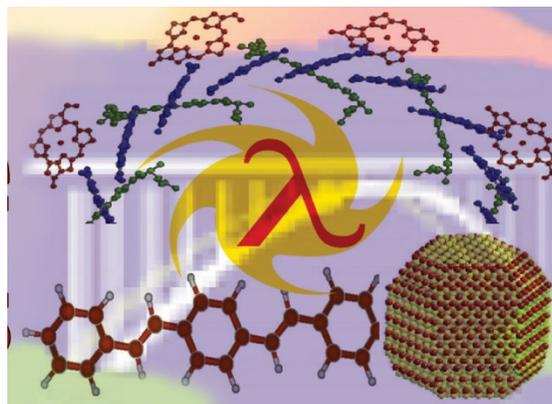

Updated 6/3/16
Conference Program



The 7th International Conference on

Excited State Processes in Electronic and Bio Nanomaterials

ESP-2016

June 13 – June 16, 2016

Santa Fe, New Mexico, USA

<http://cnls.lanl.gov/esp2016>

The conference is sponsored by Center for Nonlinear Studies (CNLS); Center for Integrated Nanotechnologies (CINT); Theoretical, Chemistry and Materials Physics and Applications at Los Alamos National Laboratory; and supported by the U.S. Department of Energy.

*Conference organizer: Sergei Tretiak
Conference e-mail: serg@lanl.gov*

The Advisory Committee: Enrique Batista, Stephen Doorn, Victor Klimov, Aditya Mohite, Tammie Nelson, Avadh Saxena

Conference coordinator: Kacy Hopwood & Rose Romero, cnls-conferences@lanl.gov

Location: Hilton Santa Fe Historic Plaza, 100 Sandoval Street

Santa Fe, New Mexico 87501

(505) 988-2811

(oral presentations, poster session, banquet)

	Monday, June 13	Tuesday, June 14	Wednesday, June 15	Thursday, June 16
8:00AM	WELCOME 8:10AM-8:30AM			
8:30AM	VARDENY 8:30AM-9:05AM	LAURET 8:30AM-9:05AM	ZIMANYI 8:30AM-9:05AM	TOMANEK 8:30AM-9:05AM
9:00AM	MAZUMDAR 9:05AM-9:40AM	HOEGELE 9:05AM-9:40AM	KILINA 9:05AM-9:40AM	BROVELLI 9:05AM-9:40AM
9:30AM	GIERSCHNER	PIRYATINSKI	MELLO-DONEGA	HOLLINGSWORTH
10:00AM	9:40AM-10:15AM	9:40AM-10:15AM	9:40AM-10:15AM	9:40AM-10:15AM
10:30AM	GU 10:15AM-10:35AM	OLIVIER 10:15AM-10:35AM	MAKAROV 10:15AM-10:35AM	BLANCON 10:15AM-10:35AM
	BREAK 10:35AM-10:55AM	BREAK 10:35AM-10:55AM	BREAK 10:35AM-10:55AM	BREAK 10:35AM-10:55AM
11:00AM	STINGELIN 10:55AM-11:30AM	WANG 10:55AM-11:30AM	LAW 10:55AM-11:30AM	RAPPE 10:55AM-11:30AM
11:30AM	ALAM 11:30AM-12:05PM	ONOE 11:30AM-12:05PM	EFROS 11:30AM-12:05PM	FIDLER 11:30AM-12:05PM
12:00PM	KOVALENKO 12:05PM-12:40PM	NIENHAUS 12:05PM-12:25PM	STRANKS 12:05PM-12:40PM	AHMED 12:05PM-12:25PM
12:30PM		LUNCH		LUNCH
1:00PM	LUNCH	12:25PM-2:00PM	LUNCH	12:25PM-2:00PM
2:00PM	12:40PM-2:10PM	ZHENG 2:00PM-2:35PM	12:40PM-2:10PM	LANZANI 2:00PM-2:35PM
2:30PM	PREZHDO 2:10PM-2:45PM	VARGANOV 2:35PM-3:10PM	2:10PM-2:45PM	KILIN 2:35PM-3:10PM
3:00PM	NESBITT 2:45PM-3:20PM	BATISTA	SHUAI 2:45PM-3:20PM	DUNLAP
3:30PM	SLIPCHENKO 3:20PM-3:55PM	3:10PM-3:45PM	BAZAN 3:20PM-3:55PM	3:10PM-3:45PM
	BREAK	BREAK 3:45PM-4:05PM	BREAK	BREAK 3:45PM-4:05PM
4:00PM	3:55PM-4:15PM	SHREVE 4:05PM-4:40PM	3:55PM-4:15PM	SPANO 4:05PM-4:40PM
4:30PM	DYER 4:15PM-4:50PM	BATHE	4:15PM-4:50PM	BITTNER
5:00PM	KRYLOV 4:50PM-5:25PM	4:40PM-5:15PM	SCHARFF 4:50PM-5:25PM	4:40PM-5:15PM
5:30PM	CURUCHET 5:25PM-6:00PM	VELIZHANIN 5:15PM-5:35PM	MYERS 5:25PM-5:45PM	WILHELM 5:15PM-5:35PM
				CLOSING REMARKS
6:00PM			BANQUET	
7:00PM		POSTER SESSION 7:00PM	6:30PM	

Monday, June 13

Session chair: **Sergei Tretiak** (LANL)

08:10am – 08:30am **Welcome (John Sarrao, Angel Garcia)**

Session Title: Polymers I

Session chair: **Sergei Tretiak**

08:30am – 09:05am **Valy Vardeny** (Univ. Of Utah)

“Transient Magneto-Spectroscopy Studies of Photoexcitations in Pristine and D-A Blends Based on Low Bandgap π -Conjugated Copolymers”

09:05am – 09:40am **Sumit Mazumdar** (Univ. of Arizona)

“Theory of Primary Photoexcitations in Low Bandgap Donor-Acceptor Copolymers”

09:40am – 10:15am **Johannes Gierschner** (Madrid Institute Adv. Studies)

“Controlled Light Emission in Organic Single Crystals for Optoelectronic Applications”

10:15am – 10:35am **Kevin Gu** (Stanford)

“Controlling Domain Size, Crystallinity, and Performance of Organic Photovoltaics via Solution Shearing”

10:35am – 10:55am **Break**

Session Title: Quantum Dots & Semiconductors I

10:55am – 11:30am **Natalie Stingelin** (Imperial College)

“A Close Look at Charge Generation and its Dependence on Microstructure”

11:30am – 12:05pm **Muhammad Alam** (Purdue)

“Is there any Exciton (bottleneck) in an Excitonic Solar Cells: My Journey from OPV to Perovskite Solar Cells”

12:05pm – 12:40pm **Maksym Kovalenko** (ETH Zurich)

“Highly-Luminescent Colloidal Nanocrystals of Cesium Lead Trihalide Perovskites (CsPbX₃, X=Cl, Br, I)”

12:40pm – 2:10pm **Lunch**

Session chair: **Joel Kress** (LANL)

02:10pm – 02:45pm **Oleg Prezhdo** (USC)

“Excited state dynamics at nanoscale interfaces: time-domain ab initio studies”

02:45pm – 03:20pm **David Nesbitt** (JILA)

“Two-Photon Excited Fluorescence Intermittency in Single CdSe/ZnS Quantum Dots: A Novel Role for Hot Exciton States”

03:20pm – 03:55pm **Lyudmila Slipchenko** (Purdue)

“Excitation Energy Transfer and Vibronic Couplings in Multichromophores”

03:55pm – 04:15pm **Break**

Session Title: Metal-organic & Biological Systems I

04:15pm – 04:50pm **Brian Dyer** (Emory)

“Ultrafast Energy Flow in Protein Structures”

04:50pm – 05:25pm **Anna Krylov** (USC)

“Two-photon absorption spectroscopy of molecular switches: Insights from theory”

05:25pm – 06:00pm **Carles Curutchet** (Univ. of Barcelona)

“Modelling Environment Effects in Photosynthetic Energy Transfer”

Tuesday, June 14

Session Title: Carbon Nanotubes, Graphene & Nanomaterials

Session chair: **Steven Doorn** (LANL)

08:30am – 09:05am **Jean-Sebastian Lauret** (ENS Cachan)

“Optical properties of carbon nanostructures”

09:05am – 09:40am **Alex Hoegele** (LMU Munich)

“Photophysics of localized excitons in cryogenic carbon nanotubes”

09:40am – 10:15am **Andrei Piryatinski** (LANL)

“Exciton Dynamics and Related Photon Emission Properties of Semiconductor Carbon Nanotubes”

10:15am – 10:35am **Jean-Hubert Olivier** (Duke)

“Photo-Induced Hole and Electron Transfer Reactions in Well-Defined Nanoscale Objects that Feature Electronically Homogeneous Single-Walled Carbon Nanotubes Wrapped by Redox Active Polymers”

10:35am – 10:55am **Break**

10:55am – 11:30am **Hsing-Lin Wang** (LANL)

“Synthesis of Nanographene Self-Assemblies with Optimized Electronic Structure and Facilitated Electron Transfer for Highly Efficient Energy Storage”

11:30am – 12:05pm **Jun Onoe** (Nagoya)

“Physicochemical Properties of One-Dimensional Periodic Uneven-Structured Nanocarbon Synthesized by Electron-Beam-Induced C60 Polymerization”

12:05pm – 12:25pm **Lea Nienhaus** (MIT)

“Visualizing Single Molecule Absorption at the Nanometer Scale”

12:25pm – 2:00pm **Lunch**

Session Title: Metalorganic & Biological Systems II

Session chair: **Enrique Batista** (LANL)

02:00pm – 02:35pm **Ming Zheng** (NIST)

“Differentiating Left- and Right-handed Carbon Nanotubes by DNA”

02:35pm – 03:10pm **Sergey Varganov** (Univ. of Nevada)

“Nonadiabatic Transition State Theory: Application to Intersystem Crossings in the Active Sites of Metal-Sulfur Proteins”

03:10pm – 03:45pm **Victor Batista** (Yale)

“Studies of Natural and Artificial Photosynthesis”

03:45pm – 04:05pm **Break**

04:05pm – 04:40pm **Andrew Shreve** (UNM)

“Energy Transfer, Electronic Coupling and Light-Harvesting in Assemblies of Chromophores”

04:40pm – 05:15pm **Mark Bathe** (MIT)

“Programming synthetic nanoscale excitonic circuits using DNA”

05:15pm – 05:35pm **Kirill Velizhanin** (LANL)

“Excitonic Effects in 2D Semiconductors: Path Integral Monte Carlo Approach”

07:00pm **Poster Session**

Wednesday, June 15

Session Title: Quantum Dots & Semiconductors II

- Session chair: **Han Htoon** (LANL)
- 08:30am – 09:05am** **Gergely Zimanyi** (UC Davis)
"The Full Spectrum Boost Project: The Intermediate Band Mechanism and the Metal-Insulator Transition in Nanoparticle Solar Cells"
- 09:05am – 09:40am** **Svetlana Kilina** (North Dakota State)
"Surface Chemistry of Semiconductor Nanostructures: Theoretical Perspectives"
- 09:40am – 10:15am** **Celso de Mello-Donaga** (Utrecht Univ.)
"Synthesis and Spectroscopy of Ternary Copper Chalcogenide Nanocrystals"
- 10:15am – 10:35am** **Nikolay Makarov** (LANL)
"Mechanism for Highly Efficient Intra-Gap Emission from CuInSexS2-x Quantum Dots"
- 10:35am – 10:55am** **Break**
- 10:55am – 11:30am** **Matt Law** (UC Irvine)
"Matrix Engineering, State Filling, and Charge Transport in PbSe Quantum Dot Solids"
- 11:30am – 12:05pm** **Alexander Efros** (NRL)
"Radiative Recombination from Dark Excitons: Activation Mechanisms and Polarization Properties"
- 12:05pm – 12:40pm** **Sam Stranks** (MIT)
"Relationship between Microscale Photophysics, Structure, and Local Chemistry of Metal Halide Perovskites"
- 12:40pm – 2:10pm** **Lunch**

Session Title: Polymers II

- Session chair: **Ping Yang** (LANL)
- 02:10pm – 02:45pm** **Greg Scholes** (Princeton)
"Coherence in Ultrafast Chemistry"
- 02:45pm – 03:20pm** **Zhigang Shuai** (Tsinghua)
"Boosting OLEDs Efficiency through Theoretical Understanding and Computational Study"
- 03:20pm – 03:55pm** **Gui Bazan** (UC Santa Barbara)
"Regioregular Narrow Bandgap Conjugated Polymers for Low Energy Loss Organic Solar Cells"
- 03:55pm – 04:15pm** **Break**
- Session chair: **Tammie Nelson** (LANL)
- 04:15pm – 04:50pm** **Joe Subotnik** (U Penn.)
"A Surface Hopping Theory of Electrochemistry"
- 04:50pm – 05:25pm** **Jason Scharff** (LANL)
"Excited State Processes in Novel Energetic Materials"
- 05:25pm – 05:45pm** **Thomas Myers** (LANL)
"Explosive Chromophores for Photo-Thermal and Photo-Chemical Laser Initiation"
- 06:30pm** **Banquet**

Thursday, June 16

Session Title: Perovskites and Semiconductors III

Session chair: **Aditya Mohite** (LANL)

08:30am – 09:05am **David Tomanek** (Michigan State Univ.)

“Unusual 2D Semiconductors and their Unexpected Properties”

09:05am – 09:40am **Sergio Brovelli** (Milan)

“Permanent Excimer Superstructures by Supramolecular Networking of Metal Quantum Clusters”

09:40am – 10:15am **Jennifer Hollingsworth** (LANL)

“Nano-engineering Core/Shell Quantum Dots for Ultimate Control Over Light-emission Processes”

10:15am – 10:35am **Jean-Christophe Blancon** (LANL)

“The Effects of Electronic Impurities and Electron-Hole Recombination Dynamics on Large Grain Organic-Inorganic Perovskite Photovoltaic Efficiencies”

10:35am – 10:55am **Break**

Session chair: **Jianxin Zhu** (LANL)

10:55am – 11:30am **Andre Rappe** (U Penn.)

