainesville, Florida.

A series of Pt-acetylde oligomers and polymers have been investigated towards the objective of understanding structure-property relationships that control the linear and non-linear optical properties of the materials. Recent investigations have explored the effects of aggregation on the absorption and photoluminescence properties, and how the coupling of multiple Pt-acetylde chromophores into a single molecular framework influences the non-linear optical properties of the materials. The talk will highlight recent findings in this area.

#### 9:00 AM \*DD3.2

**Binary Optical Memory Applications of Luminescent Metal-Organic Materials.** Felix N. Castellano, Chemistry & Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio.

The design, synthesis, and optical characterization of several metal-organic photoluminescent molecules and assemblies capable of serving as nondestructive readout optical memories when dispersed in inert polymer matrices will be presented. The inorganic portion of each molecule is based on transition metal complexes displaying metal-to-ligand charge transfer (MLCT) excited states. The organic complement is a photochromic species that serves as an energy transfer quencher of the MLCT-based luminescence in one of its photochromic states. These particular systems are capable of serving as nondestructive luminescence readout binary optical memories when dispersed in polymer matrices, where two-dimensional micron scale images are recorded and read using photons of different color. This presentation will overview our recent progress in this area, emphasizing some of our latest molecular designs and readout concepts including binary discrimination based upon luminescence lifetimes. Recent near-field scanning optical microscopy approaches will also be discussed.

#### 9:30 AM DD3.3

**Approaches to Photoactive Paddlanes Based Upon Metal**

**Acetylene Coordination Chemistry.** Wiley J. Youngs, Jered C. Garrison, Carol A. Quezada, Paul C. Custer and Claire A. Tessier; Chemistry, University of Akron, Akron, Ohio.

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 paddlanes. Preliminary studies of the photoactive properties of these complexes will be presented.

#### 9:45 AM DD3.4

**Structure Property Characterization of Nonlinear Optical Materials.** Joy Elizabeth Rogers<sup>1,2</sup>, Jonathan E. Slagle<sup>1,3</sup>, Daniel G. McLean<sup>1,4</sup>, Kristi M. Gossett<sup>1,5</sup>, Weijie Su<sup>1,3</sup>, Benjamin C. Hall<sup>1,6</sup>, Thomas M. Cooper<sup>1</sup>, Aaron R. Burke<sup>1,5</sup> and Paul A. Fleitz<sup>1</sup>; <sup>1</sup>Materials and Manufacturing Directorate, Air Force Research Laboratory, WPAFB, Ohio; <sup>2</sup>UES, Inc., Dayton, Ohio; <sup>3</sup>AT&T Government Solutions, Dayton, Ohio; <sup>4</sup>Science applications International Corporation, Dayton, Ohio; <sup>5</sup>Anteon Corporation, Dayton, Ohio; <sup>6</sup>Universal Technology Corporation, Dayton, Ohio.

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 chromophores 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 poly-ynes and various metallated 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 poly-ynes that differ only by the phenyl-ethynyl ligand 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 benzo and naphtho 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

**Photophysics and optical limiting properties of platinum(II) 4'-aryltetrapyridyl arylacetylde complexes.** Wenfeng 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 phenylacetylde complexes are promising broadband optical limiting materials. In order to better understand the structure-property relationship, a series of platinum(II) terpyridyl arylacetylde 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 the aryl substituent on the acetylde ligand. Except for the complexes that contain electron-donating substituents on the phenyl ring of the acetylde 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 acetylde ligand. In addition, most of the complexes exhibit clear optical limiting for nanosecond laser pulses at 532 nm. Similar to the photophysical properties, the optical limiting performances of these complexes are influenced significantly by the different substituents on the terpyridyl ligand and on the acetylde ligand.

#### 10:45 AM DD3.6

**Chiral Metalloccycles for Sensing and Catalytic Applications.** Wenbin Lin, Dept of Chem, Univ of North Carolina, Chapel Hill, North Carolina.

Coordination driven self-assembly of inorganic 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 promises 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 applications in chiral sensing and asymmetric catalysis. Our proof of principle experiments use 1,1'-bi-2-naphthol (BINOL) 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 rational design of a variety of conjugated chiral metallocycles of various sizes as well as their applications in chiral sensing, asymmetric catalysis, and light-emitting devices.

#### 11:00 AM DD3.7

##### Optical and Electronic Properties of Metal-containing

**Poly-yne and their Organic Precursors.** Paul Robert Raithby, Marek Jura, Olivia Koentjoro, Emma Louise Sharp, Hazel Ann Sparkes and Paul John Wilson; Chemistry, University of Bath, Bath, United Kingdom.

Organic poly-ynes 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-yne 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-yne polymers with the general formula  $\text{trans}[(\text{R3P})_2\text{Pt-CC-X-CC}]_n$  (X = a range of aromatic and heteroaromatic 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 reduced by introducing electron withdrawing groups 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 of these and their organic precursors onto metal surfaces. We will report the results of these studies including the formation of polymers of gold poly-ynes where the chains are formed through gold-gold interactions, and where absorption and emission spectroscopy show differences between solution and solid-state studies. The results of the absorption of these poly-yne polymers and of related metal nanoparticles onto gold surfaces are also described, and the electronic properties of the systems are reported. References 1. Burroughes, J. H., Bradley, D. D. C., Brown, A. R., Marks, R. N., Mackay, K., Friend, R. H., Burn, P. L., Holmes, A. B., Nature 1990, 347, 539; Tessler, N., Denton, G. J. and Friend, R. H., Nature 1996, 382, 695. 2. Younus, M., Kohler, A., Cron, S., Chawdhury, N., Al-Mandhary, M. R. A., Khan, M. S., Lewis, J., Long, N. J., Friend, R. H., Raithby, P. R., Angew. Chem., Int. Ed. Engl. 1998, 37, 3036; Chawdhury, N., Kohler, A., Friend, R. H., Wong, W.-Y., Lewis, J., Younus, M., Raithby, P. R., Corcoran, T. C., Al-Mandhary, M. R. A., Khan, M. S., J. Chem. Phys. 1999, 110, 4963. 3. Khan, M. S., Al-Mandhary, M. R. A., Al-Suti, M., Ahrens, B., Mahon, M. F., Male, L., Raithby, P. R., Boothby, C. E., Kohler, Dalton Trans. 2003, 74. 4. Wilson, J. S., Chawdhury, N., Al-Mandhary, M. R. A., Younus, M., Khan, M. S., Raithby, P. R., Kohler, A., Friend, R. H., J. Am. Chem. Soc. 2001, 123, 9412. 5. Walzer, K., Marx, E., Greenham, N. C., Less, R. J., Raithby, P. R., Stokbro, K., J. Am. Chem. Soc. 2004, 126, 1229.

#### 11:15 AM DD3.8

**Platinum (II) Complexes as Phosphorescent Materials for Organic Light Emitting Diodes.** Biwu Ma<sup>1</sup>, Simona Garon<sup>2</sup>, Jian Li<sup>2</sup>, Arnold Tamayo<sup>2</sup>, Xiaofan Ren<sup>2</sup>, Bert Alleyne<sup>2</sup>, Peter I. Djurovich<sup>2</sup> and Mark E. Thompson<sup>2,1</sup>; <sup>1</sup>Materials Science, USC, Los Angeles, California; <sup>2</sup>Chemistry, USC, Los Angeles, California.

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 strongly emissive triplet excited states. The emission of monomeric square planar platinum complexes can be tuned to give monochromatic blue, green and red emission in fluid solution, by changing the cyclometallated ligands. However, in the solid state, the luminescence 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. Using this intermolecular interaction 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 aggregate or dimer emission and thus broad emission lines. 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 pyrazole bridged platinum complexes as phosphorescent dopants. The metal-metal distance in the dinuclears is strongly tied to 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 center triplet/metal ligand charge transfer) excited state to low-energy MMLCT (metal-metal-to-ligand 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<sup>1</sup>, Quan Ren<sup>2</sup>, Guanghui Zhang<sup>1</sup>, Xinqiang Wang<sup>1</sup>, Yanling Wang<sup>1</sup>, Tingbin Wang<sup>1</sup>, Hongliang Yang<sup>2</sup>, Y. T. Chow<sup>3</sup>, Andy Chan<sup>3</sup> and P. L. Chu<sup>3</sup>; <sup>1</sup>The State Key Lab of Crystal Materials, Shandong University, Jinan, Shandong, China; <sup>2</sup>Department of Optics, Shandong University, Jinan, China; <sup>3</sup>Department 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 molecules or radicals like in organic crystals. In this paper, some results on new crystals and nano-composited films are reported and reviewed.  $\text{ZnCd}(\text{SCN})_4$  (abbreviated as ZCTC, space group I4- ) crystal is a new organometallic nonlinear optical material. The dielectric and nonlinear optical parameters were measured,  $\epsilon_{11}=7.3$ ,  $\epsilon_{33}=7.8$ ;  $d_{14}=3.2$  pm/V,  $d_{15}=7.6$  pm/V; UV transparency cutoff occurs at 290 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:  $n_o^2=3.30681+0.02564/(\lambda^2-0.05141)-0.02564/(0.05141-\lambda^2)$   $n_e^2=2.88293+0.02001/(\lambda^2-0.03114)-0.02001/(0.03114-\lambda^2)$  Growth mechanisms and surface morphology of organometallic crystal were discussed. Another examples are organometallic and organic nanocomposited waveguide using for electro-optical or all-optical switch.  $\text{ET}_2\text{I}_3$ , ET,  $\text{ET}_2\text{Cu}(\text{SCN})_2$ , DBOT-DTT, DMACB nanocrystals were already prepared. Two and three dimension waveguides in 1.55  $\mu\text{m}$  and 1.32  $\mu\text{m}$  were successfully achieved. The electro-optic coefficient, third-order optical 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 basic units (guest) of electro-optical or all optical polymer films, 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 non-central symmetrical 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 excitons. But, the recombination injected electrons and holes inevitably form both singlet and triplet excitons under electrical excitation. Statistically, the singlet-to-triplet (S1/T1) exciton ratio is restricted to 1:3. Recent experimental and theoretical studies have indicated that the S1/T1 ratio can be increased if the electron-hole capture process becomes spin-dependent. In this presentation, we report a dramatic enhancement of the singlet fraction (>75%) based on EL and photoluminescence (PL) measurements by employing direct ferromagnetic exchange interaction to affect the spin configuration of the injected electrons and holes. This is achieved by doping CoPt ferromagnetic nanowires into a conjugated polymer poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEHPPV), in which spin-polarized charge transfer from the CoPt nanowires leads to a net magnetic moment in nonmagnetic MEHPPV chains. The singlet formation is enhanced by the local ferromagnetic exchange field from the induced magnetic moment in the MEHPPV chain. On the other hand, we found the local ferromagnetic exchange field largely affects the singlet-triplet energy transfer. Therefore, the

approach of magnetic doping not only presents a new pathway to enhance polymer EL efficiency, but also makes conjugated polymers promising as spintronic 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 Thompson<sup>1</sup>, Stephen Forrest<sup>2</sup>, Julie Brown<sup>3</sup>, Xiaofan Ren<sup>1</sup>, Russel Holmes<sup>2</sup>, Arnold Tamayo<sup>1</sup>, Jason Brooks<sup>3</sup>, Peter Djurovich<sup>1</sup>, Tissa Sajoto<sup>1</sup> and Biwu Ma<sup>1</sup>; <sup>1</sup>Department of Chemistry, University of Southern California, Los Angeles, California; <sup>2</sup>Department of Electrical Engineering, Princeton University, Princeton, New Jersey; <sup>3</sup>Universal 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 complexes (i.e. Pt, and 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 monomer and dimer/excimer states of Ir and Pt dopants. The result is an emission spectrum that covers the entire visible spectrum, giving true white illumination. The Pt complexes are square planar 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 structure. We have recently found that it is possible to prepare a binuclear Pt complex that is stable in solution, readily sublimates and gives an emission spectrum matching the aggregate species in our white OLEDs. The photophysics, structure and OLED properties of this binuclear 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

##### Luminescent Metal Alkynyls - 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 oligo- and poly-ynes 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 emissive origins elucidated. Correlations of the luminescence behavior with the electronic and structural effects of the metal complexes have also been made. Through rational design and assembly strategies, these metal alkynyls may serve as ideal building blocks for the design and construction of luminescent molecular rods and materials as well as may find potential applications in chemosensing and luminescence signalling.

#### 2:30 PM \*DD4.3

##### T1 and Tn triplet states in organic and Pt-containing conjugated polymers.

Anna Kohler<sup>1</sup>, Ning Zhang<sup>1</sup>, David Beljonne<sup>2</sup>, Mohammed K. Al-Suti<sup>3</sup> and Muhammad S. Khan<sup>3</sup>; <sup>1</sup>Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom; <sup>2</sup>Materia Nova, University of Mons, Mons, Belgium; <sup>3</sup>Department 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(PBu<sub>3</sub>)<sub>2</sub>CC-R-CC]<sub>n</sub>. 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-polymers (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 localised while the Tn state is highly delocalised. We have 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 yet different sidechains, we have further explored the role of chain conformation on 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 Holder<sup>1,2</sup> and Ulrich S. Schubert<sup>1,2</sup>; <sup>1</sup>Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology (TU/e), 5600 MB Eindhoven, Netherlands; <sup>2</sup>Dutch Polymer Institute (DPI), 5600 AX Eindhoven, Netherlands.

New metal-containing and emissive materials find applications in various research fields but are recently in the focus for displays. 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 d6 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 lifetimes in the region of several microseconds. 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 polymeric iridium(III) complexes via the so-called bridge-splitting method is described. [3] Therefore the respective dimeric precursor complexes [Ir(ppy)<sub>2</sub>C]2 (ppy = phenylpyridine) and [Ir(ppy-CHO)<sub>2</sub>C]2 (ppy-CHO = 4-(2-pyridyl)benzaldehyde) were coordinated to a bipyridine carrying poly(e-caprolactone) (PCL) tails as well as to terpyridine functionalized poly(ethyleneglycol) 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) centers to the bipyridine macroligand and the respective terpyridine functionalized polymers. The photophysical and electrochemical properties of the iridium(III) containing polymers revealed color-shifts depending on the substituents of the cyclometalating ligands. Processing features of the materials will be shown. Excitation of films of the light-emitting polymers at 365 nm yielded yellow emission. [1] Newkome, G. R.; Patri, A. K.; Holder, E.; Schubert, U. S. Eur. J. Org. Chem. 2004, 2, 235. [2] Schubert, U. S.; Eschbaumer, C. Angew. Chem. Int. Ed. 2002, 41, 2892. [3] Neve, F.; Crispini, A.; Campagna, S.; Serroni, S. Inorg. Chem. 1999, 38, 2250.

#### 3:45 PM DD4.5

##### Phosphorescence quantum efficiency and intermolecular interaction of iridium(III) complexes in co-deposited films with organic semiconducting hosts.

Yuichiro Kawamura<sup>1</sup>, Kenichi Goushi<sup>2</sup>, Jason Brooks<sup>3</sup>, Julie J. Brown<sup>3</sup>, Hiroyuki Sasabe<sup>2,1</sup> and Chihaya Adachi<sup>2,1</sup>; <sup>1</sup>CREST program, Japan Science and Technology Agency, 1-32-12 Higashi, Shibuya, Tokyo, Japan; <sup>2</sup>Department of Photonics Materials Science, Chitose Institute of Science and Technology, 758-65 Bibi, Chitose, Hokkaido, Japan; <sup>3</sup>Universal 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 lead to highly efficient OLED devices that are able to utilize both singlet and triplet electrogenerated 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 ( $\eta_{EL}$ ) as high as 19%. Considering losses in efficiency due to light out-coupling from the substrate, it is believed that the internal efficiency ( $\eta_{int}$ ) of this green phosphorescent device approaches 100%. In this study, The solid state photoluminescent quantum efficiencies ( $\eta_{PL}$ ) for three Ir(III) complexes used as dopants in OLEDs are reported herein: The green emitting complex, *fac*-tris(2-phenylpyridinato)iridium(III) (Ir(ppy)<sub>3</sub>), the red emitting bis[2-(2'-benzothienyl)pyridinato-N,C<sup>3'</sup>]

(acetylacetonato)iridium(III) ( $\text{Btp}_2\text{Ir}(\text{acac})$ ), and the blue complex bis[(4,6-difluorophenyl)pyridinato- $\text{N},\text{C}^2$ ] (picolinato)iridium(III) (Flrpic) were prepared as co-deposited films with a 4,4'-bis(N-carbazolyl)-2,2'-biphenyl (CBP) host. The maximum  $\eta_{\text{PL}}$  values for  $\text{Ir}(\text{ppy})_3$ ,  $\text{Btp}_2\text{Ir}(\text{acac})$ , and Flrpic were respectively  $97 \pm 2\%$  (at 1.5 mol%),  $51 \pm 1\%$  (at 1.4 mol%), and  $78 \pm 1\%$  (at 15 mol%). We also found that the maximum  $\eta_{\text{PL}}$  of Flrpic reached  $99 \pm 1\%$  when doped into the high triplet energy host m-bis(N-carbazolyl)benzene (mCP) at an optimal concentration of 1.2 mol%. This suggests that the triplet energy of Flrpic can be effectively confined by using a host material having a high enough triplet energy. As the doping concentrations are increased, concentration quenching significantly decreases the  $\eta_{\text{PL}}$  of all the complexes. The radiative decay rates at each concentration are found to be independent of the average distance between two adjacent Ir(III) complexes, and the concentration quenching rate ( $k_{\text{CQ}}$ ) 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  $\text{Ir}(\text{ppy})_3$  in CBP, 0.74 nm for  $\text{Btp}_2\text{Ir}(\text{acac})$  in CBP, and 1.14 nm for Flrpic in mCP.