“Understanding the Photovoltaic Efficiency of Organometallic Perovskites”

11:30am – 12:05pm **Andrew Fidler** (LANL)

“Charge carrier dynamics in quantum-dot solids probed by ultrafast photocurrent spectroscopy”

12:05pm – 12:25pm **Towfiq Ahmed** (LANL)

“Optical Properties of Organometallic Perovskite: An ab initio Study using Relativistic GW Correction and Bethe-Salpeter Equation”

12:25pm – 2:00pm **Lunch**

Session Title: Polymers III

Session chair: **Anders Niklasson** (LANL)

02:00pm – 02:35pm **Guglielmo Lanzani** (IIT)

“Controlling Life with Photons”

02:35pm – 03:10pm **Dmitri Kilin** (North Dakota State)

“Dynamics of Electronic Excitations at Interfaces”

03:10pm – 03:45pm **David Dunlap** (UNM)

“Disorder in Organic Semiconductors Due to Fluctuations in Space Charge Density”

03:45pm – 04:05pm **Break**

04:05pm – 04:40pm **Frank Spano** (Temple)

“Molecular Aggregate Photophysics Beyond the Kasha Model: Introducing a New Design Paradigm for Organic Materials”

04:40pm – 05:15pm **Eric Bittner** (Univ. of Houston)

“Charge-separation at Donor/Acceptor interfaces: coherent or not coherent, that is the question”

05:15pm – 05:35pm **Philipp Wilhelm** (Regensburg)

“Molecular Polygons Tune Intramolecular Strain in the π -System of Organic Semiconductors”

05:35pm – 05:40pm **Closing Remarks**

Transient Magneto-Spectroscopy Studies of Photoexcitations in Pristine and D-A Blends Based on Low Band-Gap π -Conjugated Copolymers*

Z. Valy Vardeny¹

Uyen N. V. Huynh¹, Yaxin Zhai¹, and Sumit Mazumdar²

¹*Department of Physics & Astronomy, University of Utah, Salt Lake City, UT 84112, USA*

²*Department of Physics, University of Arizona, Tucson, AZ, 85721, USA*

We have used both cw and picosecond-to-millisecond transient spectroscopies for studying the photoexcitations dynamics in several low band-gap π -conjugated copolymers (such as PTB7, for example) that have been extensively used in organic photovoltaic (OPV) applications with high power conversion efficiencies. We obtained two primary photoexcitations that are generated within ~ 150 fs (our time resolution). These are singlet exciton (SE; S_1) and triplet-triplet (1TT) pair, respectively; the latter species is a precursor for singlet-fission into two individual triplet excitons (TE). The SE has been considered to be the only primary photoexcitation in regular π -conjugated polymers, and is related with a transient photoinduced absorption (PA) band that peaks at an energy value close to the exciton binding energy (~ 0.4 eV) in the copolymer. The TT pair, on the other hand is an usual photoexcitation species in low band-gap π -conjugated copolymers [ref.1]. It has an absorption band close to that of TE, and may readily dissociate into two individual TE at time that depends on the energy proximity of the TT state to that of SE.

We have used the technique of transient magneto-photoinduced absorption (t-MPA) in a broad time domain for identifying the photoexcitations in the pristine copolymers and copolymer/fullerene blends. We found that the SE and TT-pairs show identical t-MPA(B) response (where B is the magnetic field strength), but opposite in sign. This shows that the photogenerated SE and TT-pairs are 'magnetically correlated'. In addition, the existence of t-MPA also shows that the TT-pair is indeed composed of two spin-carrying species, and is thus not a simple singlet state. We also found that the t-MPA(B) response of the TE in the microsecond-millisecond time domain shows a pronounced 'spectral narrowing' that reveals a unique spin dynamics in the copolymer chains.

We further studied the charge photogeneration in blends of donor-acceptor (D-A) based on the low band-gap π -conjugated copolymers and fullerene molecules. We found that the TT pair easily dissociate into polaron-pair and triplet exciton at the D-A interfaces. This finding may be one of the reasons for the obtained high power conversion efficiency in OPV devices based on low bandgap copolymers.

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* This work was supported by the AFOSR grant No 11976864.

[1] K. Aryanpour, T. Dutta, U. N. V. Huynh, Z. V. Vardeny, and S. Mazumdar, *Phys. Rev. Lett.* **115**, 267401 (2015).

Theory of Primary Photoexcitations in Low Bandgap Donor-Acceptor Copolymers

S. Mazumdar¹

Karan Aryanpour¹, Tirthankar Dutta¹, Souratosh Khan¹, Uyen N. V. Huynh², Z. Valy Vardeny²

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Donor-Acceptor (DA) pi-conjugated copolymers have generated intense recent interest as the primary photon absorbers in organic photovoltaic solar cells. The power conversion efficiencies (PCEs) of organic solar cells with DA copolymers as optically excited electron donor materials and fullerenes as acceptors have exceeded 10%. There is thus intense interest in the development of structure-property correlations that will facilitate further enhancement of the PCE.

It is generally assumed that the high PCEs of solar cells with DA copolymers as the active donor materials is due to the small optical gap E_g of these materials. Multiple recent experimental observations indicate that small E_g is not the only reason for the high efficiency. First, ultrafast dynamics studies have indicated that the low energy absorption band in several copolymers is composed of two distinct absorptions. Second, generation of triplet excitons in picosecond time scale and intramolecular singlet fission has been claimed in the DA copolymer PBTDO1. Finally, Huynh et al. have found two distinct transient photoinduced absorptions (t-PAs), PA1 at 0.4 eV and PA2 at 0.82 eV, in the DA copolymer PDTP-DFBT, in contrast to a single t-PA from homopolymers [1]. The two t-PA bands show an unprecedented magnetic field response.

We present here a generic theory of primary photoexcitations in the DA copolymers [2]. We show that because of the combined effects of strong electron correlation and broken symmetry, there is considerable mixing between a charge-transfer exciton and an energetically proximate triplet-triplet state with an overall spin singlet. The triplet-triplet state, optically forbidden in homopolymers, is allowed in DA copolymers. For an intermediate difference in electron affinities of the D and A moieties, the triplet-triplet state can have a stronger oscillator strength than the charge-transfer exciton. We discuss all experimentally observed features, including the possibility of intramolecular singlet fission, in the light of our theory.

[1] U. N. V. Huynh, T. P. Basel, L. Dou, G. Li, S. Mazumdar, E. Ehrenfreund, Y. Yang, and Z. Valy Vardeny, arXiv:1510.04773.

[2] K. Aryanpour, T. Dutta, U. N. V. Huynh, Z. V. Vardeny and S. Mazumdar, Phys. Rev. Lett., Vol. 115, (2015), pp. 267401.

Controlled Light Emission in Organic Single Crystals for Optoelectronic Applications

Johannes Gierschner

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The last years have seen a boost in small molecule based conjugated materials for innovative (opto)electronic applications. Targeted design of such materials requires nevertheless a systematic understanding of structure-property relationships; this however can only be achieved if all intra- and intermolecular parameters can be controlled. We are therefore systematically investigating a library of luminescent single crystals based on distyrylbenzenes, by integrating optical spectroscopy and quantum chemistry to unveil features and fates of molecular excitons.[1] Our studies give detailed insight in the conditions for effective & color-tuned spontaneous and stimulated light emission,[1,2] stressing the cooperative effect of molecular properties, intermolecular arrangement and morphology.[3-5] This knowledge forms a unique basis to create novel functional materials for organic (opto)electronic applications by targeted design.

[1] J. Gierschner, S. Y. Park, *J. Mater. Chem. C* 1 (2013) 5818.

[2] J. Gierschner, S. Varghese, S. Y. Park, *Adv. Opt. Mater.* 4 (2016) 348.

[3] M. Wykes, S. K. Park, S. Bhattacharyya, S. Varghese, J. E. Kwon, D. R. Whang, I. Cho, R. Wannemacher, L. L?er, S. Y. Park, J. Gierschner, *J. Phys. Chem. Lett.* 6 (2015) 3682.

[4] M. Wykes, R. Parambil Mangattu, D. Beljonne, J. Gierschner, *J. Chem. Phys.* 143 (2015) 114116.

[5] J. Gierschner, L. L?er, B. Mili?n-Medina, D. Oelkrug, H.-J. Egelhaaf, *J. Phys. Chem. Lett.* 4 (2013) 2686.

Controlling Domain Size, Crystallinity, and Performance of Organic Photovoltaics via Solution Shearing

Kevin Gu

Stanford University

To continue to improve the efficiency of organic photovoltaics (OPVs), it is imperative to develop a comprehensive understanding of the detailed processing-morphology-performance relation beyond correlating morphology with performance. Solution shearing provides a highly tunable lab-scale fabrication technique to study coating conditions that can be potentially used to guide massively scalable roll-to-roll printing. A systematic experimental investigation of a model polymer/fullerene OPV system highlights the critical role of processing parameters on morphological characteristics and device performance. Increasing temperature during fabrication simultaneously increased phase separation domain size and decreased the relative degree of crystallinity in those domains, leading to decreased photocurrent. Domain size, polymer crystallinity, and power conversion efficiency can all be varied by upwards of a factor of two. Further, a temperature-dependent description of the relative importance of diffusion to evaporation is presented in the context of spinodal decomposition (spontaneous phase separation). Experimental results of printing parameters vs domain size correlate well with computational predictions. The profound effect of processing parameters on morphology and composition suggests that controlling fabrication parameters is a powerful method for tuning performance in polymer/fullerene OPVs.

Disorder in Organic Semiconductors Due to Fluctuations in Space Charge Density

David Dunlap¹

Tzu-Cheng Wu¹, Susan Atlas¹, and Steve Valone¹, Andrei Piryatinski²

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²*Los Alamos National Laboratory, Los Alamos, NM*

In organic semiconductors the charge mobility is many orders of magnitude lower than in inorganic counterparts due to weak (Van der Waals) molecular interactions and high energetic and spatial disorder. In many applications the density of injected charges is low, so that long-range Coulomb interactions between a moving charge with the static electric field set up by randomly oriented and randomly distributed permanent dipoles has been shown to lead to correlated Gaussian energetic disorder. However, another important source of static energetic disorder is the random field set up by permanently trapped (space) charge. Analytic models for which the energetic landscape has been calculated for randomly placed positive and negative charges have indicated anomalously large energy fluctuations, but this is because correlations between trapped charges have been largely ignored. In this work we introduce a mean-field model in which the dynamical correlations of the trapped charges can be calculated analytically. The model allows for a determination of the disordered electric field landscape set up by thermal fluctuations in the trapped charge distribution. We show that, in many systems of interest, charge transport will be thermally activated due to the energetic disorder caused by space charge fluctuations alone. Remarkably, in such a case, the activation energy depends only on the distance a charge hops, and is completely independent of the space charge density.

Is there any Exciton (Bottleneck) in an Excitonic Solar Cells: My Journey from OPV to Perovskite Solar Cells

Muhammad A. Alam

School of Electrical and Computer Engineering, Purdue University, West Lafayette, Indiana

The discovery dye sensitized and bulk heterojunction solar cells in early 1990s introduced a new class of PV technology that rely on (i) distributed photogeneration of excitons, (ii) dissociation of excitons into free carriers by the heterojunction between two organic semiconductors (OSC), and (iii) collection of free carriers through electron and hole transport layers. The success of the approach is undisputed: the highest efficiency OPV cells have all relied on variants of BHJ approach. Yet, three concerns related to the use of a pair of OSCs, namely, low Voc, process sensitivity, and reliability, suggest that the technology may never achieve efficiency-variability-reliability metrics comparable to inorganic solar cells. This encourages a reconsideration of the prospect of Single semiconductor OPV (SS-OPV), a system presumably doomed by the exciton bottleneck. I will explain how this reconsideration (and a chance meeting at a restaurant) helped define our journey from OPV to perovskite solar cells.

Nano-Engineering Core/Shell Quantum Dots for Ultimate Control Over Light-Emission Processes

Jennifer Hollingsworth

Han Htoon

Los Alamos National Laboratory, Center for Integrated Nanotechnologies, Los Alamos, NM

I will discuss advanced synthetic tuning or nano-engineering of semiconductor nanostructures as an important strategy for realizing novel functionality. Most notably, I will review our experiences with so-called giant core/shell QDs (gQDs) that, due to their internal nanoscale structure, exhibit a range of fundamentally interesting and useful behaviors, including being non-blinking and non-photobleaching,[1-5] as well as remarkably efficient emitters of multiexcitons as a result of extreme Auger recombination suppression.[6,7] I will describe recent work using compositional alloying to 'color-tune' gQD emission, multiple-shell constructs to achieve dual-color excitonic emission, and shape-tuning to realize dual-color multiexcitonic emission all with strong blinking suppression and enhanced single-nanostructure photostability. Finally, I will show how new synthesis and characterization[8] tools can dramatically facilitate our ability to establish structure-function correlations for the intelligent design of functional photonic nanostructures.

[1] Chen, Y. et al. J. Am. Chem. Soc. 2008, 130, 5026.

[2] Vela, J. et al. J. Biophotonics 2010, 3, 706.

[3] Dennis, A. M. et al. Nano Lett. 2012 12, 5545.

[4] Ghosh, Y. et al. J. Am. Chem. Soc. 2012, 134, 9634.

[5] Acharya, K. P. et al. J. Am. Chem. Soc. 2015, 137, 3755.

[6] Mangum, B. D. et al. Nanoscale 2014, 6, 3712.

[7] Gao, Y. et al. Adv. Optical Mater. 2015, 3, 39.

[8] Orfield, N. J. et al. ACS Nano 2016, 10, 1960.

Excited State Dynamics at Nanoscale Interfaces: Time-Domain Ab Initio Studies

Oleg Prezhdo

University of Southern California, Los Angeles, USA

Photo-induced processes at various interfaces form foundation of photovoltaic and photo-catalytic applications. They require understanding of dynamical response of novel materials on atomic and nanometer scales. Our non-adiabatic molecular dynamics techniques, implemented within time-dependent density functional theory, allow us to model such non-equilibrium response in real time. The talk will focus on photo-initiated charge and energy transfer at interfaces involving organic and inorganic nanoscale materials. Examples include TiO₂ sensitized with organic molecules, water, semiconductor quantum dots, graphene and hybrid organic-inorganic perovskites, GaN/water interface, carbon nanotube bundles, mixtures of C₆₀ with inorganic particles, etc. Photoinduced charge separation across such interfaces creates many challenges due to stark differences between molecular and periodic, and organic and inorganic systems. Our simulations provide a unifying description of quantum dynamics on nanoscale, characterize the rates and branching ratios of competing processes, resolve debated issues, and generate theoretical guidelines for development of novel systems for solar energy harvesting.

Two-Photon Excited Fluorescence Intermittency in Single CdSe/ZnS Quantum Dots: A Novel Role for Hot Exciton States

David J. Nesbitt

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The combination of ultrafast laser excitation, confocal microscopy and time correlated single photon counting methods provides a powerful platform for quantitative exploration of excitonic behavior in quantum dot nanocrystals. In particular, a major channel for fluorescence intermittency (“blinking”) in quantum dots is thought to arise from Auger ionization of the biexciton state promoting charge transfer to quantum dot surface, the mechanism and kinetics of which have been of considerable relevance to prospects for practical device applications. After a brief introduction to confocal microscopy methods and quantum dot blinking kinetics, this talk will focus primarily on power dependence, kinetics, and statistics of ultrafast, two photon-excited fluorescence intermittency from single CdSe/ZnS quantum dots, which highlight several new aspects of the blinking dynamics. As one example, a nearly quadratic ($n = 2.3(2)$) rather than quartic ($n = 4$) power dependence is observed for the on-state blinking dwell times, which suggests the presence of a novel $2 + 1$ “hot exciton” ionization/blinking mechanism due to partially saturated 1-photon sub-bandgap excitation out of the 2-photon single exciton state. The kinetic results can be analyzed within a simple kinetic model framework to predict photoionization quantum yields from “hot” exciton states ($4(1) \times 10^{-6}$) comparable with experimental estimates (10^{-6} - 10^{-5}) of conventional Auger ionization efficiencies out of biexcitonic states.