#### 4:00 PM DD4.6

**Unusual phosphorescence decay characteristics of  $\text{Ir}(\text{ppy})_3$  in a solid matrix.** Kenichi Goushi<sup>1,2</sup>, Yuichiro Kawamura<sup>2</sup>, Jason Brooks<sup>3</sup>, Julie J. Brown<sup>3</sup>, Hiroyuki Sasabe<sup>1,2</sup> and Chihaya Adachi<sup>1,2</sup>; <sup>1</sup>Photonics Materials Science, Chitose Institute of Science and Technology, Chitose, Hokkaido, Japan; <sup>2</sup>Japan Science and Technology Agency, Shibuya, Tokyo, Japan; <sup>3</sup>Univocal Display Co., Ewing, New Jersey.

Organic phosphors have been used as electroluminescence (EL) materials in organic light emitting diodes (OLEDs) and have attracted considerable attention due to their high EL efficiency. OLEDs using phosphors can overcome the limitations on internal quantum efficiency of 25% in fluorescence-based OLEDs. In particular, OLEDs using iridium (Ir) complexes ((2-phenylpyridine)iridium derivatives) have demonstrated very high-efficiency electrophosphorescence approaching an internal quantum efficiency of 100%. To understand the detailed luminescence mechanism of *fac* tris(2-phenylpyridine) iridium ( $\text{Ir}(\text{ppy})_3$ ), we investigated the time resolved phosphorescence spectrum of  $\text{Ir}(\text{ppy})_3$  in both 4, 4'-N, N'-dicarbazole-biphenyl (CBP) and polymethylmethacrylate (PMMA) host matrices. From a measurement of the temperature dependence of the phosphorescence intensity and the lifetime of  $\text{Ir}(\text{ppy})_3$  in these hosts, we observed that the phosphorescence intensities are independent of temperature, while the lifetimes significantly increase at temperatures below  $T \cong 50$  K. These characteristic temperature dependences of the transient phosphorescence lead us to conclude that the non-radiative transition rate ( $k_{nr}$ ) from the triplet excited state is very small compared with the radiative transition rate ( $k_r$ ) 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  $S_0$  is proportional 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 rationalize the characteristic temperature dependence 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

**Lanthanide Sensitized Quantum Dots with Tunable Fluorescent Lifetimes.** Thomas A. Schmedake and Thomas Michael Barnard; 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 (see for instance Proc. Nat. Acad. Sci., USA 91, 10024-10028, (1996)). The lanthanides are tethered to the quantum dots via a thiol terminated ligand of variable length to control the distance separating the II-VI quantum dot and the lanthanide sensitizer. The distance separating the donor-acceptor pair determines the rate of energy transfer from the lanthanide to the quantum dot. The result is a multiexponential fluorescent signal from the quantum dot that includes a tunable long tau contribution from the lanthanide pumping. The use of these new materials in "bar-coding" applications will be demonstrated.

#### 4:30 PM DD4.8

**Novel Electron Transporting Materials and Their Use in Organic Light-Emitting Diodes.** Simona Garon, Sudhakar Madhusoodhanan, Eugene Polikarpov and Mark E. Thompson;

University of Southern California, Los Angeles, CA, California.

New concepts for the molecular design of amorphous molecular materials for use in organic light-emitting diodes (OLEDs) have been presented and novel electron-transporting amorphous molecular materials were investigated. These materials permitted the fabrication of thermally stable, high performance OLEDs. Here we investigated the characteristics of fluorene trimer ( $\text{F}_3$ ) doped by weight with dibenzo18-crown-6 ether (DBC) as new electron transport layer for OLEDs. Amorphous ter(9,9-diarylfuorene)s show an interesting ambipolar carrier transport and high electron mobility in the order of  $10^{-3} \text{ cm}^2/(\text{Vs})$  magnitude making them suitable to use as electron transport layer (ETL) in organic light-emitting diodes. The  $\text{F}_3$  doped with DBC aluminum (III) tris (8-hydroxyquinoline), ( $\text{Alq}_3$ ), based OLED (NPD 50nm/ $\text{Alq}_3$  30nm/ $\text{F}_3$ :DBC (15% by weight) 20nm/Li 1nm/Al 100nm) gave a peak external quantum efficiency of 2.2% at 100  $\text{Cd/m}^2$ . Lithium or LiF incorporation prior the cathode deposition as monolayer film has been shown to be an effective electron injector due to a low work function value. We selected to use dibenzo18-crown-6 ether as trapping agent for Li ion since crown ethers have high affinity toward alkali metals and DBC prevents the metal ion to diffuse deeply in the  $\text{Alq}_3$  layer. Different percentage of DBC doping level has been investigated with annealing procedures to verify the effect in devices performance. Application to efficient electrophosphorescent organic light-emitting diodes (PHOLEDs) has been developed and discussed.

#### SESSION DD5: Plasmonics

Wednesday Morning, December 1, 2004  
Room 310 (Hynes)

#### 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 metallodielectric 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 fringing field of the resonant 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.** Yongqiang 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. 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. Our theory is based on the Lagrangian formulation of semiclassical



electrodynamics, where we treat the nanoparticle optical response quantum-mechanically within the jellium model. We discuss the insights obtained from such microscopic analysis for understanding light confinement in subwavelength structures and near-field mediated electromagnetic energy transport through resonant excitation of surface plasmon polariton modes. We also discuss light scattering by charged metal nanoparticles.

#### 9:15 AM DD5.3

**Local Plasmon Resonance Properties of Highly Ordered Metal Nano-Dot Array Prepared Using Anodic Porous Alumina.** Futoshi Matsumoto<sup>1</sup>, Kazuyuki Nishio<sup>1,2</sup> and Hideki Masuda<sup>1,2</sup>; <sup>1</sup>Kanagawa Academy of Science and Technology, Kanagawa, Japan; <sup>2</sup>Department of Applied Chemistry, Tokyo Metropolitan University, Tokyo, Japan.

Highly ordered metal dot array with controlled nanometer-sized diameter and spacing have recently attracted growing interests, because discrete metal nano-dots with nanometer-sized diameter such as Au and Ag show characteristic optical properties which are applicable to high-sensitive optical detection of biomolecules through surface-enhanced Raman spectroscopy and surface plasmon resonance spectroscopy and the arrays composed of highly ordered metal nano-dots are expected to improve the optical properties. In the present study, the 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 arrays fabricated were studied. Anodic porous alumina membranes formed by anodizing aluminum in an acid 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 size 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 height 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 as mask for vacuum evaporation was shown to be possible. [1] H. Masuda, et al., Jpn. J. Appl. Phys., 35, L126 (1996). [2] H. Masuda, et al., Adv. Mater., 12, 1031 (2000). [3] H. Masuda and K. Fukuda, Science, 268 146 (1995). [4] H. Masuda, et al., Appl. Phys. Lett., 71, 2770 (1997).

#### 9:30 AM DD5.4

**Percolation-Enhanced Supercontinuum and Second-Harmonic Generation from Metal Nanoshells.** Aiqing Chen, Rohde A. Charles and Miriam Deutsch; University of Oregon, Eugene, Oregon.

Nanometer-sized metal particles have been the focus of extensive studies owing to their greatly amplified nonlinear optical (NLO) response. These amplifications are attributed mainly to large enhancements of surface-induced electric fields at the nanoparticles' surface plasma resonance (SPR). Additionally, localization of plasmon fields into "hot-spots" in semicontinuous metal films manifests in extremely large local EM fields and giant enhancements of surface 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 (typically 10-30nm) surrounding dielectric core particles. These systems exhibit unique linear extinction spectra, tunable through appropriate design of their core-shell thickness ratios. We have developed a new chemical deposition technique to fabricate silica-core/silver-shell monodisperse colloidal spheres. Silica spheres with highly controllable size distributions and diameters in the range of 100nm-1000nm are grown by the Stober method. On these we grow granular and uniform silver nanoshells (20-50nm) using a variation of the Tollen's reaction. This deposition protocol does not require functionalization of the silica for the attainment of complete silver shells. The optical response of disordered aggregates of metal-coated spheres, as well as of single metallodielectric spheres will be discussed in detail. In particular, strong nonlinear optical response has been observed under illumination with ultrashort 850nm laser pulses. We observed a frequency-doubled signal at 425nm, and an intense white-light scattered background. Both signals were absent when illuminating uncoated silica spheres. The SHG is attributed to dipole effects induced at the metal surfaces, as well as quadrupole contributions. The continuum generation is related to the enhanced Kerr nonlinearity observed in random metallodielectric films near the percolation threshold. These unique systems allow us to address for the first time percolation-enhanced NLO scattering in microscopic spherical geometries. In such environments additional enhancements

should exist from coupling of geometrical (Mie) resonances to localized plasmon modes. The prospects of observing strong NLO enhancements in ordered arrays of these spheres (photonic crystals) will also be discussed.

#### 10:15 AM DD5.5

**Single Nanoparticle Sensors Improved by Gold Nanoshells.** Gunnar Raschke<sup>1</sup>, Thomas A. Klar<sup>1</sup>, Sandra Brogl<sup>1</sup>, Andrei S. Susha<sup>1</sup>, Andrey L. Rogach<sup>1</sup>, Jochen Feldmann<sup>1</sup>, Alfons Nichtl<sup>2</sup> and Konrad Kuerzinger<sup>2</sup>; <sup>1</sup>Photonics and Optoelectronics Group, Physics Department and CeNS, Ludwig-Maximilians-Universitaet Muenchen, Munich, Bavaria, Germany; <sup>2</sup>Roche Diagnostics GmbH, Nonnenwald 2, Penzberg, Bavaria, Germany.

Miniaturisation of molecular sensors is a rapidly growing field in biooptical 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 noble metal nanoparticles are dominated by a pronounced resonance in their light scattering spectra caused by a collective oscillation of the conduction band electrons. The spectral position of this nanoparticle plasmon resonance (NPPR) depends on intrinsic nanoparticle parameters like their shape and material composition. Even more important, the resonance position also depends sensitively on the refractive index of the nanoparticles' surrounding, rendering it suitable as a nanoscale sensor for its dielectric environment. Molecular binding events close to the surface of a nanoparticle change the dielectric environment and can therefore be deduced from the shifted scattering spectrum of a functionalized, single gold nanoparticle [1]. To increase the sensitivity of single nanoparticle molecular sensors, we investigate the NPPR of gold nanoshells. These nanoshells are composed of a thin gold layer coated on dielectric Au<sub>2</sub>S nanoparticles [2, 3]. Our measurements reveal that molecular identification indeed can be improved threefold by the use of gold nanoshells instead of solid spherical nanoparticles: (i) the 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 [3] and (iii) the scattering spectra show sharper resonances. In particular, we find a narrow homogeneous NPPR linewidth of typically 180 meV for a single Au<sub>2</sub>S/Au nanoshell. By comparing our data with Mie-theory calculations, we conclude that roughly half of the homogeneous linewidth is due to scattering of electrons at the surface of the gold shell. The observed surface scattering is much less than previously expected from extinction measurements on ensembles of nanoshells. Thus, gold nanoshells may also improve SERS and increase nonlinear optical effects to a larger extent than expected. [1] G. Raschke, S. Kowarik, T. Franzl, C. Sönnichsen, T. A. Klar, J. Feldmann, A. Nichtl, and K. Kürzinger, Nano Letters, 3, 935 (2003) [2] H. S. Zhou, I. Honma, H. Komiyama, J. W. Haus, Phys. Rev. B 50, 12052 (1994) [3] R. D. Averitt, D. Sarkar, N. J. Halas, Phys. Rev. Lett. 78, 4217 (1997)

#### 10:30 AM DD5.6

**Nonlinear Transmission of Surface Plasmon Polariton Modes in an Optical Nanowire.** Nicolae Coriolan Panoiu and Richard M. Osgood; Applied Physics and Applied Mathematics, Columbia University, New York, New York.

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 plasmon 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 is 75 nm, and the thickness of the spherical shells, made from dielectrics with Kerr optical nonlinearity such as polymers or semiconductor materials, is 10 nm. The FDTD algorithm is fully rigorous and incorporates both the nonlinear optical response of the dielectric shells as well as the frequency dispersion of the metallic spheres, which is considered to obey the Drude model. In the linear limit, the optical nanowire supports two surface plasmon polariton modes, a transverse one with  $\lambda_t = 333.36$  nm, for which the electric field is perpendicular to the axis of the wire and a longitudinal one with  $\lambda_l = 307.5$  nm, for which the electric field is along the axis of the nanowire. Furthermore, our numerical simulations show that for an input power  $P_0 = 100$  MW/cm<sup>2</sup>, the wavelength of the transverse surface plasmon polariton mode is shifted by  $\Delta\lambda = 43.5$  nm when the Kerr coefficient is increased from  $n_2 = 10^{-18}$  m<sup>2</sup>/W to  $n_2 = 8 \cdot 10^{-14}$  m<sup>2</sup>/W. Conversely, if the dielectric shell is made of a material with Kerr coefficient  $n_2 = 1.5 \cdot 10^{-17}$  m<sup>2</sup>/W (e.g. GaAs-based semiconductors) the transverse surface plasmon polariton mode is shifted by  $\Delta\lambda = 12.9$  nm when the input power varies between  $P_0 = 100$  MW/cm<sup>2</sup> and  $P_0 = 130$  GW/cm<sup>2</sup>. Finally, the potential use of these nonlinear effects to

design nanoscale active optical devices is discussed.

#### 10:45 AM DD5.7

**Plasmonic Characterization and Actuation of Opto-electronic Molecular Switches.** Nick Melosh and Ken Shimizu; Materials Science and Engineering, Stanford, Stanford, California.

Although molecular optical or electronic switches promise to deliver fast and economic solutions to increasing computing demands, these nanoscale devices are limited by our understanding of the physics within current architectures, and the difficulty of designing an optical molecular device structure. We report results on a new plasmonic device that allows us to both characterize 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. Shahbazyan; 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 radial contractions 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 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 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 to nanoshell aspect ratio. Supported by NSF under grants DMR-0305557 and NUE-0407108, by NIH under grant 5 SO6 GM008047-31, and by ARL under grant DAAD19-01-2-0014. 1. N. Del Fatti et al., J. Chem. Phys. 110, 11484 (1999). 2. J. Hodak et al., J. Chem. Phys. 111, 8613 (1999).

#### 11:15 AM DD5.9

**Gold Nanorod Nucleation from Colloid Seeds.** Hongwei Liao<sup>1</sup> and Jason H. Hafner<sup>1,2</sup>; <sup>1</sup>Chemistry Department, Rice University, Houston, Texas; <sup>2</sup>Physics 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 mechanism. The 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 colloid seed particles 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 stages under simple conditions 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.** Futao Kaneko<sup>1,2</sup>, Susumu Toyoshima<sup>3</sup>, Yasuo Ohdaira<sup>1,2</sup>, Kazunari Shinbo<sup>1,2</sup> and

Keizo Kato<sup>2,3</sup>; <sup>1</sup>Electrical and Electronic Engineering, Niigata University, Niigata, Japan; <sup>2</sup>Center for Transdisciplinary Research, Niigata University, Niigata, Japan; <sup>3</sup>Graduate School of Science and Technology, Niigata University, Niigata, Japan.

Emission light due to surface plasmon (SP) excitations has been investigated in Kretschmann configuration of prism/metal thin film/organic 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. Intensities and spectra 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- (light) 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

**Synthesis and Characterization of Functionalized Guanidines for Development of Electro-Optic Materials with Highly Desirable Properties.** Nicholas Buker<sup>1</sup>, Larry R. Dalton<sup>1</sup>, Kimberly A. Firestone<sup>1</sup>, Alex K.-Y. Jen<sup>2</sup> and Marnie Haller<sup>2</sup>; <sup>1</sup>Chemistry, University of Washington, Seattle, Washington; <sup>2</sup>Materials Science and Engineering, University of Washington, Seattle, Washington.

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  $\pi$ -electron system that connects electron rich moieties (donors) to electron deficient functionalities (acceptors). Hyperpolarizability ( $\beta$ ), is the critical parameter that defines molecular NLO behavior. Optimization of NLO chromophores has proven to be a challenging task because enhancement of  $\beta$  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 Prakash Bhatambrekar<sup>1</sup>, Scott Hammond<sup>1</sup>, Jessica Sinness<sup>1</sup>, Olivier Clot<sup>1</sup>, Harrison L. Rommel<sup>1</sup>, Antao Chen<sup>3</sup>, Bruce Robinson<sup>1</sup>, Alex K.-Y. Jen<sup>2,1</sup> and Larry Dalton<sup>1</sup>; <sup>1</sup>Chemistry, University of Washington, Seattle, Washington; <sup>2</sup>Materials Science and Engineering, University of Washington, Seattle, Washington; <sup>3</sup>Applied 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 Sinness<sup>1</sup>, Olivier Clot<sup>1</sup>, Nishant Bhatambrekar<sup>1</sup>, Scott R. Hammond<sup>1</sup>, Harrison L. Rommel<sup>1</sup>, Bruce H. Robinson<sup>1</sup>, Alex K-Y. Jen<sup>2</sup> and Larry R. Dalton<sup>1</sup>; <sup>1</sup>Chemistry, University of Washington, Seattle, Washington; <sup>2</sup>Materials 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 ( $r_{33}$ ). This deficiency of order represents one major obstacle that must be overcome before E-O device commercialization can be achieved. This lack of order is in part due to the large dipole moments of high  $\mu\beta$  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 to give a three dimensional structure in order 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 Matsui<sup>1</sup>, Masaya Mitsuishi<sup>1</sup>, Atsushi Aoki<sup>2</sup> and Tokuji Miyashita<sup>1</sup>; <sup>1</sup>Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Miyagi, Japan; <sup>2</sup>Graduate 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 assembly (polymer nanosheet) 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 gates (AND and EXOR). One nano-sheets diode 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. Firstly, to produce the AND logic gate, we assembled these film 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 nano-sheet photodiodes so that the direction of each photocurrent flow becomes opposite. For selective photoexcitation of the phenanthrene chromophore in the array cathodic photocurrent was generated by the interlayer charge-transfer reaction between phenanthrene and dinitrobenzene unit. Selective photoexcitation of the anthracene at 380 nm produced anodic photocurrent was observed similarly. Furthermore, when both chromophores were irradiated simultaneously, the output photocurrent was canceled out because the photocurrent direction was opposite between photodiode 1 and 2, resulted in a very small value. Therefore, the assembly of nano-sheets operates as an EXOR logic gate. Notably, these polymer sheets 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-Peryrene-Phenanthroline Structure.**

Yutaka Ohmori, Taichiro Morimune and Hirotake Kajii; 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 structure for high speed photo-detectors. The organic nano structures were fabricated using organic molecular deposition system (OMBD). Organic hetero-structure consists of ITO (Indium-Tin-Oxide) anode, CuPc (copper phthalocyanine) and BPPC (N,N'-bis(2,5-di-tert-butylphenyl)-3,4,9,10-perylene-dicarboximide), 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 band width, optical signals of moving picture can be detected using optical transmission with red light emitting diode (620 nm). Photo detectors using copper 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.

### 3:30 PM \*DD6.6

**Size-Dependence of the Linear and Nonlinear Optical Properties of GaN Nanoclusters.** Andrew C. Pineda<sup>1,2,3</sup> and Shashi P. Karna<sup>4</sup>; <sup>1</sup>Space Vehicles Directorate, Air Force Research Laboratory, KAFB, New Mexico; <sup>2</sup>Chemistry, The University of New Mexico, Albuquerque, New Mexico; <sup>3</sup>Center for High Performance Computing, The University of New Mexico, Albuquerque, New Mexico; <sup>4</sup>Weapons and Materials Directorate, U.S. Army Research Laboratory, Aberdeen Proving Ground, Maryland.

The linear and nonlinear optical (NLO) properties of III-V binary semiconductors have been a subject of active research since the late 1960s. Recent advancements in (a) experimental techniques to fabricate/produce stable nanometer-size binary atomic clusters composed of group III and group V elements and (b) techniques and tools to probe response properties of nano-scale objects, have attracted a great deal of attention in the linear and NLO properties of III-V nanoclusters due to their potential applications in future technologies. An important issue in a bottom-up approach to fabricating nanoclusters for future technological applications is an understanding of the evolution of response properties with cluster size. In order to develop such an understanding, we have undertaken a systematic study of the electronic and geometrical structures and the optical properties of III-V nanoclusters by first-principles ab initio time-dependent Hartree-Fock calculations. In this paper, we present the results of our first-principles quantum mechanical studies of the electronic structure, stability, and linear and NLO properties of Ga<sub>m</sub>N<sub>n</sub> atomic clusters, with values of m and n ranging between 1 and 17. Our calculated results suggest that the linear and NLO properties both exhibit strong dependence on the cluster size and shape. However, the size-dependence is more pronounced for the NLO properties than that for the linear optical properties.

### 4:00 PM DD6.7

**Long-Range Absorption Enhancement in Organic Tandem Thin Film Solar Cells Containing Silver Nanoclusters.** Barry P. Rand<sup>1</sup>, Peter Peumans<sup>2,1</sup> and Stephen R. Forrest<sup>1</sup>;

<sup>1</sup>Department of Electrical Engineering and the Princeton Institute for the Science and Technology of Materials (PRISM), Princeton University, Princeton, New Jersey; <sup>2</sup>Department of Electrical Engineering, Stanford University, Stanford, California.

The interest in using organic materials for solar energy conversion has grown rapidly due to the demand for inexpensive, clean, and renewable energy sources. One factor limiting device performance is that the absorption length of organic materials is typically an order of magnitude larger than the exciton diffusion length. One solution to this problem is to stack multiple, very thin layer photovoltaic (PV) cells in tandem separated by a thin metallic nanocluster layer [1]. Each subcell is sufficiently thin to allow for a large percentage of excitons to dissociate, while the device is thick enough to realize a high absorption efficiency. Inclusion of nanoclusters leads to a significant enhancement in power conversion efficiency beyond that expected in the case where the clusters simply act as charge recombination centers [1]. This work indicates that the enhancement of the incident optical field persists into an organic dielectric for distances of up to 10 nm from the center of a random array of approximately 5 nm diameter nanoparticles. Furthermore, the enhancement exists far from the resonant particle surface plasmon excitation energy. We model these effects based on finite element calculations to elucidate the role that cluster spacing, shape, and embedding media play in determining plasmon enhancement. Dipole interactions between clusters explain the long-range enhancement, and

simulations for silver island films are shown to agree with experiment. The plasmonic enhancement has a wide spectral range, and accounts for the higher than expected power efficiencies of tandem organic solar cells based on an organic heterojunction of copper phthalocyanine (CuPc) and 3,4,9,10-perylene-tetracarboxylic bis-benzimidazole (PTCBI) [1]. [1] A. Yakimov and S. R. Forrest, Appl. Phys. Lett. 80, 1667 (2002).

#### 4:15 PM DD6.8

**Current-Voltage Characteristics in Organic Semiconductor Crystals: Space Charge vs. Contact-Limited Carrier Transport.** Johan Reynaert<sup>1,2</sup>, V. I. Arkhipov<sup>1</sup>, G. Borghs<sup>1</sup> and P. Heremans<sup>1</sup>; <sup>1</sup>MCP, IMEC, Leuven, Belgium; <sup>2</sup>ESAT, KULeuven, Leuven, Belgium.

Numerous experimental studies, mostly based on time-of flight (TOF) technique, showed that the conductivity mechanism in organic crystals is (trap-controlled) 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 perylene 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 same material or a crystalline layer with a 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-hexylthiophene) and Al interface.** Keiichi Kaneto, Mitsuru Ujimoto and Wataru Takashima; Life Science and Systems Engineering, Kyusshu Institute of Technology, Kitakyushu, Japan.

A photo induced memory cell is constructed on a glass substrate by deposition of 1nm Al on 20 micro m channel length of Au electrode array, followed by spin coat with poly(3-hexylthiophene) 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-hexylthiophene)/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-Sullivan<sup>1</sup>, Jonathan S. Steckel<sup>2</sup>, LeeAnn Kim<sup>1</sup>, Mounqi G. Bawendi<sup>2</sup> and Vladimir Bulovic<sup>1</sup>; <sup>1</sup>Department of Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts; <sup>2</sup>Department 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, constraints inherent in this solution based process prevent the production of LEDs with truly monochrome 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 Berggren<sup>1</sup>, Miaoxiang Chen<sup>1</sup>, Erik Perzon<sup>2</sup>, Mats Andersson<sup>2</sup> and Robinson Nathaniel<sup>1</sup>; <sup>1</sup>ITN, Linköping University, Norrköping, Sweden; <sup>2</sup>Chalmers 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-D 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-D 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 Lee<sup>1,2</sup>, John Rogers<sup>1</sup> and Graciela Blanchet<sup>2</sup>; <sup>1</sup>Materials Science and Engineering, University of Illinois, Urbana, Illinois; <sup>2</sup>CR&D, Dupont, Wilmington, Delaware.

It was shown that active matrix circuit could be achieved on flexible substrates using micro-contact printing.[1] 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 12// x 12// large area PDMS (Polydimethylsiloxane) stamp from positive photoresist master. The stamp is then used to print high resolution Au lines onto flexible substrates using standard thiol 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 photoresist when the photoresist 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, Proc. Nat. Acad. Sci. USA 98, 4835 (2001); J. A. Rogers, Science 291, 1502 (2001). [2] G. Blanchet et al. Appl. Phys. Lett. 82, 463 (2003).

#### 8:45 AM DD7.4

**Achievement of Extremely High Current Density of 12000A/cm<sup>2</sup> into Organic Thin Films with High Thermally Conductive Substrates.** Hidetoshi Yamamoto<sup>1</sup>, Hiroki Kasajima<sup>1</sup>, Wataru Yokoyama<sup>1</sup>, Hiroyuki Sasabe<sup>1,2</sup> and Chihaya Adachi<sup>1,2</sup>; <sup>1</sup>Department of Photonics Materials Science, Chitose Institute of Science and Technology, 758-65 Bibi, Chitose, Hokkaido, Japan; <sup>2</sup>CREST 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  $E_{th}$  10μJ/cm<sup>2</sup>, corresponding to a current density of 3000A/cm<sup>2</sup> for realization of electrical ASE. However, with the conventional organic light emitting diode (OLED) structure of α-NPD/Alq<sub>3</sub>, it brakes down at a maximum current density of only  $J_{max}$  10A/cm<sup>2</sup>. 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 low thermal stability. 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 (< 1×10<sup>-4</sup> 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 100nm-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  $J_{max}$  = 12222A/cm<sup>2</sup>, the highest ever reported. Here, we employed a 25 nm-thick Copper phthalocyanine (CuPc) thin film sandwiched between an ITO anode and a MgAg/Ag cathode with an active electrode dot size (S) of  $S = 2.0 \times 10^{-5}$  cm<sup>2</sup> (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 organic 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 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 ( $J \leq 1000 \text{ mA/cm}^2$ ), the significant difference of the J-V characteristics was observed in high current density region ( $J > 1000 \text{ mA/cm}^2$ ). These results suggest that the J-V characteristics are controlled by the trap-free space charge limited current (SCLC) [ $J = (9/8)\mu\epsilon\epsilon_0(V^2/d^3)$ ] in the high current density region, while the J-V characteristics are controlled by the trapped charge limited current (TCLC) [ $J = V^{m+1}$ ] in the low current density region.

9:00 AM **DD7.5**

**Blue Luminescence and Electroluminescence from (CdS)ZnS Core-Shell Nanocrystals.** Jonathan S. Steckel<sup>1</sup>, Seth Coe-Sullivan<sup>2</sup>, John P. Zimmer<sup>1</sup>, Nathan E. Stott<sup>1</sup>, Vladimir Bulovic<sup>2</sup> and Mouni G. Bawendi<sup>1</sup>; <sup>1</sup>Chemistry, MIT, Cambridge, Massachusetts; <sup>2</sup>Electrical Engineering and Computer Science, 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 (CdSe)ZnS core-shell nanocrystals, but blue QD-LEDs have remained elusive due to a lack of blue emitting core-shell material. The ideal blue emission spectrum of an LED for a flat panel display application would have a narrow bandwidth and a wavelength such that its coordinates on the Commission International d'Eclairage (CIE) Chromaticity Diagram would lie to the outside of the current National Television System Committee (NTSC) standard color triangle. For a gaussian emission spectrum with a full width at half maximum (FWHM) of 30 nm and a maximized perceived power, the ideal wavelength of blue emission for display applications is 470 nm. We 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  $\leq 28$  nm), with quantum yields of 20-30%. We also demonstrate saturated blue electroluminescence (CIE<sub>x</sub> = 0.18, CIE<sub>y</sub> = 0.13) from these core-shell materials by embedding them in an organic thin film device.

9:15 AM **DD7.6**

**New Wide Band Gap Host Materials for Blue Dye-Doped OLEDs.** Linda Susan Sapochak, Angasa 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 to the triplet state of the phosphor. Although internal quantum efficiencies have reached >90% this has only been achieved for green emission. Development of power efficient blue OLEDs based on this technology has been particularly challenging because the host material must exhibit triplet level emission < 450 nm (energy > 2.75 eV) to achieve efficient (exothermic) energy transfer without sacrificing charge transporting properties. Current amine-based host materials (i.e., aryl bridged dicarbazoles) do not meet these requirements. Blue shifted emission and higher triplet state energies can be achieved by replacement of the N-heteroatoms in triaryl diamines with phosphoryl (P=O) groups. The C-N bonds in triaryl amines are approximately trigonal planar and although the aryl rings are twisted the lone pair electrons on N are delocalized in the aryl rings. In contrast, the rigid tetrahedral geometry about the P-atom prevents communication between the bridging and outer aryl groups resulting in higher absorption and emission energies. Photophysical properties, physical properties (thermal and chemical stability) and preliminary device results will be presented for a series of aryl bridged diposphine oxide materials. Exploitation of this new class of wide band gap host materials for blue electrophosphorescent OLEDs will be discussed.

9:30 AM **DD7.7**

**New Blue Light Emitting Polymers and High Energy Hosts for Triplet Emission.** Andrew Bruce Holmes<sup>1,3</sup>, Khai Leok Chan<sup>1,3</sup>, Sung Yong Cho<sup>1,3</sup>, Nicholas R. Evans<sup>1</sup>, Chris S. K. Mak<sup>1,3</sup>, Scott E. Watkins<sup>1,3</sup>, Richard H. Friend<sup>2</sup>, Anna Hayer<sup>2</sup> and Anna Koehler<sup>2</sup>; <sup>1</sup>Melville Laboratory, University of Cambridge, Cambridge, United Kingdom; <sup>2</sup>Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom; <sup>3</sup>Bio21 Institute, University of Melbourne, Parkville, Victoria, Australia.

Much interest has been focused on the use of poly(fluorene)

derivatives as the emissive layer in blue polymer light emitting devices, but they suffer from the evolution of an unwanted long wavelength emission in the green region of the visible spectrum which has been attributed to the presence of ketone (fluorenone) defects. In this paper we describe the synthesis of a poly(dibenzosilole) blue light emitting polymer which shows considerable resistance to thermal and oxidative degradation. In a second aspect of this presentation a variety of high energy triplet host polymers based on carbazole and twisted biphenyl comonomers are described and their potential for promoting energy transfer to phosphorescent iridium complexes is reported. In particular a comparison is made between blends of phosphors and covalently linked host-guest complexes.