Dynamics of Electronic Excitations at Interfaces

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Atomistic modeling of broad range of excited state dynamics and charge transfer reactions at metal-to-semiconductor interfaces,[1] supported metal clusters in aqueous environment,[2] as well as in organic-inorganic lead-halide perovskites[3] and laser crystals[4] is performed by a range of methodologies including reduced density operator method, with nonadiabatic coupling being computed on-the-fly along nuclear trajectory.[5] A solution for non-equilibrium density of electrons is used for determining the dynamics of formation of surface charge transfer states, computing surface photo-voltage, and rates of energy and charge transfer.[6] An average over long *ab initio* molecular dynamics trajectories provides inhomogeneous broadening of spectral lines.[7] A modification of this methodology helps to evaluate distribution of products in photoassisted reactions.[8]

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Ultrafast Energy Flow in Protein Structures

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Energy flow through a protein structure is often anisotropic, following specific pathways rather than a diffusive transport mechanism. It is also possible that proteins are evolved for efficient energy flow through collective motions of the protein structure. Whether energy flows preferentially through a specific set of protein residues or through collective vibrational states, either mechanism is sensitive to the protein architecture and the specific distribution of conformations that is present. We have investigated the dynamics and structural anisotropy of energy flow in enzymes as probes of allosteric coupling and to determine how energy flow is influenced by the conformational distribution. We have developed a pump-probe method to measure the ultrafast flow of energy through proteins that is straightforward in concept: a short laser pulse (~100 fs) is absorbed by a heater dye bound to the interior of the protein (e.g. the active site of an enzyme), and is then converted to vibrational energy through rapid internal conversion. The "hot" ground state of the heater dye then cools by transferring energy to the protein, and ultimately that heat flows through the protein and out to the solvent. Ultrafast infrared spectroscopy is used to track the dynamics of heating the protein and the solvent, since the spectra of both are sensitive to temperature, a property that we have exploited in extensive studies of protein folding dynamics using a laser induced T-jump. These experiments provide a direct measure of the dynamics of energy transport through the protein structure. The transient IR spectrum provides information about the anisotropy of the energy flow, through transient changes in specific backbone amide vibrations. Thus we measure both the dynamics and anisotropy of the heat flow from active site to exterior of protein. Using this approach, we have studied energy flow in heme proteins, including hemoglobin and catalase. The dynamics of heat flow depend on the conformational distribution of the protein, which can be altered by the binding of allosteric effectors.

Two-Photon Absorption Spectroscopy of Molecular Switches: Insights from Theory

Anna Krylov

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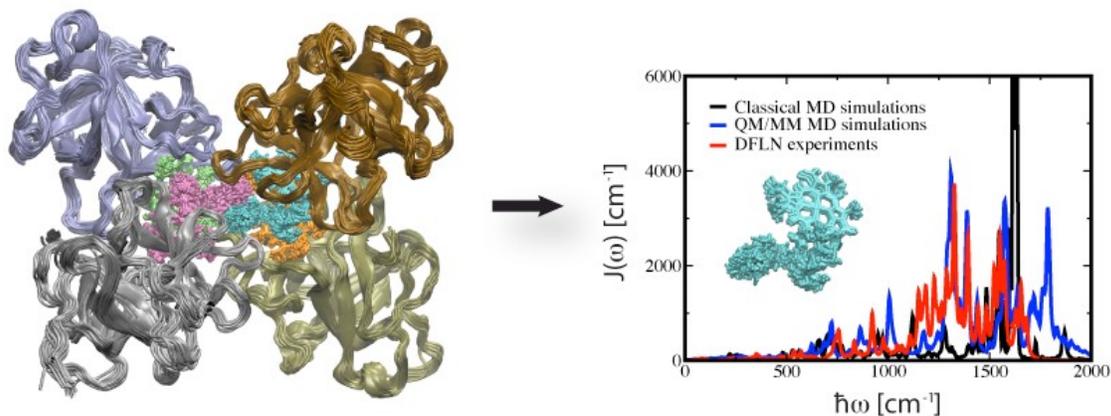
Non-linear spectroscopies have revolutionized many areas of material and life sciences. For example, techniques based on two-photon absorption (2PA) enable 3D and super-resolution imaging, nanosurgery, and targeted cell deactivation. This lecture will discuss 2PA spectra of several prototypical molecules (ethylene, toluene, stilbene, and phenanthrene). The choice of stilbene and phenanthrene is motivated by their potential applications as molecular switches, which stimulated recent experimental studies by Elles and coworkers. Ethylene and toluene can be viewed as building blocks of stilbene. We employ the recently developed implementation for calculating 2PA cross-sections using equation-of-motion coupled-cluster wave functions with single and double substitutions (EOM-CCSD). We also analyze the electronic structure of the states that give rise to the dominant features in the 2PA spectra using wave function analysis tools. We compare the computed 2PA spectra with the 1PA ones as well as with the experimentally measured spectra (for stilbene and phenanthrene).

Modelling Environment Effects in Photosynthetic Energy Transfer

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The environment plays an important role in the light harvesting dynamics of photosynthetic pigment-protein complexes. Specific pigment-protein interactions modulate the energy levels of the pigments, thus defining the spatial pathways of energy transfer in a given complex. On the other hand, the heterogeneous polarizable properties of the environment screen interpigment electronic couplings, a key quantity that determines exciton delocalization and migration dynamics. Moreover, coherent energy transfer recently observed in several photosynthetic complexes as well as organic materials has been suggested to arise from the structured-nature of the spectral density of electronic- vibrational coupling, which quantifies the coupling of electronic excitations to the nuclear vibrations in the system.



Here we overview a combined QM/MM-MD strategy we have developed that allows exploring the impact of the environment in full atomic detail on site energies, electronic couplings and spectral densities, accounting for mutual polarization effects among the chromophores and their environment through polarizable force fields.¹ We discuss the main insights unveiled by this strategy by investigating the properties of several pigment-protein complexes, including phycobiliproteins from cryptophyte algae,² the Fenna-Matthews-Olson (FMO) complex of green sulfur bacteria³ and the water-soluble chlorophyll binding protein (WSCP) of higher plants.⁴

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Optical Properties of Carbon Nanostructures

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In the last fifteen years, research on graphene has been extensively developed. It is commonly accepted that graphene shows unique physical properties such as high carriers' mobility, which promises numerous applications in nanoelectronics. However, graphene is a zero-bandgap semiconductor. Therefore, a graphene layer on its own is not appropriate for applications such as light-emitters for instance. Semiconducting form of sp² carbon can be obtained by size reduction that leads to 1D (carbon nanotubes, graphene nanoribbons) or 0D (graphene quantum dots) semiconductors. In this talk, we will first report on our recent results on the optical properties of carbon nanotubes at cryogenic temperatures. In particular, some insight into broadening mechanisms and exciton localization will be reported [1, 2]. Finally, preliminary results on the optical properties of graphene nanoribbons with a defined structure, both on ensemble and at the single object level, will be presented [3].

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Photophysics of Localized Excitons in Cryogenic Carbon Nanotubes

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LMU Munich

Pristine semiconducting carbon nanotubes are commonly pictured as one-dimensional solid-state systems that host diffusive excitons at room temperature. At cryogenic conditions, however, the photophysics of carbon nanotubes are dominated by exciton localization stemming from accidental disorder or deterministic covalent side-wall functionalization. On the basis of our photoluminescence studies of individual carbon nanotubes at low temperatures I will discuss the spectral signatures of exciton localization and highlight the effect of the dielectric environment on the spectral characteristics of single nanotube emission.

Exciton Dynamics and Related Photon Emission Properties of Semiconductor Carbon Nanotubes

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Semiconductor single-walled carbon nanotubes (CNTs) are near-perfect 1D materials with great potential for applications in opto-electronic and photonic devices. Their unique optical properties are determined by highly mobile interacting excitons. We address the following aspects of the exciton dynamics in CNTs. Motivated by experiment, we examine competition between exciton diffusion dynamics and their local interactions resulting in the exciton-exciton annihilation. [1] Our model reveals important dependence of the exciton emission profile on exciton population prepared by optical pulse and further applied to interpret the photon counting statistics typically available from 2nd order photon correlation measurements. The findings have strong implications toward development of CNT-based room-temperature single photon sources. Increase in the CNT emission quantum yield can be achieved via coupling of the exciton states with plasmonic mode of a metal nanotip placed near a CNT. We examine such an effect theoretically and demonstrate that near-field interaction between the exciton and surface plasmons occurs in a weak coupling regime, the effect of the exciton population transfer to the metal tip is fast resulting in the radiation distribution dominated by surface plasmon emission for the tip-CNT separation of a few tens of nanometers, the directionality of the radiation diagram can be controlled by varying the separation distance and position of the tip. Finally, we examine effect of the exciton states modulation by external periodic potential produced due to the acoustic wave propagating along CNT substrate. [3] We demonstrate that the potential induces dynamical gaps in the single particle dispersion leading to the redistribution of the oscillator strength and subsequent fluorescence quenching. The simulations also show exciton energy Stark red shift as well as reduction in the binding energy. Comparison of our results with reported experimental studies is provided.

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Photo-Induced Hole and Electron Transfer Reactions in Well-Defined Nanoscale Objects that Feature Electronically Homogeneous Single-Walled Carbon Nanotubes Wrapped by Redox Active Polymers

Jean-Hubert Olivier

Jaehong Park

Duke University

Single-walled carbon nanotube (SWNT)-based nanohybrid compositions based on (6,5) chirality-enriched SWNTs [(6,5) SWNTs] and a chiral n-type polymer (S-PBN(b)-Ph4PDI) that exploits a perylenediimide (PDI)-containing repeat unit are reported; S-PBN(b)-Ph4PDI-[(6,5) SWNT] superstructures feature a PDI electron acceptor unit positioned at 3 nm intervals along the nanotube surface, thus controlling rigorously SWNT-electron acceptor stoichiometry and organization. Time-resolved pump-probe spectroscopic studies demonstrate that S-PBN(b)-Ph4PDI-[(6,5) SWNT] electronic excitation generates PDI⁻ via a photoinduced CS reaction ($\tau_{CS} = 0.4$ ps, $\tau_{CR} = 0.97$). These experiments highlight the concomitant rise and decay of transient absorption spectroscopic signatures characteristic of the SWNT hole polaron and PDI⁻ states. Multiwavelength global analysis of these data provide two charge-recombination time constants ($\tau_{CR} = 31.8$ and 250 ps) that likely reflect CR dynamics involving both an intimately associated SWNT hole polaron and PDI⁻ charge-separated state, and a related charge-separated state involving PDI⁻ and a hole polaron site produced via hole migration along the SWNT backbone that occurs over this timescale.

In contrast to S-PBN(b)-Ph4PDI-[(6,5) SWNT] nanohybrids, selective photoexcitation of a SWNT superstructure in which a (porphinato)zinc (PZn)-based polymer wraps the nanotube surface triggers the formation of SWNT electron polaron and PZn radical cation states. Despite the disparate driving forces for photoinduced CS and thermal CR reaction in S-PBN(b)-Ph4PDI-[(6,5) SWNT] and S-PBN-PZn-[(6,5) SWNT] superstructures, similar magnitude CS ($\tau_{CS} = 0.4$ ps) and bi-exponential CR values ($\tau_{CR} = 22$ and 307 ps) are determined in these experiments. These intriguing results provide mechanistic insights into the factors that govern photo-induced charge transfer reactions in these well-defined polymer-wrapped [(6,5) SWNT] superstructures.

Synthesis of Nanographene Self-Assemblies with Optimized Electronic Structure and Facilitated Electron Transfer for Highly Efficient Energy Storage

Hsing-Lin Wang

Hung-Ju Yen, Edward Holby, Sergei Tretiak, Gang Wu

Los Alamos National Laboratory, Los Alamos, NM

Traditional graphene anodes in lithium ion batteries (LIBs) suffer from significant performance loss due to the restacking of graphene layers. In our lab, we have synthesized a series of 2D and 3D nanographenes with various functional groups attached to the edge of the nanographene basal planes. Among other potential applications, these high-surface area nanographenes have an excellent cyclic durability and a much enhanced charge capacity as novel anode materials for LIBs. Moreover, the theoretical charge capacity of these nanographenes exceeds 2000 mAh/g due to an increased edge to surface ratio and oxygen-containing functional groups. These exceptional metrics observed within the novel assemblies is primarily due to the robust structure with high surface areas and optimal d-spacing which allows for facilitated Li adsorption/desorption and diffusion. Moreover, optimized electronic structure and facilitated electron transfer has led to energy storage three times the capacity of graphite, suggesting that the optimal design of conjugated nanographenes are promising for next generation LIBs with superior energy storage efficiency.

Physicochemical Properties of One-Dimensional Periodic Uneven-Structured Nanocarbon Synthesized by Electron-Beam-Induced C₆₀ Polymerization

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Department of Materials, Physics, and Energy Engineering, Nagoya University

One-dimensional (1D) periodic uneven-structured C₆₀ polymer (see Fig. 1), which has been synthesized by electron-beam (EB) irradiation of pristine C₆₀ films, exhibits the electronic, optical, and phonon properties arising from 1D metal.^{1–19} Since the 1D C₆₀ polymer has both positively and negatively Gaussian curvatures (k), it can be regarded as a new nanocarbon allotrope that differs from conventional nanocarbons such as graphene ($k = 0$), fullerenes ($k > 0$), nanotubes ($k = 0$ in body, $k > 0$ at cap edge), and the hypothetical Mackay crystal ($k < 0$). Thus, the 1D C₆₀ polymer can be expected to show novel properties different from those of the nanocarbon allotropes. Indeed, it is interesting to note that the 1D C₆₀ polymer shows geometric curvature effects on the electronic properties, which have never been confirmed experimentally since the theoretical prediction in 1950s.

In this talk, in addition to the geometric curvature effects on the Tomonaga-Luttinger Liquid states,^{15,16} we will present the shape effects of p-electron conjugation on the electron-phonon coupling strength for nanocarbon allotropes¹⁷ and the anomaly in the resistivity of the 1D C₆₀ polymer at a low temperature.¹⁴ More recently, we have found that the sub-nanospace (0.3 nm) between adjacent 1D metallic polymer chains in the film acts as a specific reaction field for carbon dioxides at room temperature when the film is exposed to environmental air, which has not been observed for a pristine C₆₀ film with almost the same-size space.²⁰ This topic will be also presented.

We believe that the 1D periodic uneven-structured C₆₀ polymer not only exhibits novel physical and chemical properties different from those of the other nanocarbon allotropes but also plays a role of opening a new interdisciplinary between modern mathematics and materials science.

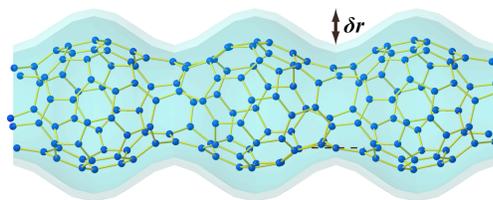


FIG. 1. Schematic illustration of 1D periodic uneven-structured C₆₀ polymer.

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Visualizing Single Molecule Absorption at the Nanometer Scale

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Nanomaterials such as quantum dots (QD) and carbon nanotubes (CNT) bear great promise for applications in (opto)electronic devices. Their unique optical and electronic properties allow for a wide spread of applications ranging from electronic switches and transistors, to photovoltaics, displays and cameras, light sources such as LEDs and lasers, to catalysis. Understanding the fundamental optical and electronic properties is of high importance for future applications.

The high spatial resolution of the scanning tunneling microscope makes it a powerful tool to investigate single molecules deposited on a variety of conductive or semi-conductive surfaces. By adding laser absorption, we are able to simultaneously examine single molecules with high spatial and high energy resolution. Our method of single molecule absorption detected by scanning tunneling microscopy (SMA-STM) relies on backside illumination to cut down on tip heating effects. The evanescent wave of a laser undergoing total internal reflection nearly saturates excitation of molecules on the surface, thus changing the net local density of states enough for STM detection. The excitation laser is amplitude modulated, allowing for simultaneous detection of the STM current (image) and its derivative (absorption signal) by a lock-in amplifier. As expected, SMA-STM performed on QDs and CNTs deposited by dry contact transfer onto a Pt-Au film, resulted in a strong, phase dependent absorption signal. Theoretical calculations aid in the explanation of the observed shapes of excited electron density in PbS QDs Stark-shifted so that different electronic states contribute to the absorption signal. Semiconducting-to-metallic transitions in CNTs have been imaged and identified directly by SMA-STM, and also characterized by I-V curves.