9:45 AM **DD7.8**

**Highly Luminescent Composite Films from Core-Shell Oxide Nanocrystals.** Valerie Buissette, Melanie Moreau, Thierry Gacoin and Jean-Pierre Boilot; Solid State Chemistry Group, Laboratoire de Physique de la Matière Condensée, CNRS Ecole Polytechnique, Palaiseau, 91128, France.

Luminescent nanocrystals could find interesting applications for the elaboration of light emitting transparent materials. This requires the synthesis of nanoparticles with optimized properties such as luminescence efficiency, surface passivation and functionalization to ensure dispersion within a transparent dielectric host matrix. The work described here is based on a new aqueous colloidal synthesis of lanthanide phosphate nanoparticles  $\text{LnPO}_4 \cdot x\text{H}_2\text{O}$  ( $x = 0.7$ ), where Ln = La, Ce, Tb, Eu, through the use of a mixture of lanthanide salts and sodium tripolyphosphate TPP precursors in water. Hydrolysis of TPP groups and subsequent growth of lanthanide phosphate particles are observed after aging at 90°C. This leads to well-dispersed TPP-capped colloids of  $\text{LnPO}_4 \cdot x\text{H}_2\text{O}$  exhibiting the rhabdophane type structure and average sizes below 10 nm. These transparent solutions show violet (Ln = La and Ce), green (Ln = La, Ce and Tb) or red (Ln = La and Eu) luminescence under UV excitation (254 nm). Concerning (La, Ce, Tb)PO<sub>4</sub>·xH<sub>2</sub>O rhabdophane nanoparticles, the luminescence quantum yields are high (45%) compared to other colloidal luminescent systems in water (20-30%), but significantly lower than for the equivalent bulk material (93%). The partial quenching of the luminescence observed in aqueous colloids is essentially related to OH groups located at the surface. Another difference is that Ce-Tb energy transfers are strongly reduced in the case of nanoparticles compared to the bulk materials. The weak efficiency of energy transfers in nanoparticles, which has been previously demonstrated in the YVO<sub>4</sub>:Eu system (J. Phys. Chem. B, 107 (2003) 6754-59), is probably associated with their intrinsic characteristics such as surface effects and structural distortions. Improvement of the luminescence properties of the nanocrystals was achieved through the elaboration of core/shell nanostructures, following the principles previously developed for CdSe quantum dots. Extension of our synthetic process allows the growth of a lanthanum phosphate crystalline phase at the surface of the luminescent nanoparticles. 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 organically modified silica shell using a functionalized silane precursor. Concentrated sols 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 Bin Hu; Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee.

The co-existence 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-S0 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 Forster 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 the S-T energy transfer in the mixtures of phosphorescent Ir-dye and fluorescent material (fluorene polymer) by using different organic solvents for spin cast. The 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-orbital coupling and thus dramatically influence the S-T energy transfer, presenting a new pathway to improve the organic electroluminescence efficiency.

**10:45 AM DD7.10**

**Self-Assembling Luminescent Amphiphiles.** Marina Sofos<sup>1</sup>, James F. Hulvat<sup>1</sup>, Keisuke Tajima<sup>2</sup> and Samuel I. Stupp<sup>1,2,3</sup>; <sup>1</sup>Materials Science and Engineering, Northwestern University, Evanston, Illinois; <sup>2</sup>Department of Chemistry, Northwestern University, Evanston, Illinois; <sup>3</sup>Feinberg School of Medicine, Northwestern University, Chicago, Illinois.

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) asymmetrically end-substituted with a hydrophilic poly(ethylene glycol) (PEG) block and a hydrophobic 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 hydrophile 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.

**11:00 AM DD7.11**

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

Luminescence in oxide/polymer nanocomposites is a well-described phenomenon. The poor variation width of emission wavelength of these 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 ZrO<sub>2</sub> and HfO<sub>2</sub> are used as ceramic kernels. Chlorides, bromides, iodides, or metalorganic, halide free compounds, were used as precursors for the oxide core. Anthracene, or its halide containing derivatives, is 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. Nanocomposites made from chloride precursors generally contain 1 to 2 at% chlorine. Whereas the residual bromine content of nanocomposites made from bromine precursors is approximately 0.1 at%. In case of iodine, residual iodine from the precursor is not detectable. Therefore, one has to assume that chlorine is somehow incorporated in the polymer coating or the ceramic core, too. For nanocomposites made from a metalorganic precursor, coated with 9,10-dichloroanthracene, a chlorine content of 0.5 at% is determined. The luminescence spectra of the halide free nanocomposite powders are similar to the anthracene molecule spectrum except for the strongest line at 420 nm. Halide-free ZrO<sub>2</sub> or HfO<sub>2</sub> kernels, coated with 9,10-dichloroanthracene exhibit luminescence spectra resembling to a superposition of 9-chloro- and 9,10-dichloroanthracene. Obviously a loss of chlorine occurs during synthesis. The nanocomposite powders made from chloride precursors differ totally from the spectra described above. The materials exhibit excimer like spectra with a broad maximum at 540 to 545 nm. Using bromide or iodide precursors, the materials exhibit luminescence spectra of halide-free nanocomposites with reduced intensity. The luminescence intensity decreases with increasing atomic number of the halide. Suspensions of the chlorine containing nanocomposites in ethanol exhibit modified anthracene like spectra. This is a strong indication for dechlorination by hydrogen-chlorine exchange in ethanol. Suspensions of this material in water lead to spectra showing a superposition of excimer spectrum and modified anthracene spectrum, indicating partial dechlorination. The concept of ceramic/lumophore/polymer nanoparticles leads to a large variety of tunable effects. Halides in the system exhibit a strong influence on luminescence that can be exploited technically.

**11:15 AM DD7.12**

**Organic light-emitting transistors using ambipolar FET characteristics.** Takahito Oyamada<sup>1</sup>, Hiroyuki Uchiuzou<sup>1</sup>, Kazumi

Matsushige<sup>2</sup>, Hiroyuki Sasabe<sup>1</sup> and Chihaya Adachi<sup>1</sup>; <sup>1</sup>Department of Photonics Materials Science, Chitose Institute of Science and Technology (CIST), Chitose, Japan; <sup>2</sup>Kyoto university, Kyoto, Japan.

To realize organic light-emitting transistors (OLETs) having efficient light-emission, we fabricated a OLET structure based on a co-deposited film of p-type and n-type materials which leads ambipolar characteristics with efficient hole and electron double injection and transport into the organic active layer. Using this structure, we demonstrate ambipolar FET characteristics with substantial electroluminescence (EL). We investigated the Luminance (L) - Drain current (I<sub>d</sub>) - Drain voltage (V<sub>d</sub>) characteristics of OLETs by changing the molecular ratio of p-type and n-type materials. In the organic co-deposition process, two organic sources were independently controlled in a high-vacuum (<1×10<sup>-3</sup> Pa) thermal evaporation system. A 70-nm-thick co-deposited film of thiophene and naphthalene derivatives are used as p- and n- type semiconductors. The molecular ratios of thiophene and naphthalene derivatives are 3:2, 1:1, 2:3 and 1:2, respectively. A highly doped n<sup>+</sup>-Si (100) wafer which has 300nm-thick-SiO<sub>2</sub> layer (C<sub>i</sub>=1.18×10<sup>-8</sup> F) was used as a gate electrode. Source and drain comb bottom electrodes composed of Cr (0.5nm)/Au (30nm) were formed on the SiO<sub>2</sub>/n<sup>+</sup>-Si layer using conventional photolithography and lift-off techniques. The channel length and width of the electrodes were 4 mm and 25 μm, respectively, with the comb number of 20. With the optimum ratios of p-type and n-type semiconductors, we obtained ambipolar characteristics. Holes and electrons are injected and transported simultaneously into the organic layer and EL with increasing I<sub>d</sub> was clearly observed. The light emission (L) - drain voltage (V<sub>d</sub>) characteristics demonstrates that the threshold voltage for EL is equal to the onset of ambipolar characteristics where the I<sub>d</sub>-V<sub>d</sub> changes from saturation mode into dispersion mode. The external quantum efficiency (η<sub>ext</sub>) of the light emitting devices was estimated to η<sub>ext</sub>≈10<sup>-4</sup>%. Although the η<sub>ext</sub> is still low, the optimization of device parameters such as p/n ratio, channel length and width, and doping techniques surely increases η<sub>ext</sub>.

**11:30 AM DD7.13**

**Ambipolar Injection in a Submicron Channel Light-Emitting Tetracene Transistor with Distinct Source Drain Contacts.** J. Reynaert<sup>1,2</sup>, D. Cheyts<sup>1,2</sup>, D. Janssen<sup>1</sup>, G. Borghs<sup>1</sup>, J. Genoe<sup>1</sup> and P. Heremans<sup>1</sup>; <sup>1</sup>MCP, IMEC, Leuven, Belgium; <sup>2</sup>ESAT, KULeuven, Leuven, Belgium.

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 fabricated an 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.

SESSION DD8: Nanocomposite Optical Materials  
Thursday Afternoon, December 2, 2004  
Room 310 (Hynes)

**1:30 PM DD8.1**

**Nanoparticle-Based Scintillators for Radiation Detection.** Suree Saengkerdsub Brown, Hee-Jung Im, Michelle D. Pawel, Adam J. Rondinone and Sheng Dai; Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

The usage of commercially available inorganic scintillators (particle sizes: μm), despite their high efficiencies and stability, suffers from low solubilities in both inorganic and organic matrices. The opaque materials containing inorganic scintillators have low scintillation efficiencies due to light scattering. The requirement of growing large crystals has been addressed, however, cannot always be met. Organic scintillators (e.g., 2,5-Diphenyloxazole or PPO) although soluble in organic matrices, cannot be simply incorporated with inorganic and hydrophilic materials. The rapid advancement in nanoparticle syntheses and surface modification offers the opportunity for the usage of nanoparticles as new and improved class of transparent scintillators. Organic nanoparticles (e.g., polystyrene) dispersed in hydrophilic media were applied to encapsulate organic scintillators and wavelength shifters (e.g., PPO and POPOP). Several types of highly photoluminescent inorganic nanocrystals, including core-shell (CdSe)ZnS, and doped materials Y<sub>2</sub>O<sub>3</sub>:Ce, ZnS:Ag, and LaPO<sub>4</sub>:Ce, emit light in the blue to UV range which can be effectively detected

by photomultiplier tube in radiation detection. Nanoparticles containing a highly efficient neutron absorber, Li-6, were synthesized for the purpose of neutron detection. Surface 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<sup>1</sup>, Abhijit Sarkar<sup>2</sup>, Purnima Basu Neogi<sup>3</sup>, Harsheetal Liddar<sup>1</sup>, Jianyou Li<sup>1</sup>, Padmarekha Vemuri<sup>1</sup>, Terry Golding<sup>1</sup>, Hadis Morkoc<sup>5</sup> and Brian Gorman<sup>4</sup>; <sup>1</sup>Physics, University of North Texas, Denton, Texas; <sup>2</sup>Michigan Molecular Institute, Midlands, Michigan; <sup>3</sup>Biology, University of North Texas, Denton, Texas; <sup>4</sup>Material Science and Engineering, University of North Texas, Denton, Texas; <sup>5</sup>Virginia 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 functional 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. Guanosine 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 act as donors and acceptors of H-bonds. 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 biological semiconductor occurs 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 3 - 3.5 eV and electron effective mass  $m_e > 2 m_0$  (similar to GaN). SAGC were then successfully self-assembled on GaN/AlN QD matrix. Electron transport properties at the interface were investigated using photocurrent spectroscopy. The radiative energy transfer between the GaN quantum dots and SGCA 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. We intend to fabricate an array 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 SAGC molecule acting as a cross-linker. FDTD 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. Liddell; Materials Science and Engineering, Cornell University, Ithaca, New York.

Symmetry reduction is an important approach to the design of novel photonic crystal 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 600 nm to 3 microns can be synthesized by precipitation induced clustering of preformed monodispersed spheres in acidic aqueous solutions of metal salts and thioacetamide by varying reactant concentration, temperature and time. Here we present a method that enhances control of the size and clustering of spheres in the regime below 600 nm during a secondary reaction by varying the amount of primary reaction supernatant added. Uniform spheres and multimers ranging in the size from 70 nm to 1.2 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 nitrate system. Further characterization by x-ray and electron diffraction showed that the particles were built up from nanocrystallites. The relationship between the particle size, porosity, and refractive index were studied by modeling UV-Vis spectra using the MIE scattering method. Monodispersed zinc sulfide spheres and multimers in the size range from 100 nm to 600 nm can be used as high 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/Zelite Nanocomposites.** Andreas Goldbach<sup>1</sup>, Lennox E. Iton<sup>2</sup> and Marie-Louise Saboungi<sup>1</sup>; <sup>1</sup>Centre de Recherche sur la Matiere Divisee, Orleans, France; <sup>2</sup>Materials 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 nanopores is stabilized through bonding to the zeolitic cations and also through cyclization [2]. The low-frequency Raman spectra yielded the first insight into the intrinsic length scale of the Se dynamics in chain-type nanocomposites [3], and indicated that the microscopic dynamics of ring-type nano-composites are markedly different. The Se band gap broadens from the bulk value of 2 eV up to 3 eV in confinement but it can be narrowed again through interaction with transition metal counter-cations [4]. Thus, the band gap of the confined semiconductor can be tailored within the whole optical range. Also, the photo-stability of the nanocomposites depends on the Se structure. The photodecomposition is a delicate function of the counter-cation and highly selective, yielding charged and neutral degradation products of differing composition [5]. [1] A. Goldbach, L. Iton, M.-L. Saboungi, Chem. Phys. Lett. 281 (1997) 69. [2] A. Goldbach, M.-L. Saboungi, L. Iton, D. L. Price, Chem. Comm. 1999 997. [3] A. Goldbach, M.-L. Saboungi, Eur. J. Phys. E 12 (2003) 185. [4] A. Goldbach, M.-L. Saboungi, L. Iton, D. L. Price, J. Chem. Phys. 115 (2001) 11254. [5] A. Goldbach, L. Iton, M. Grimsditch, M.-L. Saboungi, J. Am. Chem. Soc. 118 (1996) 2004; J. Phys. Chem. B 101 (1997) 330.

#### 2:30 PM DD8.5

**Study on the Novel Synthetic Material for Nano-Hybrid Layered Zr-P Derivatives.** Tsung-Yen Tsai, Fang-Jung Hsu 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 offer the 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 of inorganic/organic hybrid nanocomposites in the near future.

#### 3:15 PM DD8.6

**Preparation of Organic Dye Nanoparticles by Pulsed Laser Ablation in Water.** Tsuyoshi Asahi, Teruki Sugiyama, Kenichi Yuyama and Hiroshi Masuhara; Applied Physics, Osaka University, Osaka, Japan.

Organic nanoparticles consisting of aromatic and dye molecules have attracted increasing attention, as they are expected to be useful as pigments, cosmetics, drugs, and new materials for optical and electronic devices. Despite metals and semiconductors, 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.<sup>1,2</sup>

Microcrystalline powder suspended in a poor solvent is exposed to intense laser pulses, which induces fragmentation of the initial crystals. Consequently, the opaque suspension is converted into a transparent colloidal solution. In this paper, we report on the nanoparticle preparation of various kinds of organic pigments in water by using nanosecond YAG laser as a light source. We examined 5 compounds; Quinidine Yellow, Oralith Brilliant Pink R, Deep Red, quinacridone, and aluminum chloride phthalocyanine, which were used as purchased from companies. Micrometer-sized crystalline powder of the materials was added into water and sonicated for 15 min. The mixture (pigment concentration of about  $10^{-4}$  wt%) was put into a 1 cm quartz cuvette. The microcrystals were suspended in water by stirring the mixture vigorously and then exposed to the third harmonic of nanosecond YAG laser (355 nm, 7 ns, 10 Hz). Before irradiation the supernatant of all samples was almost colorless and most of microcrystals sank on the bottom of the cuvette. Upon laser irradiation above the intensity of a threshold, colored and transparent colloidal solutions were obtained. The colloidal solution exhibited characteristic visible absorption spectra of each parent pigment, and was stable for a few days. We examined laser fluence dependence of the absorption spectra, and confirmed that nanoparticle formation was realized only above a certain threshold of the laser fluence. This means that the formation is based on laser ablation of crystals dispersed in poor solvent. For characterizing prepared nanoparticles, a drop of the supernatant was dried on a silicon substrate, and then their SEM images were observed. From the statistics of many nanoparticles, we estimated the mean size and the distribution. The mean size was almost same for each pigment examined here and ranged from 40 to 60 nm. The size distribution was ranged from 10 to 16 nm. The laser ablation method in poor solvents is very simple and promising. The size distribution of produced nanoparticles is narrow and the nanoparticles can disperse well without any surfactants. Furthermore, nanoparticle formation at the suitable condition can be adjusted by laser properties such as pulse width, wavelength and so on. REFERENCES 1. Y. Tamaki, T. Asahi, and H. Masuhara, J. Phys. Chem. A, 106 (2002) 2135. 2. T. Sugiyama, T. Asahi, and H. Masuhara, Chem. Lett., 33 (2004) 724.

### 3:30 PM DD8.7

**Organic/Inorganic Hybrid Silicate Materials for Optical Applications; Highly Fluorinated Hybrid Glasses Doped with (Erbium-ions/CdSe) Nanoparticles for Laser Amplifier Material.** Kyung M. Choi<sup>1</sup> and John A. Rogers<sup>1,2</sup>; <sup>1</sup>Bell Labs, Lucent Technologies, Murray Hill, New Jersey; <sup>2</sup>Materials Science and Engineering, University of Illinois at UC, Urbana, Illinois.

A new family of organic/inorganic hybrid silicate materials, bridged polysilsesquioxanes, was designed and synthesized through a molecular-level mixing technique. Since hybrid materials in the molecular-composite level, whose domain sizes are in the nanometer-scale, and whose constituents often lose individual identities and thus create new properties, which hitherto have not been possible from single components, we obtained a set of new properties from those organically modified glasses. By modifying the Si-O-Si polymeric network, we produced controllable, porous glass materials for facile and uniform doping of various ions, metals, or semiconductor particles. By taking advantage of void volume created in those molecularly modified silicate systems, novel optical materials with designed properties can thus be achieved. Via a chemical strategy, we designed hexylene- or fluoroalkylene-bridged polysilsesquioxane doped with both Er<sup>3+</sup> ions and CdSe nanoparticles for the development of new laser amplifier materials. In photoluminescent experiments, a significant enhancement in fluorescent intensity at 1540 nm has been obtained from the fluoroalkylene-bridged glass. Analysis by NMR indicates a dramatically enhanced degree of condensation and a low level of hydroxyl environment in the fluoroalkylene-bridged glass matrix. The presence of CdSe nanoparticles, by virtue of their low phonon energy, also appears to significantly influence the nature of the surrounding environment of Er<sup>3+</sup> ions in those modified silicate systems, resulting in the increased fluorescent intensity. We developed this hybrid glass material as an erbium ion-doped laser amplifier material based on organically modified silica. We also developed a hybrid glass doped with transition metal particles, which generates a huge acoustic wave. We determined five-times higher thermal conductivity of the new hybrid glass. The new hybrid glass also shows 45% of diffraction efficiency compared to that of methanol (25%), which means the compressibility of the new hybrid glass is as effective as liquid. From the examinations, this material is also suggested as a laser device such as diffraction beam modulator.

### 3:45 PM DD8.8

**Buffer System as Effective Means to Focus the Particle Size and Modulate the Morphology.** Chun-hua Yan, Xiao-Cheng Jiang, Wei Feng and Ling-Dong Sun; State Key Lab of Rare Earth Materials Chemistry and Applications & PKU-HKU Joint Lab on Rare Earth Materials and Bioinorganic Chemistry, Beijing, China.

Last decade has witnessed great progress in controlling the size and shape of nanocrystals, which not only established ideal models for studying the quantum confinement effects, but also represented an important step toward practical applications on the basis of their tunable size and morphology dependent properties. In our effort to enable a more facile synthesis and a direct yield of uniform particles, we found that a simple acetate buffering system is very efficient in controlling the size and shape of the nanocrystals. Ceria was taken as the start point. The formed particles are well crystallized and dispersed despite their small size, and exhibit the tendency to form local superstructures. Up to now, the observation of large-scale superlattices is only limited to systems consisting of surfactant modified nanocrystals. In our case, although the formation of superstructures is just local behaviors, it is still quite amazing when considering the absence of any surfactant, and reveals the high quality of as-prepared samples. As the temperature increased to 220 degree C, the shape of nanocrystals evolved from spherical to cubic. Generally, high temperature favors Ostwald ripening process which improves the crystallinity at the sacrifice of uniformity. With further increasing the temperature to 260 degree C, larger nanocubes with well-defined facets and broader size distributions could be produced. With the addition of large amount of buffer, particles with cubic morphology could be produced, which were composed of almost completely {100} faces, originating from the stronger interaction between acetate ions and {100} faces. And as the amount of buffer decreased, only nonuniform irregular particles could be produced, the shape of these particles could be identified as truncated octahedron. This shape evolution from cube to truncated octahedron is mainly concerned with the increase of the ratio of the growth rate along [100] to that along [111], in accordance with the decrease of acetate concentration and weakened interaction with {100} faces. The function of the buffer system is studied. Acetate coordinated compounds act as suitable precursors for the nucleation and posted growth in the system, furthermore, acetate ions also worked as an efficient and stable capping reagent to modify the growth habit of crystals. According to this speculation, the other system, such as rare earth orthoborate, is also studied. It is proved that the buffer system works well for a series of systems.

### 4:00 PM DD8.9

**Microscopic Theory of Surface-Enhanced Raman Scattering in Noble-Metal Nanoparticles.** Vitaliy N. Pustovit and Tigran V. Shahbazyan; Department of Physics, Jackson State University, Jackson, Mississippi.

We study the effect of quantum confinement on surface-enhanced Raman scattering (SERS) from molecules adsorbed on small noble-metal particles. The main SERS mechanism has electromagnetic origin and is due to a strong surface plasmon (SP) local field acting on a molecule near the metal surface. Recent observations of an enormous enhancement of the single-molecule Raman scattering [1,2] as well as the emerging possibilities of nanoparticle-based Raman sensors have prompted a new interest in single particle SERS and, in particular, in finite-size effects in small nanoparticles. We developed a first quantum-mechanical description of SERS in noble-metal nanoparticles that takes into account the effect of the confining potential on the density profile of sp-band and d-band electrons. The spillover of delocalized sp-electrons beyond the classical nanoparticle boundary results in an incomplete embedding of sp-electron distribution in the background of localized d-electrons whose density profile follows more closely the classical shape. In the absence of d-electron population in the nanoparticle surface layer, the effective dielectric constant is reduced relative to the bulk, leading to an underscreening of sp-electrons in the surface layer [3]. We performed numerical calculations of the local field and Raman enhancement factor, based on time-dependent local-density approximation (TDLDA), in small Ag nanoparticles. We found that, the effect of underscreening of sp-electrons in the surface layer leads to a substantial increase in the SP local field acting on a molecule located in a close proximity to the metal surface. This additional enhancement of the Raman signal is more pronounced for small nanoparticles due to the larger volume fraction of the underscreened region. Supported by NSF under grants DMR-0305557 and NUE-0407108, by NIH under grant 5 SO6 GM008047-31, and by ARL under grant DAAD19-01-2-0014. [1] S. Nie and S. R. Emory, Science 275, 1102 (1997). [2] K. Kneipp et al., Phys. Rev. Lett. 78, 1667 (1997). [3] A. Liebsch, Phys. Rev. 48, 11317 (1993).

### 4:15 PM DD8.10

**Photoelectrochemical behaviors of Pt/TiO<sub>2</sub> nanocomposite thin film electrodes prepared by PLD/Sputtering combined system.** Takeshi Sasaki, William T. Nichols and Naoto Koshizaki; Nanoarchitectonics Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan.

Platinum nanoparticle doped titanium dioxide thin films have the unique optical and chemical properties, which arise from quantum size



effects of the embedded nanoparticles in the matrix, or surface effects between the nanoparticles and the matrix. Pt/TiO<sub>2</sub> nanocomposite 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<sub>2</sub> matrix. In this study Pt/TiO<sub>2</sub> nanocomposite thin films were prepared by PLD/Sputtering combined system, where sputtering of TiO<sub>2</sub> and pulsed laser deposition of platinum were utilized. Two variations were utilized for the depositions. Sputtering of TiO<sub>2</sub> and PLD of Pt were performed sequentially to build the nanocomposite layer by layer or simultaneously to form a homogenous 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<sub>2</sub> films. Simultaneously deposited Pt/TiO<sub>2</sub> 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<sub>2</sub>. 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<sub>2</sub> matrix, which can be controlled by process parameters of PLD/sputtering combined system.

#### 4:30 PM **DDS.11**

**Fabrication of Nanocrystals and/or Nanofibers of  $\pi$ -Conjugated Organic Compounds Using the Microwave Irradiation Method.** Hitoshi Kasai<sup>1,2</sup>, Koichi Baba<sup>1</sup>, Shuji Okada<sup>1,2</sup>, Hidetoshi Oikawa<sup>2,3</sup> and Hachiro Nakanishi<sup>1,2</sup>. <sup>1</sup>Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan; <sup>2</sup>CREST, Japan Science and Technology Agency, Kawaguchi, Japan; <sup>3</sup>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 [1] is the 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 [2]. 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 will also be presented. [1] H. Kasai, H.S. Nalwa, H. Oikawa, S. Okada, H. Matsuda, N. Minami, A. Kakuta, K. Ono, A. Mukoh, H. Nakanishi, *Jpn. J. Appl. Phys.* 31 (1992) L1132. [2] K. Baba, H. Kasai, S. Okada, H. Oikawa, H. Nakanishi, *Jpn. J. Appl. Phys.* 39 (2000) L1256.

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<sup>3+</sup> Doped Y<sub>2</sub>O<sub>3</sub> and Lu<sub>2</sub>O<sub>3</sub> Nanoparticles and Processed Ceramics.** A. K. Pradhan, Kai Zhang and G. B. Loutts; Center for Materials research, Norfolk State University, Norfolk, Virginia.

Europium doped Yttrium oxide (Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup>) and Lutetium oxide (Lu<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup>) nanophosphors were synthesized by wet chemical routes using both combustion and coprecipitation 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 Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> nanophosphors with particle size that is influenced by the extrinsic stress, revealed by X-rays and Raman scattering. The influence of Eu<sup>3+</sup> activation on the Raman spectra has been illustrated. We have demonstrated the significant enhancement of emission characteristics of the ceramics synthesized from the nanoparticles using the combustion technique by controlling the vacuum sintering conditions. We have illustrated the crystallite size dependence and the influence of Eu<sup>3+</sup> activation of Lu<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> 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. Our results suggest 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 Anatolevich Eliseev<sup>1</sup>, Natalia Gennadijevna Zhuravleva<sup>1</sup>, Alexey Viktorovich Lukashin<sup>1</sup>, Ulrich Kynast<sup>2</sup> and Yuri Dmitrievich Tretyakov<sup>1</sup>; <sup>1</sup>Department of Materials Science, Moscow State University, Moscow, Russian Federation; <sup>2</sup>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 of novel hybrid luminophores combining solid state properties with optical features typical for the molecular state. The present research deals with synthesis and the investigation of optical properties of terbium and europium picolinates and dipicolinates inside the LDH matrix. The structure of LDH consists of positively charged hydroxide layers, which enables one to control the loading values of anions by variation Mg to Al ratio in the initial precursor. Thus, compounds with different content of Rare Earth complex can be obtained, allowing the investigation of the concentration (and Ln-Ln distance) dependence of properties of the complex inside the matrix. The absorptive and excitability of rare earth containing LDH were found high enough for their possible use as luminescent materials such as phosphors, signaling, sensors and lighting applications in general; their light output is maintained or improved as compared to the molecular complex. Calculated quantum efficiencies range from 30-50 % for different samples. Energy transfer studies in corresponding mixed Tb<sup>3+</sup>/Eu<sup>3+</sup> systems also revealed intra- and intermolecular communication channels, among them Ligand→Tb<sup>3+</sup>/Eu<sup>3+</sup> and Tb<sup>3+</sup>→Eu<sup>3+</sup> transfer, geometrical constraints become a governing factor; in the case of Eu<sup>3+</sup>, additionally Lattice→Eu CT states appear to participate. It was shown that Tb<sup>3+</sup>→Eu<sup>3+</sup> energy transfer strongly depends on Ln-Ln distance and complex geometry. In the frames of present study we also provide the results on formation and intercalation of EuTOPO/EuF<sub>3</sub> core-shell nanoparticles into the interlayer space of layered double hydroxides.

#### **DD9.3**

**Synthesis and Photophysics of Luminescent Platinum(II) Complexes and Materials.** Irina E. Pomestchenko 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 <sup>3</sup>MLCT or triplet  $\pi,\pi^*$  excited states in addition to equilibrated or configuration mixed excited states composed of varying degrees of <sup>3</sup>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 dynamics. 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.

#### **DD9.4**

**Novel, Efficient OLED Materials Based on Organometallic Iridium Complexes.** Shu-Tang Yeh, Kou-Hui Shen, Heh-Lung Huang, Miao-Cai Jhu, Mei-Rung Tseng and Jia-Ming Liu; Materials Research Laboratories, Industrial Technology Research Institute, Chutung, Hsinchu, Taiwan.

Abstract We studied and synthesized red emissive materials with phenyl-quinazoline framework organo-Iridium complexes. We demonstrated high efficient red phosphorescent dopants showed the

maximum PL peak around 640nm and excellent luminescent efficiency with 0.65-0.83 compared to Ir(piq)<sub>3</sub> as a unit. The device configuration of ITO/HTL/CBP:Ir-complex(6%)/BCP/Alq/LiF/Al. The electroluminescent spectrum has a maximum at a wavelength of  $\lambda_{max}$ =648nm. The luminescent efficiencies of the devices was above 1lm/W and maximum brightness were all above 10000 Cd/m<sup>2</sup>. 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 Ir-complex phosphorescent materials for OLED.

#### DD9.5

**Novel and Efficient electroluminescent organo-iridium phosphorescent OLED materials.** Heh-Lung Huang, Kou-Hui Shen, Shu-Tang Yeh, Miao-Cai Jhu, Mei-Rung 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:Ir-complex(4%)/BCP/Alq<sub>3</sub>/LiF/Al showed the EL emitting peak from 536nm to 568nm. The electroluminescent efficiencies of the devices were from 8 lm/W to 17 lm/W and maximum brightness were all above 6000 cd/m<sup>2</sup>. We demonstrated high-efficiency, high-brightness and saturated yellow to orange Ir-complex phosphorescent materials for OLED. Results and Discussions: The general synthetic protocol for yellow to orange phosphorescent complexes: PO-01, PO-02 and PO-03, which are thieno-pyridine framework organo-iridium complexes. A series of nucleophilic attack, oxidation, imination, and cyclization resulted in the thieno-pyridine framework ligands. Dimerization and acetylacetonation afforded the final phosphorescent complexes: PO-01, PO-02 and PO-03. UV absorption bands of PO-01, PO-02, and PO-03 are showing in Table 1. The two UV absorption bands from 282 to 338nm were assigned to a spin-allowed  $1\pi-\pi^*$  transition of the cyclometalated ligand (Table 1), and the bands between 393 to 398nm were assigned to a spin-allowed metal-ligand charge transfer (1MLCT). The most surprising feature of the complex is the strong intensity of the bands between 427 to 438 nm, which are assigned to spin-forbidden 3MLCT band. Therefore, the spin-forbidden 3MLCT band indicates an efficient spin-orbit coupling that is prerequisite for phosphorescent emission. Figure 1 shows the device configuration. There are anode electrode (ITO), hole transport layer, dopant emitter (PO-01, PO-02, or PO-03), host emitter (CBP), hole blocking layer (BCP), electron transport layer (Alq<sub>3</sub>), LiF, and cathode electrode (Al) in this device configuration. 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 electroluminescent efficiencies 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

Thursday Evening, December 2, 2004  
8:00 PM

Exhibition Hall D (Hynes)

#### DD10.1

**Fabrication of Organic-Inorganic Photonic Band Gap Structures via Holographic Photopolymerization.**

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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 band-gap. 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, SiO<sub>2</sub> and TiO<sub>2</sub>),

nanoparticle ionic liquids and semiconductor quantum dots. A model describing the migration of the nanoparticles into three-dimensional patterns, 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.