Differentiating Left- and Right-handed Carbon Nanotubes by DNA

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In addition to chiral angle and diameter variations, chiral single-wall carbon nanotubes (SWCNTs) may also exhibit different handedness: they may adopt either left- or right-handed helical configurations. However, a left-handed SWCNT and its right-handed mirror image structure have identical electronic configuration, and no distinguishable difference in their physical and chemical properties have been demonstrated. Here, we report the use of intrinsically chiral single-stranded DNA to differentiate left- and right-handed SWCNTs. We apply polymer aqueous two-phase systems to select special DNA-wrapped carbon nanotubes, each of which has an ordered DNA structure bound to a nanotube of defined handedness, resembling a well-folded biomacromolecule with innate stereo-selectivity. By screening over 300 DNA sequences, we are able to achieve unprecedented nanotube enantiomer selection across the entire chiral angle range. The structural basis of handedness selection is exemplified by a DNA sequence that adopts two distinct folds on a pair of nanotube enantiomers, respectively, rendering them large differences in fluorescence intensity and chemical reactivity. Our study establishes a first example of functionally distinguishable left- and right-handed nanotubes.

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Geyou Ao, Jason K. Streit, Jeffrey A. Fagan, and Ming Zheng "Aqueous Two-Phase Selection of DNA-Wrapped Carbon Nanotubes with Defined Structures and Functions" *submitted* (2016)

Nonadiabatic Transition State Theory: Application to Intersystem Crossings in the Active Sites of Metal-Sulfur Proteins

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University of Nevada, Reno

Nonadiabatic transition state theory (NA-TST) is a powerful tool to investigate the nonradiative transitions between electronic states with different spin multiplicities. The statistical nature of NA-TST provides an elegant and computationally inexpensive way to calculate the rate constants for intersystem crossings, spin-forbidden reactions and spin-crossovers in large complex systems. The basic NA-TST steps including calculations of the transition probability and coupling between electronic states, a search for the minimum energy crossing point, and computations of the densities of states and partition functions will be discussed. The shortcomings of the spin-diabatic version of NA-TST related to ill-defined state coupling and state counting will be highlighted. The application of NA-TST to intersystem crossings in the active sites of the metal-sulfur proteins [NiFe]-hydrogenase, rubredoxin and Fe₂S₂-ferredoxin will be demonstrated. We speculate that spin-forbidden nonadiabatic reaction mechanisms could play an important role in electron transfer and enzymatic catalysis involving these metal-sulfur proteins.

Studies of Natural and Artificial Photosynthesis

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Mechanistic investigations of the water-splitting reaction of the oxygen-evolving complex (OEC) of photosystem II (PSII) are fundamentally informed by structural studies of oxomanganese complexes. Many physical techniques have provided important insights into the OEC structure and function, including X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) spectroscopy as well as mass spectrometry (MS), electron paramagnetic resonance (EPR) spectroscopy, and Fourier transform infrared spectroscopy applied in conjunction with mutagenesis studies. However, experimental studies have yet to yield consensus as to the nature of the reaction mechanism responsible for oxygen evolution. Computational modeling studies, including density functional (DFT) theory combined with quantum mechanics/molecular mechanics (QM/MM) hybrid methods for explicitly including the influence of the surrounding protein, have proposed chemically satisfactory models of the fully ligated OEC within PSII that are maximally consistent with experimental results. The computational models are useful for rationalizing spectroscopic and crystallographic results and for building a complete structure-based mechanism of water-splitting as described by the intermediate oxidation states of oxomanganese complexes. This talk summarizes our recent advances in studies of the OEC of PSII and semiconductor materials functionalized biomimetic catalysts for artificial photosynthesis.

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- [5] *Biochemistry* **54**: 820-825 (2015) Computational Insights on Crystal Structures of the Oxygen-Evolving Complex of Photosystem II with either Ca²⁺ or Ca²⁺ Substituted by Sr²⁺, Leslie Vogt, M. Zahid Ertem, Rhitankar Pal, Gary W. Brudvig, and Victor S. Batista.
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Energy Transfer, Electronic Coupling and Light-Harvesting in Assemblies of Chromophores

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Molecular or nanomaterial assemblies that exhibit energy transfer, light-harvesting, or interesting electronic coupling performance can be obtained in many ways, including generation of geometrically well-defined arrangements of chromophores or preparation of random assemblies of chromophores with small intermolecular separation distances. Natural light-harvesting pigment-protein complexes provide exemplary cases of the first strategy, while co-assembly of chromophores and amphiphiles are practical materials that illustrate the second strategy. In addition, there are other types of interesting assemblies with energy transfer or electronic coupling performance, including DNA-origami-based architectures that place chromophores or particles in fixed geometric positions over relatively large distances. Working collaboratively with several other research groups, we have explored the performance and characteristics of several types of chromophore assemblies, including polymer micelles, liposomes, pigment-protein systems, and DNA-origami-based materials. Studies have included steady state and time-resolved spectroscopies, structural characterization, and modeling, aiming for an integrated experimental and theoretical understanding of material responses. Investigated topics that will be presented include understanding and predicting energy transfer efficiencies, system size effects, overall light-harvesting performance, and the development of possible technological applications.

Programming Synthetic Nanoscale Excitonic Circuits using DNA

Mark Bathe

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Associate Professor, Department of Biological Engineering, MIT

Associate Member, Broad Institute of MIT & Harvard

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Scaffolded DNA origami offers the unique ability to rationally design complex nanometer-scale molecular architectures with full control over both three-dimensional geometry and local molecular composition that is determined by programmed Watson-Crick basepairing. These scaffolds may be used to organize assemblies of chromophores to mimic aspects of highly evolved natural chromophore assemblies scaffolded by proteins in photosynthetic bacteria. A major challenge is to identify principles of molecular design that offer full control over both the position and orientation of multi-chromophore aggregates scaffolded using DNA to realize long-range, fast excitonic energy transport, high absorption cross-sections, and coherent multi-chromophore coupling that is typically exhibited by natural light-harvesting systems. Here, I will first present work in our group to enable the top-down, rational design of complex scaffolded DNA origami architectures with full control over 3D geometry on the 5-100 nanometer scale [1]. I will then present a new class of multi-chromophore aggregates that exhibit J-aggregate-like molecular organization and excitonic coupling in addition to full programmability in position and orientation within larger-scale DNA-based energy transfer circuits that we design, synthesize, and characterize [2]. Our system offers a path towards the construction of synthetic functional excitonic materials with rationally programmed optical and energy transport properties.

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Excitonic Effects in 2D Semiconductors: Path Integral Monte Carlo Approach

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One of the most striking features of novel 2D semiconductors (e.g., transition metal dichalcogenide monolayers or phosphorene) is a strong Coulomb interaction between charge carriers resulting in large excitonic effects. In particular, this leads to the formation of multi-carrier bound states (e.g., excitons, trions and biexcitons), which could remain stable at near-room temperatures and contribute significantly to optical properties of such materials. In my talk, I will report on our recent progress in using the Path Integral Monte Carlo methodology to numerically study properties of multi-carrier bound states in 2D semiconductors. Incorporating the effect of the dielectric confinement (via Keldysh potential), we have investigated and tabulated the dependence of single exciton, trion and biexciton binding energies on the strength of dielectric screening, including the limiting cases of very strong and very weak screening. The implications of the obtained results and the possible limitations of the used model will be discussed. The results of this work are potentially useful in the analysis of experimental data and benchmarking of theoretical and computational models.

The Full Spectrum Boost Project: The Intermediate Band Mechanism and the Metal-Insulator Transition in Nanoparticle Solar Cells

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The 'Full Spectrum Boost in Nanoparticle Solar Cells' Project has three major thrusts: (1) Transcending the Quantum Confinement Dilemma to optimize Carrier Multiplication (CM) in nanoparticles to enhance absorption in the high energy sector of the solar spectrum; (2) Demonstrating that colloidal nanoparticles are a promising platform to implement the Intermediate Band (IB) mechanism to enhance absorption in the low energy sector of the solar spectrum also; and (3) Increasing the carrier mobility, preferably across a Metal-Insulator Transition to enhance charge extraction efficiency. After reviewing several different mechanisms to reduce the gap in nanoparticles while preserving the enhanced Carrier Multiplication efficiency in (1), we provide a proof of concept for implementing the IB mechanism in nanoparticles for (2). We develop an ab initio calculation of the band structure of an array of CdSe nanoparticles and demonstrate the formation of a well-defined Intermediate Band. Then we demonstrate that this Intermediate Band can be doped with a cobaltocene-related ligand, to create the optimal setup for solar cell utilization. Finally, for the transport studies of (3), we present an ab initio-based Kinetic Monte Carlo simulation of hopping charge transport in nanoparticle arrays. This Monte Carlo model is then expanded with the introduction of metallic transitions between nanoparticles that have sufficiently large overlap between the orbitals of their electrons. With this expanded Kinetic Monte Carlo method, we are able to capture the Metal-Insulator Transition. The data are analyzed in two frameworks: that of Quantum Phase Transitions, and that of a Quantum Percolation theory. We demonstrate the emergence of a rich phase diagram of a metallic phase, an insulating phase, and an unexpected, anomalously low gap intermediate region between them.

Surface Chemistry of Semiconductor Nanostructures: Theoretical Perspectives

Svetlana Kilina

North Dakota State University

The significance of the surface passivation of colloidal quantum dots (QDs) on their photophysical properties is discussed. Optically forbidden nature of surface-associated states makes their direct measurements challenging. We present several examples, where calculations based on time dependent density functional theory (TDDFT) succeed in providing insights into these issues allowing for explanations of experimental trends and observables sensitive to surface defects and ligand passivation. Thus, our investigations of QD-ligand and QD-QD interactions provide an explanation of experimentally detected enhancement of on-blinking times in closely packed Si QDs and reveal the role of Cl ligands in formation of PbSe nanoplates growing along a specific crystal lattice direction. Our calculations show that photophysics of stoichiometric, magic-size CdnSen QDs is less sensitive to their passivation, compared to non-stoichiometric CdnSem. In the last, surface-driven optically inactive midgap states can be eliminated by anionic ligands, such as carboxylates, thiolates, and even hydrides, explaining better emission of metal-enriched than nonmetal-enriched QDs. Overall, our calculations provide insights into the surface chemistry of QDs and offering guidance for controlling the optical response of nanostructures by means of OD-QD and QD-ligand engineering.

Synthesis and Spectroscopy of Ternary Copper Chalcogenide Nanocrystals

Celso de Mello Donega

Ward van der Stam, Anne C. Berends

Debye Institute for Nanomaterials Science, Utrecht University

Colloidal nanocrystals (NCs) of ternary copper chalcogenides, such as CuInE_2 ($E = \text{S, Se}$), are attracting increasing attention as alternative for the well-known heavy metal based NCs (CdE and PbE , $E = \text{S, Se, Te}$), due to their readily tunable, size-dependent optical properties, lower toxicity, potentially lower costs, and very wide range of compositions [1]. However, the synthesis of colloidal NCs and hetero-NCs of ternary copper chalcogenides is still largely underdeveloped, and has yet to reach the same level of mastery available for the prototypical Cd-chalcogenide based nanomaterials. As a result, a comprehensive understanding of the optoelectronic properties of copper chalcogenides has yet to emerge.

In this presentation, we will discuss recent work by our group in which post-synthetic topotactic cation exchange reactions are exploited to convert template copper sulfide NCs and Cd-chalcogenide NCs and hetero-NCs into the CuIn -chalcogenide analogues, with preservation of the size, shape and heteroarchitecture of the parent NCs. This has allowed us access to CuInE_2 NCs and hetero-NCs with sizes, shapes and heteroarchitectures that are not attainable by direct synthesis protocols (e.g. wurtzite CuInS_2 bifrustum NCs, CuInE_2 nanorods and multipods, $\text{CuInSe}_2/\text{CuInS}_2$ dot core/rod shell nanorods and concentric core/shell QDs, $\text{CuInTe}_2/\text{CuInSe}_2$ heterobipods, etc.) [2-3]. Many of these novel nanomaterials show interesting optical properties, such as NIR PL.

We will also present our optical spectroscopic studies of these materials, with particular emphasis on CuInS_2 based core/shell QDs. The origin of the optical properties of CuInS_2 QDs has been explained by a variety of models, and is still under debate. Our time-resolved PL spectroscopy and Transient Absorption spectroscopy studies exclude Donor-Acceptor Pair and intrinsic recombination models, and are consistent with models in which the PL originates from recombination of a quantized conduction band electron state with a localized hole [4-5].

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Mechanism for Highly Efficient Intra-Gap Emission from CuInSexS2-x Quantum Dots

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Nanocrystals (or quantum dots) of ternary I-III-VI₂ semiconductors such as CuInSexS_{2-x} have been studied in the context of a number of applications including luminescent solar concentrators [1], solar cells [2], light-emitting diodes [3], and bio-imaging [4]. A large bandwidth and a long lifetime of their photoluminescence along with a large Stokes shift still pose questions about the detailed emission mechanism. Proposed emission models include donor-acceptor recombination, phonon-assisted processes facilitated by strong electron-phonon coupling, and emission due to a mixed transition involving a band-edge and an intra-gap defect state. An increasing body of literature points towards the last of these mechanisms. Furthermore, recent magneto-optical studies [5] suggest that the intra-gap state responsible for emission is likely associated with a Cu-related defect.

Here we perform systematic spectroscopic studies of CuInS₂ and CuInSexS_{2-x} quantum dots to further refine the model for emission from these materials. Ultrafast transient absorption and time-resolved photoluminescence measurements of solutions of nanocrystals reveal weak, short-lived (ps time scale) band-edge emission emerging on the blue side of the long-lived photoluminescence band. Comparison of the emission band width with the transient absorption spectrum confirms its band-edge origin. Further measurements using spectro-electro-chemistry allow us to formulate a self-consistent model describing photoluminescence from CuInSeS quantum dots as a competition between radiative decay of band-edge exciton, ultrafast trapping of the valence band holes by the 2E Cu-ion state, ultrafast relaxation of the hole from the 2E to 2T₂ Cu state, and finally radiative recombination of the conduction band electron and the 2T₂ hole. These processes are also affected by non-radiative decay channels associated with surface hole and electron trap. The same model is successful in explaining photoluminescence properties of both CuInS₂ and CuInSexS_{2-x} quantum dots. Based on our measurements we also identify timescales of various processes involved. These results help understand the mechanisms behind broad and relatively slow photoluminescence from CuInSeS nanocrystals, which should facilitate the development of practical approaches for increasing emission efficiency of these interesting nanomaterials.

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Matrix Engineering, State Filling, and Charge Transport in PbSe Quantum Dot Solids

Matt Law

University of California, Irvine

Colloidal semiconductor quantum dots (QDs) are attractive building blocks for solar photovoltaics (PV). In this talk, I will highlight our recent progress in designing PbX ($X = S, Se, Te$) QD thin film absorbers for next-generation PV. Basic requirements for QD absorber layers include efficient light absorption, charge separation, charge transport, and long-term stability. I begin by discussing QD film fabrication, charge transport physics, insights from theory, and evidence that the carrier diffusion length is short and limited by electronic states in the QD band gap. Studies of carrier mobility as a function of basic film parameters such as inter-QD spacing, QD size, and QD size distribution have led to a better understanding of charge transport within highly disordered QD films. Efforts to improve carrier mobility by enhancing inter-dot electronic coupling, passivating surface states, and implementing surface doping will be highlighted. Engineering the inter-QD matrix to produce QD/inorganic or QD/organic nanocomposites is presented as a powerful way to optimize coupling, remove surface states, eliminate hysteretic charge trapping and ion motion, and achieve long-term environmental stability for high-performance, robust QD films that feature good carrier multiplication efficiency. New results on the use of atomic layer deposition infilling of QD films to yield all-inorganic QD transistors free of the bias-stress effect will be presented, and the likely role of ion transport in QD optoelectronics discussed. The use of infrared transmission spectroscopy to understand state filling and study charge transport in QD thin film transistors will be presented.