#### DD10.2

**Two-Photon Frequency Upconversion Lasing in Dye-Doped Dual Range Photonic Bandgap Structure.** Jongseung Yoon<sup>1</sup>,

Wonmok Lee<sup>1</sup>, Edwin L. Thomas<sup>1,2</sup>, Przemyslaw P. Markowicz<sup>3</sup> and Praras N. Prasad<sup>3</sup>; <sup>1</sup>Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Institute for Soldier Nanotechnologies, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>3</sup>Department of Chemistry and Physics, Institute for Lasers, Photonics and 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.

#### DD10.3

**Fabrication of Micro-Optical Devices by Holographic Interference of High Photosensitive Inorganic-Organic Hybrid Materials.** Dong Jun 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 increased by the simple addition of photoactive molecules including a photoinitiator and a photoreactive monomer in the HYBRIMER. Thus, the high photosensitive HYBRIMER was optimized with containing a photoinitiator and a photoreactive monomer as much as over 30 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 form as the Fresnel lens. Thus, these fringes 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 diffraction mask. Thus, it will be demonstrated that the array pattern may be applied to superhydrophobic antireflection coating on glass.

#### DD10.4

**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 opening forbidden 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 lithography. Previously, there have been many demonstrations that various materials can be infiltrated into interconnected nanosize 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 with 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 to {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 infiltrated colloidal crystal that has graded or 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 the refractive index variations. 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.

Thomas A. Schmedake, Adam M. Frake and G. F. Stout; Chemistry, University of North Carolina at Charlotte, Charlotte, North Carolina.

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 on donor-acceptor distances smaller than the wavelength of light, where the Forster mechanism applies. The effect that tuning the O-DOS in sub-micron dielectric spheres has on photochemical and photophysical processes has been 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). Photoactive molecules, such as derivatives of Ru(bipy)<sub>3</sub><sup>2+</sup>, 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 Kaneko<sup>1,4</sup>, Satoru Shimada<sup>2,4</sup>, Takashi Fukuda<sup>2,4</sup>, Tatsumi Kimura<sup>2,4</sup>, Hiroyuki Yokoi<sup>4</sup>, Hiro Matsuda<sup>2,4</sup>, Tsunenobu Onodera<sup>1</sup>, Hitoshi Kasai<sup>1,4</sup>, Shuji Okada<sup>1,4</sup>, Hidetoshi Oikawa<sup>3,4</sup> and Hachiro Nakanishi<sup>1,4</sup>, <sup>1</sup>Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan; <sup>2</sup>National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; <sup>3</sup>National Institute for Material Science, Tsukuba, Japan; <sup>4</sup>Japan Science and Technology, Kawaguchi, Japan.

The ability to control the orientation of crystallites immobilized in a dispersion medium is especially important if they are to be used as optical materials. Recently, we reported the anisotropic orientation of DAST (trans-4-[4-dimethylamino]stilbazolium p-toluenesulfonate, well-known as an organic second-order nonlinear optical material) nanocrystals dispersed in decalin in a magnetic field. In this time, we report the immobilization method of oriented nanocrystals of DAST in a dispersion system that was oriented anisotropically in a magnetic field. The DAST nanocrystals dispersion in lauryl acrylate as polymerizable media with benzoin isopropyl ether as a photoinitiator was prepared using the reprecipitation method. The average size of the DAST nanocrystals prepared here was ca. 694 nm. The immobilization of oriented nanocrystals of DAST was performed in a magnetic field (<17 T) by irradiation of UV light. The polarized absorption spectra of the photocured DAST nanocrystal dispersion were measured with magnetic field (15 T). The maximum contrast in the absorption intensity at 555 nm between samples oriented with polarization angles of 0 degree (parallel) and 90 degree (perpendicular) with respect to the direction of the applied magnetic field was about 0.4. This absorption difference of the sample can be sufficiently recognized through a polarizer even in visual observation. In addition, it was also proven that the anisotropic orientation was retained over at least 6 months. In conclusion, it seems a good method for fixation of the oriented organic nanocrystals to photocure fine particles dispersion with polymerizable monomers while their orientations are controlled in a magnetic field.

#### DD10.7

##### Preparation of Polydiacetylene Nanocrystals Covered with Metal Nanoshell.

Tsunenobu Onodera<sup>1,3</sup>, Hidetoshi Oikawa<sup>1,3</sup>, Hitoshi Kasai<sup>2,3</sup>, Hachiro Nakanishi<sup>2,3</sup> and Takashi Sekiguchi<sup>1</sup>; <sup>1</sup>Nanomaterials Laboratory, National Institute for Materials Science, Tsukuba, Japan; <sup>2</sup>Institute of Multidisciplinary Research for

Advanced Materials, Tohoku University, Sendai, Japan; <sup>3</sup>CREST, Japan Science and Technology Corporation, Kawaguchi, Japan.

Organic  $\pi$ -conjugated polymers have been attracted considerable interest for the purpose of developing high-speed nonlinear optical (NLO) devices. Polydiacetylene (PDA) would be one of the most promising NLO materials owing to fast third-order NLO response in comparison with inorganics. However, the magnitude of so-called  $\chi^{(3)}(\omega)$  value is not still 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  $\pi$ -conjugated main chain of PDA. PDA used was Poly[1,6-Di-(*N*-carbazolyl)-2,4-hexadiyne] (polyDCHD), and polyDCHD nanocrystals as a core was prepared by the precipitation method as follows [ref. 3]: DCHD 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 monomer nanocrystals suspended in water were solid-state polymerized by UV-irradiation (254 nm) using handy lamp, which provided the dark blue dispersion. Next, aqueous solution of metal salt as a precursor of metal nanoshell was added to the suspension. Since ionic surfactant molecules were adsorbed on the surface of polyDCHD nanocrystals, metal ions electrostatically trapped at the surrounding of polyDCHD nanocrystals. Further, aqueous solution of reducing agent was dropwise added, and then metal nanoparticles were formed on the surface of polyDCHD nanocrystals. Finally, metal nanoshell structure was formed on the surface of polyDCHD nanocrystals through the growth of island metal deposition by the treatment with hydroxylamine. Namely, hydroxylamine 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*, **6**, 787 (1989). Ref. 2: F. Caruso, *Adv. Mater.*, **13**, 11 (2001). Ref. 3: T. Onodera *et al.*, *J. Cryst. Growth*, **229**, 586 (2001).

#### DD10.8

##### Size-effects on Fluorescence Spectra of Perylene Nanocrystals Studied by Single-Particle Microspectroscopy Coupled with Atomic Force Microscope Measurement.

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Organic nanocrystals with sizes of tens to a few hundred nanometers show size-dependent optical properties which differ from those of inorganic ones. For example, fluorescence spectrum of perylene nanocrystal below the size of 200 nm show a blue-shift of excimer (E-) emission peak and enhancement of monomer (M-) emission with decreasing of the crystal size. In this paper, we have examined fluorescence spectra and topographic shapes of individual perylene nanocrystals using a far-field fluorescence microscope coupled with an AFM system, and characterized the size-dependent fluorescence spectra of perylene nanocrystals. Perylene nanocrystals were prepared in water by a reprecipitation method. A sample for the single-particle spectroscopy was prepared by dropping the aqueous dispersion on a quartz glass substrate and then by drying it in the air. UV light (405 nm) from a high-pressure Hg lamp was incident onto the sample through a microscope objective, fluorescence from a single nanocrystal was collected through the objective and introduced to a polychromator with a liquid nitrogen cooled CCD camera in order to measure the spectrum. Topographical shapes of the same crystal were obtained with AFM measurements. The perylene nanocrystal exhibits fluorescence emission composing of two bands; one is a broad, structureless E-emission with a peak around 600 nm and the other is a weak monomer M-emission around 480 nm. The peak position of E-emissions shifts to a short wavelength and the relative intensity of the M-emission to the E-emission ( $I_M/I_E$ ) is large compared to the bulk. From the relationship between fluorescence spectra and topographical images of many nanocrystals, it is demonstrated clearly and precisely that the size-dependence is an intrinsic nature of nanometer-sized crystalline perylene. We have found that the peak wavelength and  $I_M/I_E$  are correlated to the crystal size defined by the cubic root of the volume. The shift value of peak wavelength ( $\Delta\lambda$ ) from the bulk increases with the inverse of the crystal size ( $\Delta\lambda \propto 1/\text{size}$ ), and  $I_M/I_E$  increases exponentially with decreasing of the crystal size. These size dependences will be discussed from a view point of destabilization of excimer state energy level, which arises from instability of lattice energy in nanocrystal having a large surface-to-volume ratio.

### **DD10.9**

#### **Fabrication of Rare Earth Ion (Eu<sup>3+</sup>, Tb<sup>3+</sup>)-Doped Polyimide Nanoparticles and Their Unique Luminescence Property.**

Takayuki Ishizaka<sup>2</sup>, Hitoshi Kasai<sup>1,2</sup> and Hachiro Nakanishi<sup>1,2</sup>;

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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 a 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 suit 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<sup>3+</sup>, Tb<sup>3+</sup>)-doped polyimide nanoparticles (30 nm-1 μm) using our original technique of reprecipitation method. As 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<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub>-Au Nanocomposite Films for Smart Sensor Applications.**

George Sirinakis<sup>1</sup>, Lianchao Sun<sup>2</sup>, Rezina Siddique<sup>1</sup>, Harry Efsthadiadis<sup>1</sup>, Michael A. Carpenter<sup>1</sup> and Alain E. Kaloyeros<sup>1</sup>; <sup>1</sup>College of Nanoscale Science and Engineering, University at Albany, Albany, New York; <sup>2</sup>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 yttria-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 work YSZ-Au nanocomposite films were synthesized from a YSZ and a Au target by the radio frequency magnetron co-sputtering technique in combination with a post-deposition annealing treatment in an argon atmosphere, with the annealing temperature being varied from 500-1000 °C in steps of 100 °C. The microstructure and the optical properties of the resulting films were characterized by x-ray diffraction spectroscopy, scanning electron microscopy and spectroscopic ellipsometry. Results on the effect of the Au particle size on the real and the imaginary part of the refractive index of the nanostructured composites are presented. Future smart sensor systems utilizing these multifunctional material sets for harsh environment sensing applications will likewise be outlined.

### **DD10.11**

#### **Molecular Self-Assembly of Highly Two-photon Absorptive Fullerene-Diphenylaminofluorene Dyads.**

Sarika Verma<sup>1</sup>, Tanya Hauck<sup>2</sup>, Prashant A. Padmawar<sup>1</sup>, Taizoon Canteenwala<sup>1</sup>, Long Y. Chiang<sup>1</sup> and Kenneth P. H. Pritzker<sup>2</sup>; <sup>1</sup>Department of Chemistry, University of Massachusetts, Lowell, Massachusetts; <sup>2</sup>Pathology and Laboratory Medicine, Mount Sinai Hospital and University of Toronto, Toronto, Ontario, Canada.

We have demonstrated the use of hydrophilic C60 derivatives in one-photon excitation based photodynamic cancer therapy (PDT) 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-chromophore

conjugates containing polar hydrophilic functional groups, such as carboxylic acid and poly(ethyleneglycol), leading to water-soluble fullerene derivatives enhances their possibility in biological applications. Accordingly, we synthesized novel A-sp3-D type amphiphilic [60]fullerene-diphenylaminofluorene-poly(ethyleneglycol) conjugates, namely, C60(>DPAF-PEG). Compound C60(>DPAF-PEG) consists of a fullerene cage as the electron acceptor (A) moiety and diphenylaminofluorene segment as the donor (D) moiety, showing high two-photon absorption (2PA) cross-sections in nanosecond regime. Here, we present molecular self-assembly of these amphiphilic two-photon active fullerene materials at different concentration in aqueous solutions. Resulting nanoparticles were characterized by dynamic light scattering, turbidity measurements and transmission electron microscopy.

### **DD10.12**

#### **Cylindrical Gold Nanoshells on Polymer Fibers.**

Tanja Kmecko<sup>1</sup> and Kenneth J. Balkus, Jr.<sup>1</sup>; <sup>1</sup>Chemistry, University of Texas at Dallas, Richardson, Texas; <sup>2</sup>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 nanostructures on cross-linked polyethylenimine (PEI) nanofibers in order to prepare conductive and transparent fibers. The synthesis and optical properties of polyethylenimine fibers encapsulated with a cylindrical thin gold shell will be present and discuss. The synthesis involved the immersion of the PEI fibers into aqueous solution of chloroauric acid (HAuCl<sub>4</sub>) and room temperature reduction of HAuCl<sub>4</sub> with tetrakis(hydroxymethyl)phosphonium chloride (THPC). By varying the amount of HAuCl<sub>4</sub>, we observed a change in the gold shell thickness. The nanoshells were characterized by SEM/EDX, TEM and UV-VIS spectroscopy.

### **DD10.13**

#### **Amine-assisted Bottleneck Etching of CdSe Nanocrystals.**

Rongfu Li<sup>1</sup>, Jeunghoon Lee<sup>1</sup>, Baocheng Yang<sup>2</sup>, David N. Horspool<sup>3</sup>, Mark Aindow<sup>3</sup> and Fotios Papadimitrakopoulos<sup>2,1</sup>; <sup>1</sup>Institute of Materials Science, Polymer Program, Univ. of Conn., Storrs, Storrs, Connecticut; <sup>2</sup>Department of chemistry, University of Connecticut, Storrs, Connecticut; <sup>3</sup>Department of Metallurgy and Materials Engineering, University of Connecticut, Storrs, Connecticut.

The bottleneck chemical etching of CdSe nanocrystals (NCs) in 3-amino-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 bottleneck behavior was observed with distinct plateaus in the peak position of photoluminescence (PL). These plateaus are 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 SeO<sub>2</sub> entities, that are readily solubilized in the basic APOL/H<sub>2</sub>O 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<sup>1,2</sup>, Rongfu Li<sup>1,2</sup>, Baocheng Yang<sup>1,2,3</sup>, Thomas A. P. Seery<sup>2,3</sup> and Fotios Papadimitrakopoulos<sup>1,2,3</sup>; <sup>1</sup>Nanomaterials Optoelectronics Laboratory (NOEL), University of Connecticut, Storrs, Connecticut; <sup>2</sup>Institute of Material Science, University of Connecticut, Storrs, Connecticut; <sup>3</sup>Chemistry, University of Connecticut, Storrs, Connecticut.

The preparation of water-soluble CdSe nanocrystal/poly(allylamine) clusters with size between 50 and 200 nm by using 3-amino-1-propanol (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 red-shift as APOL dispersion of 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 compactness of the internal structure, probed by 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 $\pi$ -Conjugated Polymers Involving Metal Nanoparticles.**

**Akito Masuhara**<sup>1,2</sup>, **Satoshi Ohnishi**<sup>1</sup>, **Hitoshi Kasai**<sup>1,2</sup>, **Yoshikazu Shinohara**<sup>1</sup>, **Shuji Okada**<sup>3,2</sup>, **Hidetoshi Oikawa**<sup>4,2</sup> and **Hachiro Nakanishi**<sup>1,2</sup>; <sup>1</sup>IMRAM, Tohoku Univ., Sendai, Japan; <sup>2</sup>CREST, JST, Tokyo, Japan; <sup>3</sup>Faculty of Engineering, Yamagata, Univ., Yonezawa, Japan; <sup>4</sup>NIMS, Tsukuba, Japan.

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-precipitation and their optical properties and morphology 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-hexadiyne (DCHD) as shells were prepared, interesting visible absorption change was observed in the course of the solid-state polymerization of DCHD stimulated by UV irradiation. The excitonic absorption peak of produced poly(DCHD) 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 NPs 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 phthalocyanine-copper(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.**

**Thalladi**; Department of Chemistry and Biochemistry, Worcester Polytechnic Institute, Worcester, Massachusetts.

Nonlinear optical (NLO) materials form the backbone of photonic and optoelectronic devices. We are pursuing octupolar NLO materials; these materials are not dipolar, yet they are noncentrosymmetric and exhibit significantly large molecular and crystalline nonlinearities. Octupolar materials offer several acentic templates with two- and three-dimensional symmetries. The most efficient of these is the cubic template in which donor (**D**) and acceptor (**A**) groups are situated at alternate corners. We developed a hierarchical self-assembly strategy for the synthesis of cubic octupoles: this strategy involves the covalent synthesis of *trans*-**A<sub>2</sub>D<sub>2</sub>**-porphyrins, their metallation with zinc and other transition metals, and dimerization of metallated porphyrins using linear diaza ligands. We synthesize *trans*-**A<sub>2</sub>D<sub>2</sub>**-porphyrins in a modular fashion by a reaction between **D** (or **A**) substituted dipyrromethane and **A** (or **D**) substituted aryl aldehyde. The dipyrromethane itself is formed from the condensation of aryl aldehyde and pyrrole. We can make a large number of *trans*-**A<sub>2</sub>D<sub>2</sub>**-porphyrins simply by changing **A** and **D** groups. We chose zinc for metallation because it binds to the four inner pyrrole N-atoms of the porphyrin macrocycle and also to another ligand in the axial direction, with a particularly high affinity for aza ligands. Cofacial dimers of porphyrins, the cubic octupoles, are formed by coordination self-assembly between metalloporphyrin and linear diaza ligands (e.g., pyrazine and bipyridyl). We present the structural characterization of a number of derivatives with different **A** and **D** groups by NMR, UV, and powder and single crystal X-ray diffraction methods, and nonlinear characterization by harmonic light scattering and Kurtz powder methods. We are in the process of exploring the generality of this hierarchical self-assembly strategy to calixarene based systems.

#### **DD10.17**

##### **Effects of Porosity on Optical Properties of Chiral GLAD**

**Films.** **Jason Sorge**, **Andy C. van Popta**, **Jeremy C. Sit** and **Michael J. Brett**; Electrical and Computer Engineering, University of Alberta,

Edmonton, Alberta, Canada.

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  $>80^\circ$  with respect to substrate normal) and substrate shadowing to allow fabrication of thin films with nanometer scale control. The GLAD technique has been utilized to fabricate porous chiral nanostructures such as 3D square spiral photonic crystals<sup>1</sup> 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 vice versa. The results of a study investigating the effect of porosity on the selective transmission of circularly polarized light through helical titanium dioxide films are presented. A set of helical films with similar helical geometry (thickness 990 nm comprising 3 turns with pitch 330nm) but with widely different porosities was fabricated. It was found that film porosity has a substantial influence on both the magnitude of the selective transmission and the frequency at which the maximum selective transmission occurs. **I. S.R. Kennedy, M.J. Brett, H. Miguez, O. Toader, and S. John** Photonics and Nanostructures 1, 37-42 (2003)

SESSION DD11: Poster Session: Organic and Hybrid  
Light Emitting Devices: Electrical and Optical  
Properties

Thursday Evening, December 2, 2004

8:00 PM

Exhibition Hall D (Hynes)

#### **DD11.1**

##### **Transparent Copolyimide Films for Micro - and Optoelectronic Applications.** **Arlen Valozhyn**<sup>1</sup>, **Ewa**

**Schab-Balcerzak**<sup>2</sup> and **Bozena Jarzabek**<sup>2</sup>; <sup>1</sup>Institute of Electrical Engineering, Technical University of Szczecin, Szczecin, Poland; <sup>2</sup>Centre 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 comonomers, for example, aliphatic diamines or cyclic dianhydrides allowed to obtain a compromise between processability and thermal properties of PI. A series of aliphatic-aromatic polyimides (CPI) have been synthesized by high temperature copolycondensation of the aliphatic diamines H<sub>2</sub>N(CH<sub>2</sub>)<sub>n</sub>NH<sub>2</sub>, where n = 4,6,7,9,10,12, 4,4'-methylenebis(2,6-dimethylaniline) with cyclopentanetetracarboxylic dianhydride. 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 causes enhancement of the transparency, decrease the dielectric constant and improvement of solubility but on the other hand the thermal stability of such polyimides may be reduced. But the use of the alicyclic monomers may be a good compromise between processability and thermal properties. Soluble, in most cases uncolored semi-aromatic polyimides which form flexible films have been synthesized. The glass transition temperature of the CPI is in the range of 189-330°C. Temperature of 10% weight loss in nitrogen for these polymers is in the range of 425-495°C. Most of synthesized CPI films are thermostable material and seem to be for very interesting material for optical applications, for example, as cover for solar cells, orientation films in liquid crystal display devices and optical waveguides for communications interconnectors.

#### **DD11.2**

##### **Fast-Switching, High-Contrast Electrochromic Thin Films Prepared via Electrostatic Self-Assembly.** **Jaime Grunlan**<sup>1,2</sup>,

**James Coleman**<sup>3,2</sup> and **Li Shu**<sup>2</sup>; <sup>1</sup>Mechanical Engineering, Texas A&M University, Pasadena, California; <sup>2</sup>Avery Research Center, Avery Dennison Corporation, Pasadena, California; <sup>3</sup>Albion LLC,

A variety of electrochromic films have been produced recently using the electrostatic self-assembly (ESA) technique. ESA thin films, typically  $< 1\mu\text{m}$ , are created by alternately exposing a substrate to positively- and negatively-charged molecules or particles in water. Positive and negative depositions are continuously repeated until the desired number of *bilayers* (or cationic-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 nm-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 ( $> 1\mu\text{m}$ ). Unfortunately, many of these films have been prepared using intrinsically conductive polymers 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 tend to switch states very slowly 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 ( $\text{WO}_4^{2-}$ ) 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-ITO were 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 ( $10^4 \text{ S/cm}$ ) that reduces the switching speed to 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. Further improvements could be achieved by negatively stabilizing the ITO in an effort to deposit from the same 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 Patterning Method. Mi Kyung Kim<sup>1</sup>,

Jeong-Ik Lee<sup>1</sup>, Duck Il Kim<sup>1</sup>, Hye Yong Chu<sup>1</sup>, Chi Sun Hwang<sup>1</sup>, JiYoung Oh<sup>1</sup>, Sang-He Ko Park<sup>1</sup>, Yong Suk Yang<sup>1</sup>, Suk-Kyung Kim<sup>2</sup>, Do-Hoon Hwang<sup>2</sup> and Hyung-Jong Lee<sup>3</sup>; <sup>1</sup>ETRI, Daejeon, South Korea; <sup>2</sup>Kumoh National Univ. of Tech., Gumi, South Korea; <sup>3</sup>Zen Photonics Co., 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 been not yet commercialized in the area of multi-color displays due to the restriction of high-resolution patterning techniques. The patterning method of conjugated polymers attracting increased interest from some researchers. Their approaches include microcontact printing, screen printing, ink jetting, the photolithographic method, the laser-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 technology uses the application of generating acid upon photolysis 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 polyfluorene, which can be cured photochemically to yield an insoluble form, have been synthesized using Ni(0) mediated Yamamoto polymerization. The relationship between patterning property and several variables such as the exposure time of UV light, and the baking temperature and time, has been studied 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 Chu; 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

accomplishment of flexible display. A-SiNx thin film is deposited as a passivation layer on the OLEDs devices fabricated on PES 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. With the film thickness of 200nm, WVTR of the film is as low as 0.18 g/m<sup>2</sup>.day (at 38degree 100%RH). Moreover, the barrier characteristics are improved much through the post-treatment using H<sub>2</sub> plasma. We found that the deterioration of the barrier characteristics of the film originated from the pin-hole 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 30nm AlO film, the WVTR decrease as low as 0.07 g/m<sup>2</sup>.day. The life-time of the OLEDs is improved much with a minor degradation of emission characteristics of the device after deposition of a-SiNx thin film. The research for the removal of the plasma damage on the OLEDs is under progress. The improvement of barrier characteristics using multilayer 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, Y.J. 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 (Alq<sub>3</sub>) layer and a metal cathode has shown the most drastic performance improvement of both drive voltage and luminance of the organic light-emitting diodes (OLED). Since then lithium fluoride has been widely used to produce the efficient OLED. Instead of lithium fluoride, we fabricated OLED with a thin cesium chloride (CsCl) interlayer between the Alq<sub>3</sub> layer and a Al cathode. We found out cesium chloride interlayer result in improved device performance. We investigated the electronic structure of Al/ cesium chloride / Alq<sub>3</sub> by x-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS). By inserting cesium chloride, tunneling effect in Al cathode to Alq<sub>3</sub> electron transport layer is more effective. cesium chloride deposition on Alq<sub>3</sub> makes the highest occupied molecular orbital (HOMO) level and the lowest unoccupied molecular orbital level shift. 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<sup>1</sup>, Holger Eichhorn<sup>2</sup>, Bryan

Bornais<sup>2</sup> and Peter R. Norton<sup>1</sup>; <sup>1</sup>The University of Western Ontario, London, Ontario, Canada; <sup>2</sup>Windsor 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 found to be excellent charge transporters, due to the proximity of the pi-orbitals of adjacent molecules. The disk-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 significantly. It has been reported, for instance, that the mobility of holes increases by several orders of magnitude because of the formation of columns.\* We have established a technique to measure the charge carrier mobility in organic materials used in OLEDs. Because of the resulting constraint on device performance, measurement of bulk charge transport in these materials has been an indispensable necessity. The ToF method is a rather direct and general measurement technique for determining mobilities of charge carriers in that it directly visualizes their field-induced transit motion through a sample from the start at one electrode to the arrival at the opposite one. While discotic molecules have been studied and measured for hole mobility, little is known about electron mobility in these molecules. We have tried to understand and measure electron mobility in the discotic molecules used for OLED fabrication. \* Adam, D., Schuhmacher, P., Simmerer, J., Haussling L., Siemensmeyer K., Etzbach, K. H., Ringsdorf, H., and Haarer, D. Nature 371, 141 (1994).

#### DD11.7

##### A Novel Light-Emitting Mixed-Ligand Iridium(III) Complex with a Polymeric Terpyridine-PEG Macroligand: Synthesis and Characterization. Elisabeth Holder<sup>1,2</sup>, Veronica Marin<sup>1,2</sup>,

Michael A. R. Meier<sup>1,2</sup> and Ulrich S. Schubert<sup>1,2</sup>; <sup>1</sup>Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology (TU/e), 5600 MB Eindhoven, Netherlands; <sup>2</sup>Dutch Polymer Institute (DPI), 5600 AX Eindhoven, Netherlands.

The study of polymeric materials with coordinating units is currently an expanding field in macromolecular chemistry. The combination of

inorganic metal-containing moieties and macromolecules lead to novel systems with new and exciting photo- and electrochemical properties as well as interesting architectures. Due to their high affinity for 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 systems with a light-emitting and electroactive center are accessible. 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 poly(ethylene glycol) (PEG) functionalized terpyridine macroligand as well as of a mixed ligand iridium(III) complex. Coupling of hexylamine functionalized terpyridine to a hydroxyfunctionalized poly(ethylene glycol) yielded a PEG-functionalized macroligand. After a bridge-splitting reaction of the orthometallated dimer  $[\text{Ir}(\text{ppy-CHO})_2\text{Cl}]_2$  (where (ppy-CHO) is 4-(2-pyridyl)benzaldehyde) and coordination to the tpy-PEG macroligand a novel polymeric monoterpyridine 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  $\text{CH}_2\text{Cl}_2$  solutions whereas as thin films on glass substrates the maxima were found to be 10 nm red-shifted. Two oxidation potentials were observed at 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 two 4-(2-pyridyl)benzaldehyde ligands gives freedom to introduce further side 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. Meier<sup>1,2</sup>, Elisabeth Holder<sup>1,2</sup>, Veronica Marin<sup>1,2</sup> and Ulrich S. Schubert<sup>1,2</sup>; <sup>1</sup>Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology (TU/e), 5600 MB Eindhoven, Netherlands; <sup>2</sup>Dutch 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 covalent 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 transition metal complexes. In particular, terpyridine 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 ligand iridium(III) complexes at the corona of these polymeric unimolecular micelles. Coupling of pentylamine functionalized terpyridine to the hydroxy functional 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  $[\text{Ir}(\text{ppy-CHO})_2\text{Cl}]_2$  (where (ppy-CHO) is 4-(2-pyridyl)benzaldehyde) and coordination to the star shaped polymers novel polymeric monoterpyridine iridium(III) complexes could be obtained. These materials might have interesting applications ranging from imaging to phase transfer catalysis or light emitting devices. [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 Abrams<sup>1</sup>, Jess Patrick Wilcoxon<sup>1</sup>, Steven George Thoma<sup>1</sup> and James M. Kraus<sup>2</sup>; <sup>1</sup>Sandia National Labs, Albuquerque, New Mexico; <sup>2</sup>Dept 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) Mn<sup>2+</sup> ions and ZnS onto their surface. Mn<sup>2+</sup> was chosen in an attempt to broaden the PL spectrum with the eventual goal of creating white emission. ZnS was chosen to modify the local Mn<sup>2+</sup> environment and aid in energy transfer between CdS and Mn. Upon deposition of Mn<sup>2+</sup> onto the surface of CdS nanoclusters, the PL broadens and slightly red-shifts. This red-shift is dependent upon the age of the nanoclusters. The PL of 1.8nm CdS nanoclusters is initially blue (470nm). Over the period of a few days to weeks, the PL intensity of these nanoclusters increases as the surface reconstructs at room temperature. Though the PL changes, the absorption edge remains the same (400nm). When ZnS is added after addition of Mn<sup>2+</sup>, there is much larger red-shift in the PL (558nm to 575nm). Deposition of ZnS aided by the adsorbed 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 ion systems. One such system of interest is Si or Ge with Mn and Sb as dopants. Preliminary work on these systems will be discussed. Acknowledgments: Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

#### DD11.10

**Investigation on the Degradation Mechanism in Organic Light Emitting Diodes using Scanning Photoelectron Microscopy.** Soo Young Kim<sup>1</sup>, Ki-Beom Kim<sup>2</sup>, Yoon-Heung Tak<sup>2</sup> and Jong-Lam Lee<sup>1</sup>; <sup>1</sup>Pohang University of Science and Technology, Pohang, South Korea; <sup>2</sup>LG 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 delayed by operating OLEDs in inert ambient, an understanding of 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 (SPEM). Because SPEM is operated in two modes, photoelectron spectroscopy from a microspot and imaging, it is considered that SPEM 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-naphthyl)-N-phenyl-amino]biphenyl ( $\alpha$ -NPD, 500 Å)/ tris(8-hydroxyquinoline) aluminum (Alq<sub>3</sub>, 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. SPEM data show that the composition of dark spot is diverse. In 3d peak appeared and the contents of C 1s 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.

#### DD11.11

**Degradation of Ru(bpy)<sub>3</sub><sup>2+</sup>-based OLEDs.** Velda Goldberg<sup>1</sup>, Michael Kaplan<sup>1,2</sup>, Leonard Soltzberg<sup>2</sup>, Joseph Genevich<sup>1</sup>, Rebecca Berry<sup>1,2</sup>, Alma Bukhari<sup>1,2</sup>, Sherina Chan<sup>1,2</sup>, Megan Damour<sup>1,2</sup>, Leigh Friguglietti<sup>1,2</sup>, Erica Gunn<sup>1,2</sup>, Karen Ho<sup>1,2</sup>, Ashley Johnson<sup>1,2</sup>, Yin Yin Lin<sup>1,2</sup>, Alisabet Lowenthal<sup>1,2</sup>, Seiyam Suth<sup>1,2</sup>, Regina To<sup>1,2</sup>, Regina Yopak<sup>1,2</sup>, Jason D. Slinker<sup>3</sup>, George G. Malliaras<sup>3</sup>, Samuel Flores-Torres<sup>4</sup> and Hector D. Abruna<sup>4</sup>; <sup>1</sup>Physics, Simmons College, Boston, Massachusetts; <sup>2</sup>Chemistry, Simmons College, Boston, Massachusetts; <sup>3</sup>Materials Science and Engineering, Cornell University, Ithaca, New York; <sup>4</sup>Chemistry and Chemical Biology, Cornell University, Ithaca, New York.

Analysis of the possible mechanisms of degradation of Ru(bpy)<sub>3</sub><sup>2+</sup>-based OLEDs has led to the idea of quencher formation in the metalloorganic area close to the cathode. It has been suggested that the quencher results from an electrochemical process where one of the bypyridine (bpy) groups is replaced with two water molecules [1] or from reduction of Ru(bpy)<sub>3</sub><sup>2+</sup> to Ru(bpy)<sub>3</sub><sup>0</sup> [2]. We have tested these and other degradation ideas using electric current-voltage measurements, UV- and IR-spectroscopy, MALDI-TOF mass spectrometry, and AF microscopy. We have taken measurements on an unoperated freshly prepared device and on the same device after extended time periods. Comparing these results with similar ones for devices operated during several hours, we are able to separate the degradation role of moisture and oxygen in the environment from the direct influence of electric current. I. G. Kalyuzny, M. Buda, J.