Radiative Recombination from Dark Excitons: Activation Mechanisms and Polarization Properties

Alexander Efros

Naval Research Laboratory

We analyze theoretically physical mechanisms responsible for radiative recombination of the ground optically passive ('dark') exciton (DE), which dominates in photoluminescence (PL) of colloidal nanocrystals (NCs) at low temperatures. The DE becomes optically active due to its mixing with the bright excitons caused by an external magnetic field, dangling bond spins or by acoustic and optical phonons. These activation mechanisms mix the DE with different bright excitons and, consequently, lead to different PL polarization properties, because they are determined by dipole orientations of the bright excitons, which the DE is coupled with. We show that the PL polarization properties of prolate and oblate shape NCs are different due to different activation mechanisms responsible for the DE recombination.

Relationship between Microscale Photophysics, Structure, and Local Chemistry of Metal Halide Perovskites

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Organic-inorganic perovskites such as $\text{CH}_3\text{NH}_3\text{PbI}_3$ are highly promising materials for a variety of optoelectronic applications, with certified power conversion efficiencies in solar cells already exceeding 22% and promising applications in light-emitting diodes, lasers and photodetectors also emerging. Nevertheless, it has recently been revealed that there is a grain to grain heterogeneity in optoelectronic properties on the microscale which limit device performance. The origin of the heterogeneous photophysical properties and their connection with local structure and chemistry is currently unclear.

Here, I will present a variety of results probing the relationship between grain structure, local chemistry and local photophysics. We probe the local photophysics of neat $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films using bulk and confocal photoluminescence (PL) measurements and correlate these observations with the local chemistry of the grains using energy-dispersive X-ray spectroscopy (EDX) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). We investigate the connection between grains that are bright or dark in emission and the local Pb:I ratios at the surface and through the grains. We investigate how the optoelectronic properties change around the phase transition temperature and how they are intimately related to the local structure, as inferred from confocal PL and bulk X-Ray Diffraction (XRD) measurements. We also examine how the photophysics, local chemistry and non-radiative decay pathways change slowly over time under illumination. Our results reveal a ?photo-induced cleaning? arising from a redistribution of iodide content in the films, giving strong evidence for photo-induced ion migration. I will discuss how immobilizing ions, reducing trap densities and achieving homogenous stoichiometries could suppress hysteresis effects and lead to devices approaching the efficiency limits.

Coherence in Ultrafast Chemistry

Greg Scholes

Princeton University

Recent experiments from my group and others have motivated reconsideration of coherent phenomena in complex systems. For example, ultrashort laser pulses were used to photoexcite superpositions of electronic absorption bands in photosynthetic light harvesting complexes. These experiments revealed how the light absorbing molecules (chromophores) interact. The surprising result is that these superpositions of states are much more resistant to dephasing than anticipated. Specifically, instead of relaxing rapidly to a statistical mixture of excitations associated locally with the chromophores, the excitation retains amplitude on both chromophores. This is a property indicative of coherence, familiar from waves and quantum states. The key advance is that despite structural and energetic disorder, transient coherent states can be prepared and observed. That is, correlations can be built into the spectroscopy of interacting molecules. These findings provoke the question: how do such correlations show up in studies of other fast light induced processes, for example electron transfer? I will report and compare some recent studies of how wavepackets evolve in different electron transfer reactions and then discuss how these experiments can be interpreted.

Boosting OLEDs Efficiency through Theoretical Understanding and Computational Study

Zhigang Shuai

Tsinghua University

Organic light-emitting diodes has aroused even stronger interests recently due to the success in organic electronics industry. We report our recent progresses in theoretical studies of OLEDs: (1) we proposed triplet-polaron collision mechanism to beat the 25% singlet limit for electroluminescence; (2) we are proposing a cross-over mechanism to rationalize the crystallization induced room temperature phosphorescence for pure organic molecules; (3) we proposed to use isotope effect as well as resonant Raman spectroscopy to probe the aggregation induced emission phenomena.

Regioregular Narrow Bandgap Conjugated Polymers for Low Energy Loss Organic Solar Cells

Guillermo Bazan

University of California, Santa Barbara

The power conversion efficiency (PCE) of solar cells and their open circuit voltage (VOC) are directly related. In the majority of conjugated polymer:fullerene bulk heterojunction (BHJ) organic photovoltaics (OPVs) the $eVOC$ is significantly lower than the energy of photons absorbed, as determined by the donor material bandgap (E_g). Minimizing E_g to $eVOC$ energy losses could appreciably increase the PCE in organic solar cells. We have found that OPVs containing the regioregular conjugated polymer PIPCP in conjunction with fullerenes exhibit very low E_{loss} , where $E_{loss} = E_g - eVOC$, while maintaining high external quantum efficiencies. This appears to be a result of very low energetic disorder, at least at the local level, as reflected by the small Urbach energy. Another important point is that the energy of the charge transfer state is nearly equal in energy to E_g , giving rise to $E_{CT} - VOC = 0.52$ eV. Our results suggest that by the use of polymers with high energetic order, the necessity of an appreciable energetic offset in OPV devices for high PCEs may need to be reconsidered and that high VOC values can be achieved in organic solar cells.

A Surface Hopping Theory of Electrochemistry

Joe Subotnik

University of Pennsylvania, Chemistry Department

In this talk, I will discuss how to propagate nuclear-electronic dynamics semiclassically near a metal surface. When you have a continuum of electronic energy levels and electronic dissipation competes with nuclear dissipation. Two different frameworks emerge for dynamics: surface hopping and electronic friction. I will discuss both methodologies and give intuition for the nuclear motion. For comparison with the more routine excited state processes that we are familiar with in solution, I will compare and contrast electrochemical dynamics with Marcus's standard theory of electron transfer and show how broadening emerges as a new phenomenon.

Excited State Processes in Novel Energetic Materials

R. Jason Scharff

Los Alamos National Laboratory, Los Alamos, NM

Explosive Chromophores for Photo-Thermal and Photo-Chemical Laser Initiation

Thomas Myers

Los Alamos National Laboratory, Los Alamos, NM

The synthesis of air stable Fe(II) explosive coordination complexes with tetrazine and triazolotetrazine ligands has been accomplished. The complexes are intensely colored secondary explosives with MLCT absorption bands in the visible region of the electromagnetic spectrum. Manipulation of the ligand electronic structure can tune the MLCT band over a wavelength range of 150nm with minimal influence on the explosive properties. Electrochemical and theoretical evidence suggest that rendering the ligand more σ donating and π accepting lowers the energy of the corresponding MLCT band and facilitates rational design of the ligand system. The optical properties of these new materials are also sensitive to their phase, exhibiting a bathochromic shift and subsequent broadening of the MLCT band in the amorphous state relative to the solution state. By manipulating the absorption properties in these complexes, materials have been developed that are more sensitive than PETN towards laser initiation while also being less sensitive than PETN towards conventional stimuli.

Unusual 2D Semiconductors and their Unexpected Properties*

David Tomanek

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Among the new class of 2D semiconductors with a direct fundamental band gap, layered black phosphorus and related phosphorene monolayers are rapidly gaining attention due to possible applications in optoelectronics [1]. Recent Quantum Monte Carlo (QMC) calculations show that the inter-layer bonding, while weak, is not well described by dispersive van der Waals (vdW) interactions[2]. As seen in Fig. 1, QMC results differ qualitatively from vdW-enhanced DFT functionals and the common designation of similar systems as “van der Waals solids” is strictly incorrect. Also other group V systems including monolayers of grey arsenic[3] and As_xP_{1-x} compounds[4] share the same nonplanarity of their structure and an intriguing dependence of their fundamental band gap on the number of layers and in-layer strain with phosphorene. Similar to 3D III-V compounds, which are isoelectronic and share many properties with group IV semiconductors such as Si, We find that also 2D IV-VI compounds such as SiS[5] are in many respects similar to layered group V allotropes and quite possibly may display superior chemical stability. Predictive *ab initio* calculations provide here a useful guidance to experimental studies.

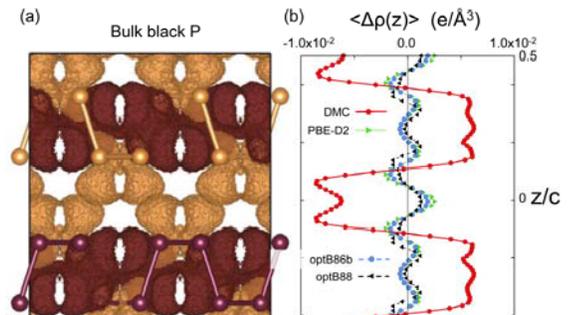


FIG 1 Calculated electron density difference representing the charge redistribution caused by assembling the bulk structure from isolated monolayers. (a) Diffusion Monte Carlo (DMC) isosurfaces bounding regions of excess electron density (dark brown) and electron deficiency (light brown), with respective values $\pm 6.5 \times 10^{-3} \text{ e}/\text{\AA}^3$. (b) $\langle \Delta\rho(z) \rangle$ for DMC and selected DFT functionals averaged across the x - y plane of the layers, with z/c indicating the relative position of the plane in the unit cell. (From Ref. [2]).

* Partly supported by the NSF/AFOSR EFRI 2-DARE grant number #EFMA-1433459.

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Permanent Excimer Superstructures by Supramolecular Networking of Metal Quantum Clusters

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Excimers are evanescent quasi-particles typically formed upon collisional intermolecular interactions and existing exclusively for their excited-state lifetime. Here, we exploit the unique structure of metal quantum clusters to fabricate permanent excimer-like colloidal superstructures made of ground-state non-interacting gold cores, held together by a network of hydrogen bonds between their capping ligands. This unprecedented aggregation state of matter, probed by spectroscopic experiments and ab-initio calculations, conveys the photophysics of excimers into stable nanoparticles, which overcome the intrinsic limitation of excimers in single-particle applications, that is, their nearly zero formation probability in ultra-diluted solutions. In vitro experiments demonstrate the suitability of the superstructures as non-resonant intracellular probes and further reveal their ability to scavenge reactive oxygen species, which enhances their potential as anti-cytotoxic agents for bio-medical applications.

B. Santiago-Gonzales, *et al.*, *Science*, in press (2016)

Highly-Luminescent Colloidal Nanocrystals of Cesium Lead Trihalide Perovskites (CsPbX₃, X=Cl, Br, I)

M. Kovalenko

ETH Zürich, Department of Chemistry and Applied Biosciences and Empa-Swiss Federal Laboratories for Materials Science and Technology

Chemically synthesized inorganic nanocrystals (NCs) are considered to be promising building blocks for a broad spectrum of applications including electronic, thermoelectric, and photovoltaic devices. We have synthesized monodisperse colloidal nanocubes (4-15 nm edge lengths) of fully inorganic cesium lead halide perovskites (CsPbX₃, X=Cl, Br, and I or mixed halide systems Cl/Br and Br/I) using inexpensive commercial precursors [1]. Their bandgap energies and emission spectra are readily tunable over the entire visible spectral region of 410-700 nm. The photoluminescence of CsPbX₃ NCs is characterized by narrow emission line-widths of 12-42 nm, wide color gamut covering up to 140% of the NTSC color standard, high quantum yields of up to 90% and radiative lifetimes in the range of 4-29 ns.

Post-synthetic chemical transformations of colloidal NCs, such as ion-exchange reactions, provide an avenue to compositional fine tuning or to otherwise inaccessible materials and morphologies. While cation-exchange is facile and commonplace, anion-exchange reactions have not received substantial deployment. Here we present fast, low-temperature, deliberately partial or complete anion-exchange in CsPbX₃ NCs. By adjusting the halide ratios in the colloidal NC solution, the bright photoluminescence can be tuned over the entire visible spectral region (410-700 nm). Furthermore, fast inter-NC anion-exchange is demonstrated as well, leading to uniform CsPb(Cl/Br)₃ or CsPb(Br/I)₃ compositions simply by mixing CsPbCl₃, CsPbBr₃ and CsPbI₃ NCs in appropriate ratios.

We also present low-threshold amplified spontaneous emission and lasing from CsPbX₃ NCs [3]. We find that room-temperature optical amplification can be obtained in the entire visible spectral range (440-700 nm) with low pump thresholds down to $5 \pm 1 \mu\text{J cm}^{-2}$ and high values of modal net gain of at least $450 \pm 30 \text{ cm}^{-1}$. Two kinds of lasing modes are successfully realized: whispering gallery mode lasing using silica microspheres as high-finesse resonators, conformally coated with CsPbX₃ NCs, and random lasing in films of CsPbX₃ NCs.



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The Effects of Electronic Impurities and Electron-Hole Recombination Dynamics on Large Grain Organic-Inorganic Perovskite Photovoltaic Efficiencies

Jean-Christophe Blancon

Wanyi Nie, Amanda J. Neukirch, Gautam Gupta, Sergei Tretiak, Laurent Cagnet, Aditya D. Mohite and Jared J. Crochet

Los Alamos National Laboratory, Los Alamos, NM

Organometallic perovskites have attracted considerable attention after promising developments in energy harvesting and other optoelectronic applications. However, further optimization will require a deeper understanding of the intrinsic photo-physics of materials with relevant structural characteristics. In this presentation, we will present an investigation of the dynamics of photogenerated charge carriers in large-area grain organometallic perovskite thin films via confocal time-resolved photoluminescence spectroscopy [1]. Our findings show that the bimolecular recombination of free charges is the dominant decay mechanism at excitation densities relevant for photovoltaic applications [2]. Bimolecular coefficients were found to be on the order of 10^{-9} cm³/s, comparable to typical direct-gap semiconductors, yet significantly smaller than what is theoretically expected. We also will provide evidence that there is no degradation in carrier transport in these thin films due to electronic defects through modeling of the photoluminescence kinetics and open circuit voltage characteristics of a photovoltaic cell. We conclude that suppressed electron-hole recombination and transport that is not limited by defects provide a microscopic model for the superior performance of large-area grain hybrid perovskites for photovoltaic applications.

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Understanding the Photovoltaic Efficiency of Organometallic Perovskites

Andrew M. Rappe

Diomedes Saldana-Greco, Fan Zheng, Liang Z. Tan, Nathan Z. Koocher

University of Pennsylvania

Halide perovskites have attracted a high and sustained level of scientific and applied interest for solar photovoltaics because they demonstrate long carrier lifetimes, high mobility, and high power conversion efficiency. The most effective materials incorporate molecular cations on the perovskite A site, making them hybrid halide perovskites, but both hybrid and inorganic halide perovskites offer impressive optoelectronic properties and pose strong scientific challenges. Despite the promise, the perovskites face multiple challenges before industrial insertion, including hysteresis and stability issues.

In this talk, I will report on key insights gleaned from theory and modeling to understand the novel couplings between mechanical, electronic, and optical responses in this class of materials. The low energy scale for vibrations and strains necessitates their explicit incorporation in electronic and optical calculations. I will present a multi-scale approach incorporating spin-orbit Hamiltonian terms, vibrational motions, thermal disorder, first-principles modeling, tight binding, molecular dynamics, and kinetic Monte Carlo. This comprehensive scheme brings a new understanding of ionic dynamics revealing emergent anharmonicity, electron-phonon coupling variations, and carrier transport and stability.

Charge Carrier Dynamics in Quantum-Dot Solids Probed by Ultrafast Photocurrent Spectroscopy

Andrew Fidler

Los Alamos National Laboratory

Quantum dots offer an attractive materials platform for advanced solar energy applications, such as third generation photovoltaics and solar windows. However, additional understanding and control of the electrical transport behavior in these materials is required for devices fabricated from quantum dots to reach their full potential. To address this issue we have conducted transient photocurrent measurements, where we incorporate quantum dots into a fast electro-optical switch to monitor the changes in the photo-generated current with 10-40 ps time resolution. With this approach we may resolve both early time intra-dot processes such as carrier multiplication and Auger recombination, as well as longer timescale trapping and recombination dynamics. In addition, this method allows us to directly study the competition between charge extraction and Auger recombination as well as the role of the electronic structure of the quantum dots in governing the early time transport behavior.

Optical Properties of Organometallic Perovskite: An ab initio Study using Relativistic GW Correction and Bethe-Salpeter Equation

Towfiq Ahmed

Theoretical Division, Los Alamos National Laboratory

We investigate the optical and vibrational properties of organometallic cubic perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ using first-principles calculations. We go beyond conventional DFT, and calculated optical conductivity using relativistic quasi-particle (GW) correction. We solve Bethe-Salpeter equations (BSE) for excitons, and found enhanced optical conductivity near the gap edge. Due to the presence of organic methylammonium cations near the center of the perovskite cell, the system is sensitive to low energy vibrational modes. We estimate the phonon modes of $\text{CH}_3\text{NH}_3\text{PbI}_3$, and further calculate the infrared absorption (IR) spectra. Our calculated low-energy phonon frequencies are in good agreement with our terahertz measurements.

Controlling Life with Photons

Guglielmo Lanzani

CNST@POLIMI Istituto Italiano di Tecnologia

Light can be used for controlling cell activity, with high space and time resolution and a virtually infinite number of configuration, free from wiring constrains. Yet there are draw backs, such as light absorption and scattering, hampering delivery into deep tissues, and a fundamental limitation: by and large living cells are transparent. In this talk we will briefly review the state of our research regarding organic bio interfaces for inducing light sensitivity in cells, both in vitro and in vivo. The coupling mechanism of the biotic/abiotic interface is still far from being understood, attempts to shed light will be introduced. The possible application of dispersed interfaces, obtained by spreading organic nanoparticles into living tissues will be discussed. Finally an update on the artificial retina project will be presented, as one of the most appealing application of this emerging technology.

Excitation Energy Transfer and Vibronic Couplings in Multichromophores

Lyudmila Slipchenko¹

Ben Nebgen²

¹*Department of Chemistry, Purdue University*

²*Department of Chemistry, University of Southern California*

Excitation energy transfer (EET) is a universal phenomenon governing photosynthesis in plants and bacteria, and exploited by humankind in photovoltaic devices and FRET spectroscopy. Thus, predictive modeling of the EET and electron-phonon interactions is essential for advancing our fundamental knowledge and technological progress. We recently developed a vibronic model that describes electron-phonon couplings in multi-chromophore systems. This model accounts for interaction among multiple vibrational modes on multiple chromophores and can describe asymmetric wave functions and inter-chromophore vibrations. Application of this model to flexible bi- and tri-chromophores diphenylmethane, diphenylethane and tricyclophane reveals that small asymmetry between chromophores dramatically affects vibronic spectra. For example, asymmetry changes localization of electronic and vibrational wave functions and intensity of vibronic transitions. Extension of this methodology to modeling synthetic and natural multi-chromophore systems will be also discussed.

A Close Look at Charge Generation and its Dependence on Microstructure

Natalie Stingelin

Imperial College London

Here we will take a close look at charge generation in organic bulk heterojunction solar cells. Focus will be on discussing the key mechanisms during charge generation in polymer:fullerene blends and how they can be linked to specific structural features of these systems, in an attempt to resolving the long-standing question of how free charges are generated in such donor:acceptor blends that are used in organic solar cells. For this we link the picture of the generally complex phase morphology of polymer:fullerene where intermixed and neat phases of the donor and acceptor material co-exist, with Stark effect spectroscopy data (performed in Natalie Banerji's laboratory at the University of Fribourg, Switzerland) obtained in the absence and presence of externally applied fields. Reconciling opposing views found in literature, we will demonstrate that the fate of photogenerated electron-hole pairs whether they will dissociate to free charges or geminately recombine is determined at ultrafast times, despite the fact that their actual spatial separation can be much slower.

Molecular Aggregate Photophysics Beyond the Kasha Model: Introducing a New Design Paradigm for Organic Materials

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Solid phases of π -conjugated molecules and polymers continue to receive widespread attention as semiconducting materials in field effect transistors, light emitting diodes and solar cells. However, despite the more than five decades of intensive experimental and theoretical research following Kasha's pioneering work on H- and J-aggregates¹ there are still a great many questions regarding the nature of the photo- excitations in molecular assemblies and how their spectral signatures are related to crystal packing and morphology. The theory of Kasha is based on the long-range Coulombic coupling between chromophores. However, in packing morphologies such as the commonly occurring π -stacking motif, the intimate contact between nearest neighbors allows for charge transfer and the creation of a short-range excitonic coupling mechanism due to wave function overlap. In this talk, it is shown how the simultaneous presence of long-range and short-range intermolecular couplings impact photophysical and transport properties in molecular π -stacks.² The effect is similar to that recently described in polymer π -stacks.³ The analysis is based on a Holstein-style Hamiltonian which includes Coulombic coupling and charge transfer. The interference between short-range and long-range couplings defines four aggregate types: HH, HJ, JH and JJ, based on the sign of the couplings. Each of the four aggregate types possess unique photophysical and transport properties. For example, HH-aggregates have constructively enhanced exciton mobilities and small radiative decay rates, making them excellent candidates for solar cell absorbers. JJ-aggregates can be superradiant at room temperature and therefore serve as good light emitting materials. The photophysical signatures of the four aggregate types include aggregation-induced changes to the vibronic progressions in the absorption and photoluminescence spectra.⁴ The vibronic progression, sourced primarily by the ubiquitous vinyl-stretching mode common to virtually all π -conjugated molecules, therefore serves as a direct probe of the nature of the excitonic coupling, as well as the exciton coherence length and mobility. Specific applications will be made to rylene π -stacks which have been intensively investigated as dye pigments and electron-transporting materials.^{5, 6} A new design paradigm for organic electronic materials is presented based on the extreme sensitivity of the short-range coupling to small (sub Angstrom) intermolecular displacements transverse to the stacking axis.^{2, 7, 8}

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Charge-Separation at Donor/Acceptor Interfaces: Coherent or Not Coherent, That is the Question

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Recent experimental evidence from ultrafast probes suggest that charge generation at in polymer/fullerene organic photovoltaics occurs promptly following the initial excitation. In my talk I will discuss our theoretical models and recent 2d-photocurrent spectroscopic measurements that indicate that mobile polarons remain entangled with the initial excitation for up to 50fs following the initial excitation. If time permits, I shall discuss our recent techniques for determining vibrational mode selectivity in electron-transfer processes that utilizes a Google-like algorithm for optimizing electron/phonon couplings.

Molecular Polygons Tune Intramolecular Strain in the π -System of Organic Semiconductors

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Conjugated polymers are a prime example for the complex interplay between morphology and function. Single-molecule spectroscopy has helped us in unraveling the large heterogeneity in this class of materials. But it has become apparent that even a single conjugated polymer chain contains such a complexity that it is difficult to derive a microscopic picture of the photo-physical processes taking place in a single chain. We therefore introduce π -conjugated polygonic model systems, which all consist of a certain number of the same chromophoric unit. If we reduce this number the degree of bending increases, which makes the investigated molecules ideal candidates to study the impact of chromophore bending on spectroscopic observables. We go from the ensemble to the single molecule level to unmask the heterogeneity within the systems. By comparing the spectroscopic properties of molecules between different groups as well as the heterogeneity within a group, we can extract the influence of bending on the spectral properties. Extrapolating the results obtained from these systems onto conjugated polymers provides a highly heterogeneous picture regarding single chromophores that can exist on a conjugated polymer chain.

Multiscale Modeling of Light Harvesting and Photoprotection in Plants

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Light harvesting by Photosystem II, the photosynthetic apparatus of plants, depends on both sub-ps exciton dynamics within individual pigment protein complexes and exciton migration across the thylakoid membrane on the >10ps timescale. While the short time dynamics of light harvesting have been extensively studied using non-linear spectroscopy, the long time spatial dynamics across the thylakoid have not been accessible because of the large number of iso-energetic pigments. We have combined information gathered from thylakoid membrane microscopy and non-linear spectroscopic measurements of isolated pigment protein complexes in vitro to describe exciton transport across an intact thylakoid membrane. This model reproduces time-resolved fluorescence measurements of PSII in vivo without free parameters and predicts an exciton diffusion length of ~50 nm, much larger than the typical disordered organic semiconductor (<10 nm). Finally, we explore the relationship between the structure of the antenna array, the exciton diffusion dynamics, and the functional behaviors of PSII as captured by photochemical yield and photoprotection.

Transient Redistribution of Ultrafast Electronic Coherences (TRUECARS)

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Conical intersections (CIs) dominate the pathways that determine the outcomes of virtually all photochemical molecular processes. The vanishing electronic energy gap combined with the fast passage through CIs greatly complicates their direct observation and the experimental evidence is generally inferred from fast reaction rates and vibrational signatures. We show that short X-ray pulses can directly detect the passage through a CI with adequate temporal and spectral sensitivity. The non-adiabatic coupling that exists in the region of a CI redistributes electronic population but also generates electronic coherence. This coherent oscillation can then be detected via a coherent Raman process that employs a composite femtosecond/attosecond X-ray pulse. This technique, dubbed Transient Redistribution of Ultrafast Electronic Coherences (TRUECARS) is reminiscent of Coherent Anti-Stokes Raman Spectroscopy (CARS) in that a coherent oscillation is set in motion and then monitored, but differs in that the dynamics is electronic (CARS generally observes nuclear dynamics) and the coherence is generated internally by passage through a region of non-adiabatic coupling rather than by an externally applied laser.

Konstantin E. Dorfman, Kochise Bennett, and Shaul Mukamel, "Detecting electronic coherence by multidimensional broadband stimulated x-ray Raman signals", *Phys. Rev. A* 92, 023826 – Published 17 August 2015

Markus Kowalewski, Kochise Bennett, Konstantin E. Dorfman, and Shaul Mukamel, "Catching Conical Intersections in the Act: Monitoring Transient Electronic Coherences by Attosecond Stimulated X-Ray Raman Signals", *Phys. Rev. Lett.* 115, 193003 – Published 5 November 2015

Nonequilibrium Solvent Effects in Born-Oppenheimer Molecular Dynamics for Ground and Excited Electronic States

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The effects of solvent on molecular processes such as excited state relaxation and photochemical reaction often occurs in a nonequilibrium regime. Dynamic processes such as these can be simulated using excited state molecular dynamics. A new method of simulating nonequilibrium solvent effects in excited state molecular dynamics using linear-response time-dependent density functional theory and apparent surface charge methods is presented. Developments include a propagation method for solvent degrees of freedom and analytical energy gradients for the calculation of forces. Molecular dynamics of acetaldehyde in water or acetonitrile are demonstrated where the solute-solvent system is out of equilibrium due to photoexcitation and emission.

Charge Transfer in the Lithium-Benzene Complex: Understanding the Role of the Hartree-Fock Exchange

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Most approximations to the exchange-correlation functional of Kohn-Sham Density Functional Theory lead to delocalization errors that undermine the description of charge-transfer phenomena. An accurate description of charge-transfer phenomena is crucial in modeling of novel electric energy storage systems such as supercapacitors, which are becoming increasingly used in the development of clean and renewable energy technology. We explore how various approximate functionals and charge-distribution schemes describe ground-state atomic-charge distributions in the lithium-benzene complex. To understand the trends, we compare with Hartree-Fock (HF) and correlated post-HF calculations, confirming that the HOMO-LUMO gap is narrower in semilocal functionals, but widened by hybrid functionals with large fractions of HF-exchange. Calculations with the equation-of-motion coupled-cluster method with single and double excitations for electron attachment provide evidence of a states crossing. When the perpendicular separation between the lithium atom and the benzene plane is closer than 1.465 Å, the long-separation ground state (Benzene + Li[•]), in which the SOMO is mainly localized over lithium, crosses with a charge-transfer state, in which the SOMO localizes exclusively over the benzene molecule. We concluded that, although charge-transfer phenomena are multi-configurational in nature, hybrid functionals with an admixture of HF-exchange are useful in describing charge-transfer in the lithium-benzene model.

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Excited State Absorption in Tetrapyrrolyl Porphyrins

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Screening materials for optical limiting properties is a necessity to drive further design principles. Population of significant amounts of excited states which absorb differently than the ground state, are fundamentally important to this process, and may be useful in design of future photo-optic devices. In this work, we examine a series of 5,10,15,20-tetra(4-pyridyl)porphyrin (TPyP) compounds for their optical limiting capabilities via DFT/RT-TDDFT methods. Utilization of the real-time propagation of the electron density allows us to model the time dependent observable quantities of the complex. Though costly, this approach can afford the entire excitation spectrum and be used to rapidly screen materials for optical limiting properties.

Optimization of Energy Transfer in DNA-Dye Excitonic Circuits

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In natural photosynthetic systems, quantum coherent effects contribute to a more efficient energy transfer pathway when light-harvesting chromophores are closely packed or aggregated (Scholes, 2011). These effects may be imitated by exploiting the J-aggregation behavior of certain dyes, such as cyanines (Wrthner, 2011). A proof-of-concept study has established that J-aggregated pseudoisocyanine (PIC) dyes can be rationally attached to DNA scaffolding in what has been termed a J-bit (Boulais, In Review). These J-bits are stable and controllable J-aggregated dye units which can self-assemble on DNA circuits in the minor groove of poly-A/T DNA sequences. In this research, we extend the previous study to determine how to optimize the excitonic behavior, and therefore, the energy transfer in these DNA-dye circuits. Since the geometry of the DNA scaffold can be precisely controlled (Dietz, 2009), the geometry of J-aggregated dyes assembled on the DNA scaffold can also be controlled. Several factors are considered in this excitonic optimization study, including the size of J-bit, and geometry factors between J-bits, such as distance and orientational dependence, as controlled by the type of DNA origami scaffold.

These factors are optimized via an in-depth computational study, involving molecular docking and molecular mechanics of the DNA-dye assemblies, and quantum dynamics of the excitonic transport behavior due to J-aggregation. Excitonic transport is calculated using a stochastic Schrodinger equation formalism (Ishizaki, 2009). The best DNA-dye candidates for efficient energy transfer are experimentally confirmed using spectroscopic techniques. Modeling these DNA-dye excitonic circuits allows a broader view of the various factors involved in efficient energy transfer, and will lead to quicker optimization and implementation of effective nanophotonic technologies.