McNeil, P. Barbara, and A. Bard. *J. Am. Chem. Soc.* **125**, 6272-6283 (2003). 2. K.M. Maness, H. Masui, R.M. Wightman, and R.W. Murray, *J. Am. Chem. Soc.* **119**, 3987-3993 (1997).

#### **DD11.12**

**An Efficient Flexible Top-emitting Electroluminescent Device on Polyester Substrate.** Li Yanqing, Tan Liwei, Hao Xiaotao, Ong Kian Soo and Zhu Furong; MNCS, Institute of Material Research and Engineering, Singapore, Singapore.

An efficient flexible top-emitting polymer light-emitting device (FTPLED) 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 semitransparent cathode. Our work involves the study of interfacial properties at polymer/electrode interface. The performance of FTPLEDs is analyzed and compared with that of the PLEDs using a conventional structure. An optical microcavity formed in the device enables to tune the emission color by varying the thickness of the active polymer layer. When a 110 nm thick polymer was used, the FTPLED exhibited superior electrical and optical characteristics with a luminance efficiency of 4.56 cd/A at a turn-on voltage of 2.5V.

SESSION DD12: Organic Photonic Bandgap Structures  
Friday Morning, December 3, 2004  
Room 310 (Hynes)

#### **8:30 AM DD12.1**

**Photonic crystals through holographic lithography: simple cubic, diamond-like, and gyroid-like structures.**

Chaitanya Ullal<sup>1</sup>, Martin Maldovan<sup>1</sup>, Edwin L. Thomas<sup>1</sup>, Gang Chen<sup>2</sup>, Yong-Jin Han<sup>2</sup> and Shu Yang<sup>2</sup>; <sup>1</sup>Materials Science, MIT, CAMBRIDGE, Massachusetts; <sup>2</sup>Bell Laboratories, New Jersey, New Jersey.

We show how to fabricate three basic photonic crystal structures with simple cubic, fcc and bcc translational symmetry by interference lithography. The structures are fabricable by beams launched from the same half space. The simple cubic structure is size scalable while the fcc structure possesses two band gaps. Both these structures are experimentally realized.

#### **8:45 AM DD12.2**

**Complex 3D Photonic Crystals Fabricated by Atomic Layer Deposition.** Jeffrey S. King, D. P. Gaillot, C. W. Neff, T. Yamashita, E. Graugnard and C. J. Summers; School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Recently we have demonstrated the potential of atomic layer deposition (ALD) for the fabrication of advanced luminescent photonic crystal (PC) structures based on the inverse opal architecture[1-3]. 3D PCs offer the potential for improvement of phosphor performance by increasing efficiency, reducing threshold, and providing emission wavelength tunability. 3D PC structures are being extensively modeled, revealing that modifications to the inverse opal structure can significantly improve photonic band gap (PBG) properties. For example, in the inverted shell structure, the width of the PBG can be increased from 4.25% to 8.6%.[4] The PBG width can also be increased to 9.6% by formation of a non-close-packed structure[5]. Using the FDTD method, we have found that the PBG in a TiO<sub>2</sub> non-close-packed structure can be as high as 5%. The performance of these structures depends critically on precisely and accurately placed high dielectric material. Using ALD, we have demonstrated infiltration of TiO<sub>2</sub> films with extremely smooth surfaces (0.2-0.4 nm RMS roughness) while maintaining a high level of control over the infiltration coating thickness, enabling formation of composite infiltrated and inverse opals with nano-scale precision. Here we report progress in fabrication of multi-layered and non-close packed PCs using ALD. Two and three-layer luminescent inverse opals were formed by the sequential deposition of thin layers of ZnS:Mn and TiO<sub>2</sub> in (111) oriented thin film silica opal templates (later removed using HF). Evidence for modification of the emission characteristics by high order PBGs has been observed by measuring normal and angular dependent photoluminescence. In addition, non-close-packed inverse opals have been formed by infiltrating heavily sintered silica opals with TiO<sub>2</sub>, etching the spheres with HF, and backfilling the resulting inverse opal. Resulting structures were characterized using specular reflectance and transmission, photoluminescence, and SEM. This work demonstrates the enormous potential that ALD offers for the realization of high performance photonic crystal structures. 1. King, J.S., C.W. Neff, S. Blomquist, E. Forsythe, D. Morton, and C.J. Summers, *Phys. Stat. Sol. (b)*, 2004. 241(3): p. 763- 766. 2. King, J.S., C.W. Neff, C.J. Summers, W. Park, S. Blomquist, E. Forsythe, and D. Morton, *App. Phys. Lett.*, 2003. 83(13): p. 2566-8. 3. King, J.S., E. Graugnard, and C.J. Summers,

Submitted for publication., 2004. 4. Busch, K. and S. John, *Physical Review E*, 1998. 58(3): p. 3896-908. 5. Doosje, M., B.J. Hoenders, and J. Knoester, *J. Opt. Soc. Am. B*, 2000. 17(4): p. 600-6.

#### **9:00 AM DD12.3**

**Fabrication of Three Dimensional Photonic Crystal with Alignment Based on Electron Beam Lithography.**

Ganapathi Subramania<sup>1</sup> and Shawn Yu Lin<sup>2</sup>; <sup>1</sup>Sandia National Laboratories, Albuquerque, New Mexico; <sup>2</sup>Department of Physics, Rensselaer Polytechnic Inst, Troy, New York.

We demonstrate the fabrication of a three dimensional woodpile photonic crystal in the near infrared using a layer-by-layer approach by electron beam lithography and spin-on-glass planarization. The alignment accuracy between the first and the fifth layer is within 10% of the lattice spacing as measured from cross section scanning electron microscopy images. Optical measurements on five layer sample yield a reflectivity peak of 66% in the 1.55 micron regime for a 660nm lattice spacing. Varying the lattice spacing to 600nm and 550nm moves the reflectivity peak to 1.32 micron and 1.21 micron respectively indicating the effect of lattice spacing on photonic gap. This method offers a way of rapid prototyping full three dimensional photonic bandgap devices with considerable flexibility of materials choice. Moreover lattice structure that can operate at wavelengths into the visible can be fabricated using this approach.

#### **9:15 AM DD12.4**

**Nonlinear spectroscopy of polymer-based nanolayered 1D photonic crystals.** Richard S. Lepkowitz<sup>1</sup>, Steven R. Flom<sup>1</sup>,

Richard G.S. Pong<sup>1</sup>, Michael J. Wiggins<sup>1</sup>, James S. Shirk<sup>1</sup>, Aditya Ranade<sup>2</sup>, Huiwen Tai<sup>2</sup>, Eric Baer<sup>2</sup> and Anne Hiltner<sup>2</sup>; <sup>1</sup>optical science division, Naval Research Lab, Washington, District of Columbia; <sup>2</sup>Macromolecular science and engineering, Case Western Reserve University, Cleveland, Ohio.

The nonlinear optical response of Lead(II)tetrakis(4-cumylphenoxy)-phthalocyanine (PbPc(CP)<sub>4</sub>) is enhanced when the dye is incorporated into a polymer-based 1D photonic crystal. This photonic crystal is composed of alternating layers of polycarbonate (PC) doped with a high concentration of PbPc(CP)<sub>4</sub> and undyed layers of polyethylene-terephthalate (PET). Under low light excitation the PET and PC/dye layers are nearly index matched, but under high excitation an index mismatch is induced. This change in index results from the nonlinear response of the dyed material under high excitation (e.g. ground-state depletion, excited-state population, and thermal heating due to absorption). This small induced change in refractive index repeated over many appropriately spaced layers produces a photonic band gap, which results in a substantial increase in reflectivity. The nanostructured material is fabricated by coextruding dyed layers of PC with undyed layers of PET and repeatedly stacking them with a novel stacking technique. The overall structure is on the order of 40-60 μm thick, and is composed of 512 layers, which results in the average layer thickness being on the order of 80 - 120 nm. This material has a quarter-wave ( $\lambda_0/4n$ ) thickness (and therefore photonic bandgap) in the range of 480 -720 nm. The wavelength dependent results in the nanosecond regime have shown a significant improvement in the nonlinear transmission of the nanostructured material over monolithic samples of the same material. This is readily verified in the spectral 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 layer thickness, the mechanism 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)<sub>4</sub> photonic bandgap material. For these measurements, the output of a Ti:sapphire regenerative amplifier (771 nm, 1 kHz rep. rate, 150 fs  $t_{FWHM}$ , 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 shown that the photonic band gap structure has a very fast rise time (< 100 picoseconds). The excited state photodynamics of the nonlinear dye are not affected by the nanolayered structure. The observed additional decrease in transmission on the order of 20% demonstrates the promise of these new materials.

#### **9:30 AM DD12.5**

**Monodispersed a-Se Spherical Colloids: A New Platform for Increasing the Complexity and Functionality of Colloidal Building Blocks.** Unyong Jeong and Younan Xia; chemistry, university of washington, seattle, Washington.

We have demonstrated the synthesis of monodispersed spherical colloids of amorphous selenium (a-Se) in large quantities. The



diameter could be well controlled by adjusting the molar ratio between selenious acid and hydrazine, covering the range from 90 to 420 nm. The high reactivity of a-Se towards various metal salt precursors was also employed to generate unique colloidal building blocks such as semiconductor core-shell particles and metal-coated dielectric spheres for photonic crystals. This presentation will discuss the synthesis of a-Se, as well as its derivatives. I will also discuss the photonic band gap properties from their 3D opaline lattices.

#### 9:45 AM DD12.6

##### **Nanofabrication of Organic and Inorganic/Organic Structures for Nanophotonics.** Alexander N. Cartwright<sup>1</sup>, William David

Kirkey<sup>1</sup>, Michael Pan<sup>1</sup>, Vincent Hsiao<sup>1</sup>, Ram Thapa<sup>1</sup>, Derrick Lucey<sup>2</sup> and Paras Prasad<sup>2</sup>; <sup>1</sup>Electrical Engineering, University at Buffalo (S.U.N.Y.), Buffalo, New York; <sup>2</sup>Chemistry, 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 characterization of these nanoparticles is presented in detail, and the feasibility of utilizing these inorganic nanoparticles as the light-emitting species within a conductive organic device structure is discussed. In addition, 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 Dot/Polymercomposites.** Stefan Richter<sup>1</sup>, Reinald Hillebrand<sup>1</sup>, Margit

Zacharias<sup>1</sup>, Ralf B. Wehrspohn<sup>2,1</sup>, Stefan Schweizer<sup>2,1</sup>, Ulrich Goesele<sup>1</sup>, Martin Steinhart<sup>1</sup>, Andrey L. Rogach<sup>3</sup>, Nikolai Gaponek<sup>4</sup>, Alexander Eychmueller<sup>4</sup> and Joachim Wendorf<sup>5</sup>; <sup>1</sup>Max-Planck-Institute Halle, Halle, Germany; <sup>2</sup>Department of Physics, University of Paderborn, Paderborn, Germany; <sup>3</sup>Department of Physics, University of Munich, Munich, Germany; <sup>4</sup>Institute of Physical Chemistry, University of Hamburg, Hamburg, Germany; <sup>5</sup>2 Institute of Physical Chemistry and Center of Materials Science, University of Marburg, Marburg, Germany.

Internal light emission in a 2D silicon photonic crystal and 2D silicon coupled cavities has been achieved. We developed a novel process based on wetting of pores of a 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. This polymer-mediated infiltration method is not limited to HgTe-quantum dots and can be applied to any colloidal quantum dots emitter.

#### 10:45 AM DD12.8

##### **Photonic Crystals: The Diamond Structures.** Martin Maldovan and Edwin L. Thomas; Materials Science, MIT, Cambridge, Massachusetts.

Certain periodic dielectric structures can prohibit the propagation of light. These artificial, so called photonic crystals are impacting how researchers can modify the interaction between 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 resultant structure to retain the large diamond gap. The basic origin of the complete photonic band gap for the champion diamond morphology is described. We also discuss current progress in 3D interference lithography to fabricate near champion diamond structures in the visible and near IR regimes.

#### 11:00 AM DD12.9

##### **Two-dimensional magneto-photonic crystal circulators.**

Zheng Wang<sup>1</sup> and Shanhui Fan<sup>2</sup>; <sup>1</sup>Applied Physics, Stanford University, Stanford, California; <sup>2</sup>Electrical 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 Faraday rotation in one-dimensional magnetic photonic crystals, where nonreciprocity in magnetic cavities is resonantly enhanced to provide optical isolation in sub-wavelength optical paths. In this paper, we study the nonreciprocity of two-dimensional magnetic photonic crystal resonators to allow further miniaturization and monolithic in-plane integration with current integrated optical devices. The nonreciprocal magnetic resonators are constructed by alternating the magnetization directions of the ferromagnetic domains in the cavities side-coupled to photonic crystal waveguides. We show analytically that the gyrotropic splitting 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. With a large overlap obtained from optimizing the domain wall structures, we can circularly hybridize two doubly-degenerate modes to form a pair of counter-rotating whispering-gallery like modes, oscillating at different frequencies. As a physical realization, we synthesize two singly-degenerate circularly-hybridized modes in a two-dimensional crystal formed of a triangular air hole lattice in yttrium iron garnet with a TE bandgap. We tune the magnetic splitting and the decay constants of the rotating modes to create a three-port optical circulator with a 30dB extinction ratio. Our numerical experiments are performed with finite-difference time-domain simulations and agree well with the analytical coupled-mode theory predictions.

#### 11:15 AM DD12.10

##### **Light Emission in 2D Photonic Quasicrystals with 8-, 10- and 12-fold Rotational Symmetries Fabricated by Interference Lithography.** Ion Bita and Edwin L. Thomas; Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Photonic quasicrystals (PQCs) are a natural extension of the notion of photonic crystals, where the refractive index spatial variation displays a quasiperiodic rather than a periodic translational symmetry. PQCs are long-range ordered materials that are not invariant under spatial translation, which represent an intermediate ordering state between perfectly periodic crystalline and perfectly random amorphous materials (e.g. the long-range order of PQCs causes sharp diffraction peaks in Bragg scattering). The study of PQCs is currently only slowly progressing, mainly due to the fundamental difficulties involved with theoretical investigations. The lack of translational order does not allow a convenient solution of Maxwell's equations, such as the use of Bloch waves in PCs. Furthermore, systematic theoretical studies are hindered by the fact that an infinity of quasiperiodic lattices can be defined, since they can be regarded as arbitrary 3D sections (2D in this work) from particular higher ( $N > 3$ ) dimensional space lattices with translational periodicity. The goal of our study is to experimentally gain insight into the optical properties of 2D quasiperiodic photonic lattices with noncrystallographic rotational symmetries, which are important for practical applications that benefit from an in-plane complete 2D photonic band gap (waveguiding, light emission, etc.). Higher rotational orders increase the circularity of the pseudo-Brillouin zone, and allow for designs where a smaller refractive index contrast is required for opening complete 2D PBGs. We have built a multiple exposure interference lithography tool for the efficient fabrication of a variety of 2D PQCs with 8-, 10- and 12-fold rotational symmetries. This tool is much more advantageous than the e-beam lithography employed by the few prior investigations (of 12-fold PQCs). We used a photosensitized chemically amplified photoresist system and a 532nm frequency doubled Nd:YAG laser to create 2D photoresist patterns uniform over large areas ( $> 5 \times 5$ mm). Optical diffraction patterns and scanning electron microscopy observations confirm the formation of the PQCs. The patterned photoresist is used as a mask for dry etching of the underlying optically transparent substrate. The light

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 PQC's in practical applications.

#### **11:30 AM DD12.11**

**Optical Properties of polystyrene opals infiltrated with cyanine dyes in the form of J-Aggregates.** Franco Marabelli<sup>1</sup>, Davide Comoretto<sup>2</sup>, Daniele Bajoni<sup>1</sup> and Matteo Galli<sup>1</sup>; <sup>1</sup>CNR-INFM and University of Pavia, Pavia, Italy; <sup>2</sup>CNR-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 Rosera Maskaly<sup>1,2</sup>, Garry R. Maskaly<sup>1,2</sup>, W. Craig Carter<sup>1</sup> and James L. Maxwell<sup>2</sup>; <sup>1</sup>Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Materials 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.