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Polymer Wrapped SWNT Hybrid Nanostructures - Exploring the Factors that Give Rise to Efficient Photoinduced Charge Carrier Generation

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Progress on the design and construction of perylene diimide (PDI) containing poly(aryleneethynylene) polymers (S-PBN(b)-Ph4-PDI) and the subsequent hybrid nanostructures formed when dispersing single walled carbon nanotubes (SWNTs) is described. Based on established design principles, a control polymer exhibited well defined periodic helical wrapping of individualized [7,5]SWNTs with a pitch length of 8 ± 2 nm. The ability to tune the excited state dynamics of the system through PDI modification is currently being explored. Of particular interest is the ability to generate multiple charge separated states on a single nanoscale object upon photoexcitation to explore: 1) how exciton density affects charge separation (CS) and charge recombination (CR) dynamics; 2) how carrier-carrier and carrier-exciton interactions compete with CS and CR; 3) if there are any unique spectroscopic signatures associated with these processes; and 4) how thermodynamic forces dictate CS and CR dynamics.

Effect of charge and surface defects on the Electronic Structure and Optical Properties of CdSe Quantum Dots

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We investigated the effect of surface defects, such as losing ligands and external charge, on the electronic structure and optical properties in thiols (CH₃SH) passivated Cd₃₃Se₃₃ quantum dots (QDs) in various solvents. Our calculations showed that a non-polar solvent such as chloroform assists in H⁺ transfer from several thiol ligands to surface selenium atoms. This process introduced trap states at the edge of the bandgap resulting in red shifts in their absorption spectra. In another study, where a polar solvent such as acetonitrile was used, we did not observe any H⁺ transfer from the thiol ligands to surface selenium atoms. We have also simulated Cd₃₃Se₃₃ QDs by passivating Se surface atoms by H ligands and Cd surface atoms by thiolate (CH₃S⁻) ligands. For full passivation of all Se surface ions by H⁺ and all Cd surface atoms by thiolate (CH₃S⁻) ligands, absorption spectra are significantly red-shifted with the lowest-energy transitions having partially optically-inactive character (semi-dark). We have also investigated the effect of the charge defects and observed an increase in the bandgap. To further understand the effect of the ligand-QD and QD-QD interactions on their optical properties, Forster Resonance Energy Transfer calculations are performed between two Cd₃₃Se₃₃ quantum dots with and without charge and surface defects providing insights into the energy transfers in these systems.

Probing and Controlling Optical Coherences in Single Nanostructures and 2D Materials

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Optical detection and coherent control of quantum interferences in nanostructures provide new insight into photo-induced phenomena and could open up novel applications in nanophotonics and optoelectronics [1]. Here, we observe and manipulate the coherent optical response of individual semiconducting single-walled carbon nanotubes (SWCNTs), Graphene and TMDs using femtosecond laser pulse shaping microscopy [2,3].

Single (5,4) SWCNTs with an average length of 400 nm excited with a pair of phase-locked 20 fs laser pulses exhibit beating patterns in their photoluminescence (PL) intensity analogous to Rabi oscillations in a two-level system. We show that light absorption of single SWCNTs can be controlled within their electronic dephasing time, varying between nanotubes from 20 to 65 fs, by tuning the relative carrier envelope phase of the pulses. For longer pulse separation coherent radial breathing mode excitations of the nanotubes with a period of 90 fs are observed. In addition, we determine the oscillator strength on the single nanotube level and estimate the coherence length of the photoexcited state.

For MoSe₂ shorter dephasing times are observed, presumably due to the simultaneous excitation of different excited states.

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Theoretical Insights into End Group Effects on Photophysics of Capped Single Walled Carbon Nanotubes

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Single Walled Carbon Nanotubes (SWCNTs) are pseudo one-dimensional nanostructures with unique chirality-dependent optical and electronic properties. As such, they are promising materials for use as active layers in a wide range of devices including photovoltaics, optoelectronics, and sensors. Chemical functionalization of SWCNTs extends their technological abilities. Due to the chemical inert nature of SWCNTs, their functionalization is expected to occur predominantly near the edges, while precise positions of functional groups is challenging to probe experimentally. We computationally investigate the direct effects on the electronic structure of the SWCNTs from passivation of the edges with various groups. Our studies compare the results of semi empirical techniques and density functional theory to determine the electronic effects of terminating the SWCNTs by functionalizing the edges with groups attached via sp² and sp³ hybridized bonds, while also differ in their electron donating/withdrawing abilities. We have found that precise functional group is not as relevant as the bond order of the connectivity at the edges of the SWCNT for determining the HOMO-LUMO gap and therefore optical properties. For the (10,5) SWCNT, the widest HOMO-LUMO gap is acquired by functionalizing the edges with two groups where the atom bonded to the SWCNT is sp² hybridized. This configuration results in electron density being distributed through the length of the SWCNT, and in contrast to other configurations doesn't result in the introduction of electronic states localized on the edges.

Photoluminescence Relaxation Dynamics of Covalently Doped Carbon Nanotubes

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New red-shifted emitting states in carbon nanotubes, introduced by stable covalently-bound dopants,[1,2] are gaining attention for their potential to boost photoluminescence quantum yields,[1,2] add new functionality,[3] and serve as single photon emitters.[4] Critical to these possibilities is the demonstration of exciton localization or trapping at individual dopant sites.[5] As a consequence of trapping, exciton dynamics are significantly altered, with photoluminescence (PL) lifetimes being extended significantly.[4] We will present a detailed study of the emission dynamics associated with dopant states introduced by aryl diazonium functionalization of semiconducting carbon nanotubes. Dopant-state PL lifetimes are found to increase by around a factor of 10 in comparison to E11 exciton lifetimes. Dependence of lifetimes on nanotube chirality, specific dopant, and dielectric environment will be presented and shown to exhibit a strong dependence on emission energy. Evidence for existence of an associated dark trap state will also be given. The results indicate multiple mechanisms for radiative and nonradiative decay. Of particular interest relevant to PL stability is the relation of PL decay to potential exciton detrapping. Possible contributing factors to detrapping, including detrapping energy, will be discussed.

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Size Dependent Photophysical and Electrochemical Properties of Silver Clusters Capped by Cytosine

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DNA are widely used to bottom-up construction of Silver nanoclusters exhibiting high stability. Understanding the redox and photophysical properties of metal nanocluster is important considering their potential application in sensing, catalysis, photophysical application. Herein, we performed Density Functional Theory (DFT) calculations to optimize silver clusters with varying sizes from 3-9 atoms, passivated by the DNA base, cytosine, in vacuum and water, in their neutral and charged forms. Time dependent DFT (TD-DFT) is used to investigate optical properties of these clusters. We observed that there is a significant difference in the overall absorption spectra between charged and neutral systems. Also, we see a difference in spectra between odd and even number in silver cluster size, with the lowest energy peaks corresponding to the dublet transitions in Si_5 , Si_7 and Si_6^+ , while the second main band originate from singlet transitions in Si_5^+ , Si_7^+ and Si_6 . Natural transition orbital plots show a significant charge transfer behavior between silver and cytosine in their first excited state near 1-2 eV. A strong peak around 3 eV is due to an ad-mix of charge transfer and silver d-d transitions. We also calculate reduction potential which reveal a significant difference of the reduction potential of ground state singlet and doublet multiplicity of odd and even number Ag cluster. It also shows a trend to increase redox potential with increasing size of the silver cluster.

Understanding the Role of Organic-Inorganic Layer Coupling in Perovskite Materials for Photovoltaics - How the Microscopic Ferroelectric Effect Impacts the Electron-Hole Recombination

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Hybrid organic-inorganic perovskite materials, since the pioneering reports of Mitzi et al. [1], have been attracting rapidly growing interest as robust active materials for the solar photovoltaics applications [2, 3]. Merging distinct properties of organic and inorganic components within a single molecular composite, hybrid perovskites offer plenteous possibilities for tuning their photophysical and electronic properties. In particular, in a recent experimental study Liao et al. (Nat. Commun., 6, 2015, 7338) showed that these materials may give rise to a new class of room-temperature ferroelectric semiconductors.

Here we report results of a non-adiabatic molecular dynamics investigation of a microscopic ferroelectric effect on hole-electron recombination in a model hybrid ferroelectric perovskite: (benzylammonium)₂PbCl₄. We find that homogenous arrangement of micro-domains originating from interacting polarized C=N bonds enhances the non-radiative hole-electron recombination through coupling with vibrations of the halide network.

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Photophysics of Triplet and Triplet-Triplet Singlet States in Acene Dimers and Crystals

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The process of singlet fission (SF), in which a photoexcited singlet exciton dissociates into two triplet excitons has been studied experimentally in aggregates as well as dimers of acene molecules. While ultrafast spectroscopy and time-resolved studies of excited state absorptions are the experimental tools of probing SF, there exist few, if any, theoretical studies of excited state absorptions in these systems. This is particularly true for the triplet-triplet state with overall singlet character, and the singlet excimer, which are believed to be intermediates in the SF process. We present high order configuration interaction calculations of excited state absorptions from the excimer, the spin triplet state, the optical exciton and the triplet-triplet state in acene aggregates and dimers [1], in order to reach understanding of the feasibility and efficiency of the SF process in various cases. Detailed comparisons to experiments are made.

[1] K. Aryanpour, A. Shukla, S. Mazumdar J. Phys. Chem. C 2015, 119, 6966-6979

Optimization and Application of Optical Gain in CdSe/Cd(1-x)Zn(x)Se(1-y)S(y) Core/Alloyed-Shell Quantum Dots

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Colloidal quantum dots (CQDs) are of considerable interest for lasing applications due to their tunable bandgaps through size and composition, and high optical gains and low lasing thresholds obtained through quantum confinement. We investigated the lasing and gain properties of CdSe/Cd(1-x)Zn(x)Se(1-y)S(y) core/alloyed-shell CQDs. The electronic potential gradient was employed to reduce the energy level mismatch between more typical CdSe/ZnS core/shell CQDs, resulting in a larger Stokes shift of PL, reduced Auger recombination and lower thresholds for laser action. Furthermore, exchange of the native oleic acid ligands with amine groups of different sizes as well as cross-linked ligand networks was used to achieve enhanced QD loading and stability in thin films. Planar waveguides constructed with such films as active layers exhibit gains as high as 650cm⁻¹ as measured by the Variable Stripe Length technique, and thresholds for ASE as low as 60 J/cm² upon optically pumping with pulsed excitation. A detailed characterization of the gain, loss and threshold behavior as a function of the excitation intensity, spectral energy and pulse width was conducted to elucidate the interesting photo-physics of these CQD films that lead to the favorable lasing characteristics and an exceptionally broad gain-bandwidth. In addition to conventional applications for optical gain materials, exotic optical phenomenon based on parity-time symmetric systems has recently been demonstrated in coupled resonators with specific values of optical gain and loss, respectively. We investigated these effects in pairs of coupled micro-disk lasers fabricated from CQDs studied here. The high gain achievable in this material caused PT-symmetry breaking at low thresholds and induced large coupling-mediated nonlinear effects on the observed laser modes.

***In Silico* Screening of Non-Fullerene Acceptor Materials for Applications of Organic Photovoltaic Devices: A Harvard Clean Energy Project Study**

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Harvard University

Organic Photovoltaics (OPVs) have shown a steady growth in efficiencies since the 1980s, and reported percent conversion efficiencies (PCEs) up to 12% are reported in multi-junction cells. OPVs are lightweight, easy to produce, and feature chemically diverse components. While PCBM is the standard fullerene n-type (acceptor) material, it is not without limitations, which include limited spectral breadth, small range of LUMO energies, and relatively high costs of industrial production. We have undertaken an *in silico* highthroughput screening utilizing the *Harvard Clean Energy Project* to explore the chemical space associated with non-fullerene acceptor materials. A library of 100,000 n-type materials including perylene diimides, tetraazabenzodifluoroanthenes, diketopyrrolopyrroles, and fluoroanthene-fused imides. This work is carried out through a tight feedback loop with experimental colleagues that synthesize target materials and create OPV devices.

Understanding Why Pure Ligand Exchange with Dithiocarbamate is Impractical

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Rationally designing ligands for quantum dots (QDs) has attracted the attention of the scientific community because the appropriate ligand can tune the optoelectronic properties of QDs for various applications. The ligands used in synthesis are typically carboxylic acid, amine, and phosphine derivatives because they are thermodynamically very stable, but these ligands are not effective in tuning the QD's properties. Ligand exchange therefore is vital and studies have shown that dithiocarbamate (DTC) is one rationally designed ligand. However, these studies have not investigated how stable the DTC is during the exchange; most work had looked at the overall effect in terms of fully exchanging native ligands. The purpose of this study is to gain fundamental knowledge of DTC and its ability to passivate CdSe QDs. Density functional theory calculations have been carried out and have provided insight into the ground state properties. These calculations have shown that DTC is less effective at ligand exchange than previously thought because during exchange methanol is used to precipitate the QDs. The calculated binding of DTC to QDs is unfavorable in methanol and experimentally the rate of decomposition in methanol is significantly higher. The present study indicates that the change in optoelectronic properties of QD's is not due to only exchange of DTC but is complicated by the binding of the products for decomposition of DTC. Future studies will highlight the effects of ligand exchange in terms of several ligands being exchange not only DTC.

Simulation of Electron and Energy Transfer Using the Fragment Molecular Orbital Method

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Modeling electron and energy transport processes in experimental organic photovoltaic systems is challenging due to both the size of the systems as well as the complexity of excited state ab-initio calculations. Here we seek to speed the simulation of electron and energy transport processes using the Fragment Molecular Orbital (FMO) method. This method breaks a single large system into many small fragments which are solved in a self-consistent manner to both intrinsically decrease the difficulty of $O(N^4)$ ab-initio calculations and also allow them to be parallelized efficiently on modern supercomputers. In the FMO method, an ab-initio calculation is performed on each fragment and each fragment pair to obtain gradient information necessary to compute a molecular dynamics trajectory. Using the dimer calculation intrinsic to the FMO method the inter-fragment non-adiabatic couplings for each time step are computed and used to determine the rate of electron and energy transfer between two fragments. This method is applied to variants of Platinum Bipyridine-Fullerene donor chromophore acceptor triads to determine the electron and energy transfer rate from the Platinum antenna complex to the Fullerene acceptor after excitation by a photon. These simulations have proven very accurate at replicating the energy and electron transfer times of these systems as observed by transient absorption spectroscopy.

Surface Hopping for Extended Molecular Systems: On-the-Fly Limiting of Essential Excited States

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The simulation of nonadiabatic dynamics in extended molecular systems involving hundreds of atoms and large densities of states is particularly challenging and computationally demanding. Nonadiabatic coupling terms (NACTs) represent a significant numerical bottleneck in surface hopping approaches. Rather than using unreliable NACT cutting schemes, here we develop “on-the-fly” state limiting methods to eliminate states that are no longer essential for the non-radiative relaxation dynamics as a trajectory proceeds. We propose a state number criteria and an energy-based state limit. The latter is more physically relevant by requiring a user-imposed energy threshold. For this purpose, we introduce a local kinetic energy gauge by summing contributions from atoms within the spatial localization of the electronic wavefunction to define the energy available for upward hops. The proposed state limiting schemes are implemented within the nonadiabatic excited-state molecular dynamics framework to simulate photoinduced relaxation in poly-phenylene vinylene (PPV) and branched poly-phenylene ethynylene (PPE) oligomers for benchmark evaluation. We find that the local kinetic energy threshold combined with the energy-based state limit provides a physically relevant approach that can be extended to any molecular system without requiring a priori knowledge of the excited state manifold. Most importantly, the observed reduction of numerical cost would reach orders of magnitude in larger molecular systems with hundreds of excited states.

Light Induced Polaron Formation in Perovskite Solar Cell Devices

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The need for an affordable, clean, and abundant source of energy has generated large amounts of research in solution processed solar cell materials. The MAPbI₃ has rapidly emerged as a top candidate for the active layer of photovoltaic devices. In the last 6 years, the efficiencies of devices made with this material have increased from 3.5% to over 20%. Despite the remarkable progress associated with perovskite materials, there are still many fundamental questions that need to be addressed regarding their lack of photo-stability over prolonged solar irradiation. Recent experiments on photo-degradation under constant illumination have found fast self-healing by resting the device in the dark for less than 1 minute. Density functional theory and symmetry analysis show that localized charge states couple to local structural lattice distortions and methyl ammonium quasitatic configurations. Once translational symmetry is lost, additional bonding configurations become symmetry allowed, triggering localized charges in the vicinity over time under constant illumination, thus seeding the formation of macroscopic charged domains and preventing efficient charge extraction. Here we present an in-depth study of polaron formation and binding energy at the atomistic level.

Long-Lived Quantum Coherence in 2D CdSe Nanoplatelets at Room Temperature

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Recent experiments on CdSe nanoplatelets synthesized with precisely controlled thickness that eliminates ensemble disorder have allowed measurement of long-lived coherence at room temperature. We have studied the exciton-exciton coherence in two-dimensional CdSe and CdSe/CdZnS core/shell systems at room temperature using atomistic molecular dynamics simulations and electronic structure calculations. We found that the longer dephasing time is a consequence of the small fluctuations in the energy gap between the two excitons. The heavy-hole and the light-hole excitons couple to the same phonon modes causing similar energy fluctuations of the two excitons which lead to the observed longer quantum coherence lifetime.

Oxidation of PbSe Quantum Dots: Insights from First-Principle Calculations

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It is known that quantum dots (QDs) exposed to air commonly demonstrate decrease in their photoluminescence (PL). However, mechanisms of QDs oxidation causing the PL quenching are not fully understood. We use density functional theory (DFT) and time dependent DFT (TDDFT) to investigate the interaction of oxygen in its molecular, atomic, and ionic forms with different surfaces of lead selenide (PbSe) QDs and its effect on the electronic and optical properties of QDs. We found that oxygen concentrations and positions at the QD facets govern an appearance of trap states at the bandgap of QDs. For 2 nm PbSe QDs, as the concentration of oxygen atoms at the surface increases, oxygens attempt to penetrate inside the QD shifting Se ions in the outer shell of the QD. In contrast, oxygen ions attempt to bind and then remove Pb ions from the QDs surface, resulting in Se-enriched QDs of smaller sizes when they are exposed at high concentrations on the QDs surface. In both cases, adsorption of oxygen atoms and ions are accompanied by additional oxygen-associated trap states appearing at the edges of the QDs bandgap. Molecular oxygen shows minor effects on both the geometry and the electronic structure of QDs.

Ultrafast Energy-Resolved Studies of Hot Electron Dynamics in Single Gold Nanorods

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Noble metal nanoparticles and nanostructures are attractive candidates for next-generation devices such as photodetectors and solar cells due to their strong and highly-tunable interactions with visible light. The design of nanosystems for specific applications is best facilitated by single-nanoparticle studies, where ensemble averaging doesn't obscure any of the detailed physics taking place. Using our unique scanning photoemission imaging microscopy (SPIM) technique, we examine the ultrafast thermalization dynamics of nascent electron distributions excited in single gold nanorods. The technique includes time-resolved pump-probe excitation and energy- and angle-resolved velocity map imaging (VMI) detection. By acquiring VMIs at a series of pump-probe delays, the full dynamical information of excited electrons within the probed excitation energy range can be characterized. We find that the lifetimes of individual electronic excitations obey an inverse-quadratic dependence on the excitation energy. While similar energy-dependent lifetimes have been observed in numerous bulk metal studies, and some studies have addressed ensemble and even single-nanostructure electronic lifetimes, this study represents the first definitive characterization of excited electron lifetimes in single nanoparticle systems, to the best of our knowledge. These findings have important implications for any applications involving electron transport out of nanoparticles, such as solar energy conversion, photodetection, and photocatalysis.

Metal-Insulator Transition in Nanoparticle Solar Cells

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Nanoparticle (NP) solids recently emerged as a promising platform for high performance electronic and optoelectronic devices, including third generation solar cells. The success of NP solids is driven by the quantum confinement effect: the electronic and optical properties can be tuned to their optimal or desired values by changing the diameter of the NPs. Unfortunately, this same nano-structure greatly hinders charge transport. Most experiments report observing a hopping conductivity, indicating that the NP film is in an insulating phase. To establish the utility of NP films for applications, it is imperative to find ways to drive NP films across a Metal-Insulator Transition (MIT) into a conducting metallic phase. Experimentally the favored methods include atomic layer deposition (ALD), chemical- and photo-doping and NP substitution. By now, several groups reported success reaching the metallic phase. At the same time, the microscopic theoretical understanding of the evolution of transport across the MIT is presently lacking. To address this challenge, we developed a band structure-based “Boosted” Kinetic Monte Carlo transport model. In our NP solid, neighboring NPs whose energies are closer than a NP-NP overlap energy, are considered to form a conducting cluster, where the electrons can transition by non-activated quantum mechanical delocalization instead of activated hopping. As this NP-NP overlap energy is increased, e.g. by ALD or by NP substitution, eventually sample-spanning percolating metallic clusters are formed that support a non-activated, metallic transport through the entire sample. We simulated the evolution of the temperature dependent electron mobility from the insulating phase to the MIT. We analyzed our results in the framework of two models: MIT as a Quantum Phase Transition, or MIT as a Percolation Transition. The two analyses yielded different MIT phase boundaries, opening the door for a possibly quite rich overall phase diagram that comprised an insulator, a metal, and an intervening anomalously low gap region.

Ultrafast Photo-induced Electron Transfer Reaction Drives Abrupt Phase Decoherence

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A coherent superposition of vibrational states generated in the reactant state of an electron transfer (ET) system carries quantum information about the transfer in the form of phase correlations. Rapid loss of phase coherences in the vibrational wavepacket is witnessed during the transition to the ET product state on a 200 fs time scale, in model system of Oxazine in electron-donating solvent. Contrarily, vibrational coherences of the excited state in a nonreactive solvent dephase at a much slower rate (>1 ps). Such an observation is in contrast to the conventional theory, that ET is a mere jump from one chemical species to the other, enabling coherences to survive when following a crude adiabatic Born-Oppenheimer approximation. This rapid phase decoherence suggests, that the population transfer from the reactant to the product state occurs strictly via curve crossing enabled by collective vibration of the modes. The created anharmonicity in the mixing region leads to wavepacket broadening and disperses it into the product potential with significantly faster dephasing. This indication of strong mode mixing or pathway interference results in decoherence of all the Franck-Condon modes in contrast to the specificity in the number of modes involved in conical intersections, an alternate curve crossing pathway.

Strong Binding of CdSe Quantum Dots to Single-Walled Carbon Nanotubes

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Experimentally monitored transient absorption of CdSe quantum dots (QDs) before and after attachment to single-walled carbon nanotubes (SWNTs) show considerably shorter lifetimes with direct covalent binding of the CdSe on SWNTs. This observation may indicate faster deactivation of charge-separated states in CdSe QDs via ultrafast electron transfer from CdSe QD to the SWNTs or formation of strongly coupled nanocomposites. The latter explanation is supported by quantum dynamics simulations of interfacial electron transfer in a fully atomistic model of the molecular assembly that matches the experimental EXAFS spectra and direct comparisons to transient absorption measurements.

One- and Two-Photon Absorption in Conjugated Energetic Molecules

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Initiating an explosive with light has been an active field of research. Common methods for optical initiation require high laser intensities that proceed through indirect mechanisms such as thermal or shock processes. Conjugated energetic molecules (CEMs), however, open the possibility for controlled and direct optical initiation using conventional lasers. CEMs combine the optical properties of carbon-based, conjugated organic molecules with high nitrogen content. Recent progress has been made to strategically alter the molecular structure of CEMs to influence their heat of formation and oxygen balance, two factors that contribute to the sensitivity and strength of an explosive material. The optical range and intensity of excitation are also affected by molecular structure. The extent to which CEMs can be used for optical initiation needs a thorough theoretical investigation. Using time-dependent density functional theory, one- (OPA) and two-photon absorption (TPA) spectra are calculated for a series of CEMs. Vertical excitation energies are compared to experimental spectra for several molecules in the study and are in good agreement. Moreover, TPA peaks are calculated to be on the order of 100 GJ. Our results were computed using the B3LYP functional and a 6-31G* basis set.

Ultimate Quantum Dot Luminescent Solar Concentrators Employing Selective Reflector

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Luminescent solar concentrators (LSCs), comprising fluorophores embedded waveguide slab and edge or side mounted photovoltaic cells (PVs), can concentrate solar light on PVs with low cost. Especially, colloidal core/shell structure quantum dots have drawn much attention due to their large stoke shift, leading to reduced re-absorption losses in LSCs. However, the optical losses during the waveguide to the PVs strikingly increase, as the size of LSC is enlarged. Hence, the attainable concentration of LSC is limited. In this work, we investigate the relationship between optical properties of selective reflector and performance of LSC to find out the way for realizing ultimate LSCs. Monte-Carlo simulation indicates that the average path length of photons elongates three times when highly reflective film ($R > 96\%$) is incorporated to the top window of large sized LSCs (geometric factor = 2000) compared to the case without it. Moreover, escaping photons from the slab are suppressed in the case implementing highly reflective film, originated from recycling them into LSCs. Thus, three times higher concentration and waveguide efficiency are expected in the device surrounded by highly reflective film that those of uncovered case. This result is verified by empirical data using same structured LSCs, which is consistent to theoretical expectation. Consequently, the implementation of LSC allow us to break the attainable concentration limit of LSC. We believe that this work will be a guideline to design highly efficient LSCs.

Biexciton Auger Recombination in CdSe/CdS Core-Shell Nanocrystals

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We present a theoretical study of positive and negative trion channels of the nonradiative Auger recombination of band-edge biexcitons in CdSe/CdS core/shell nanocrystals. The theory takes into account the biexciton fine-structure produced by the nanocrystal asymmetry and hole-hole exchange interaction. The calculations show that the growth of CdS shell upon CdSe core suppresses the rate of the Auger recombination via negative trion channel, while the more efficient positive trion channel shows much weaker dependence on the shell thickness. We find a strongly oscillatory dependence of the positive and negative trion Auger rates on core and shell sizes. These oscillations can be qualitatively explained in terms of overlap of the ground and excited carrier wavefunctions. Also, the calculations show that increase of temperature accelerates the Auger recombination in CdSe/CdS nanocrystals due to the decrease of the bulk energy gaps of CdSe and CdS. An additional effect of temperature via changes in the population of biexciton fine-structure states can be observed.

Nano Lett. 16, 2503 (2016)

**Ultrafast High-Energy Photon Imaging, a MaRIE-Driven Technology for and by
Mesoscopic Materials**

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To advance manufacturing on mesoscale will require both XFEL illumination above 30 keV (MaRIE) and high-performance imaging technologies. The existing detectors and cameras, which rely mostly on electrons or light as signals, are rather primitive on the mesoscale, i.e., dominated by random processes. Mesoscale highways for light (\sim wavelength) and electrons (\sim collection distance) will be revolutionary.

Coupled Wavepackets for Non-Adiabatic Molecular Dynamics

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Understanding and control over light-induced dynamics is critical for efforts to design functional optoelectronic materials for many applications (e.g. solar-energy harvesting). Current simulation methods for such complex non-adiabatic molecular dynamics (NAMD) are either too inefficient to be used for large-scale molecular systems, or are based on approximations that breakdown even in simple systems, especially when quantum coherence and interference are important. Quantitative and predictive simulation of NAMD requires proper treatment of coupled quantum (electrons) and semiclassical (nuclei) subsystems. Coupled Wavepackets (CW) is a novel method that extends Heller's Thawed Gaussian wavepacket dynamics to include non-adiabatic coupling between potential energy surfaces. By studying several standard test problems we demonstrate that the accuracy of the method can be systematically improved while maintaining high efficiency. The method is suitable for investigating the role of quantum coherence in the non-adiabatic dynamics of many-atom molecules.

Bottom-up Synthetic Nanographenes for Highly Efficient Lithium Storage

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Traditional graphene anodes in lithium ion batteries (LIBs) suffer significant performance loss due to the restacking of graphene layers. In this work, we have demonstrated a facile synthesis of preparing a series of graphene-derived nanomaterials. Among other potential applications, these nanomaterials achieved an excellent cyclic durability with much enhanced capacity as novel anode materials in LIBs. These exceptional metrics observed within the novel assemblies is primarily due to the robust structure along with the optimal spacing allowing for facilitated Li adsorption/desorption and diffusion. Furthermore, the significantly enhanced rate performance was achieved after optimizing the structure of the self-assemblies. Development of nanomaterials anode suggests that the optimal design of graphene materials with robust structures is very important for next generation LIBs with high-energy storage efficiencies.

Defect Control in CuInSexS_{2-x} Quantum Dots to Enhance Their Electronic Devices Performance

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Colloidal copper indium selenide sulfide (CuInSexS_{2-x}) quantum dots (QDs) are non-toxic alternatives to Cd- or Pb-based QDs for sustainable solar energy applications. The key to using QD thin films in opto-electronic devices such as solar cells is understanding their carrier transport properties. The carrier transport behavior is strongly influenced by various kinds of defects that can serve as carrier traps. To improve the electronic device performance, it is important to control the defect with reducing the number of carrier traps. In this research, we combine field effect transistor (FET) and ultrafast transient photocurrent (u-TPC) measurements to obtain a more complete picture of the nature and role of trap states in CuInSexS_{2-x} QD thin films. Pristine FET devices employing indium contacts exhibit n-type transport with decent electron mobility ($3.95 \times 10^{-3} \text{ cm}^2/\text{Vs}$), but they also indicate high concentrations of free carrier in the films. Early-time dynamical signatures revealed in u-TPC studies suggest that this high carrier density arises from the presence of trap states in CuInSexS_{2-x} QDs. In order to reduce the density of trap states that might be related to surface defects, atomic layer deposition (ALD) technique was used to infill the CuInSexS_{2-x} QD film with amorphous Al₂O₃. This process results in both higher FET mobilities ($2.0 \times 10^{-2} \text{ cm}^2/\text{Vs}$), and an elimination of trap-related decay signatures in u-TPC measurements. In addition, ALD infilling provides long term air stability of CuInSexS_{2-x}-based devices.

Monitoring Transient Gain-Saturation in Variable Stripe Length Measurements of DOO-PPV*

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The variable stripe length (VSL) technique is a simple and useful technique for determining the optical gain of thin films of novel semiconductors. However, the occurrence of gain-saturation causes deviations from the expected exponential rise in emission intensity with increasing stripe length and a subsequent underestimation of gain. We present a straightforward experimental methodology to determine the pre-saturation gain, g_0 , as well as the saturation length, LS , above which the emission intensity measured from the stripe is affected by propagation through a medium of non-constant gain in the π -conjugated polymer, DOO-PPV. By simultaneously performing transient photo-induced absorption spectroscopy (TAS) to measure the stimulated emission dynamics while measuring the emission from the stripe pump beam, we observe exciton depletion through stimulated emission at precisely the same stripe length at which gain-saturation begins to affect the VSL measurement. Meanwhile, the change in exciton population is unaffected at stripe lengths below LS but above the threshold length, LTH , for observing amplified spontaneous emission. The measured dynamics are consistent with simulations of the coupled rate-equations for the exciton and photon densities as function of position through the stripe. Furthermore, we describe how g_0 and LS may be determined from analysis of the VSL data alone, when TAS is not available.

*This work was funded by AFOSR through MURI grant RA 9550-14-1-0037.