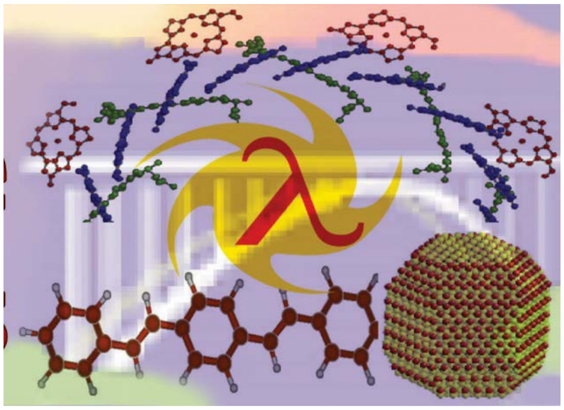
Updated 6/13/16

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, 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	**SHUAI**	**PIRYATINSKI**	**MELLO-DONEGA**	**NESBITT**
10:00AM	9:40AM-10:15AM **GU** 10:15AM-10:35AM	9:40AM-10:15AM **OLIVIER** 10:15AM-10:35AM	9:40AM-10:15AM **MAKAROV** 10:15AM-10:35AM	9:40AM-10:15AM **BLANCON** 10:15AM-10:35AM
10:30AM	**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 **PREZHDO**	**ZHENG** 2:00PM-2:35PM	12:40PM-2:10PM **SCHOLES**	**LANZANI** 2:00PM-2:35PM
2:30PM	2:10PM-2:45PM	**VARGANOV** 2:35PM-3:10PM	2:10PM-2:45PM	**KILIN** 2:35PM-3:10PM
3:00PM	**HOLLINGSWORTH** 2:45PM-3:20PM	**BATISTA**	**GIERSCHNER** 2:45PM-3:20PM	**DUNLAP**
3:30PM	**SLIPCHENKO** 3:20PM-3:55PM **BREAK**	3:10PM-3:45PM **BREAK** 3:45PM-4:05PM	**BAZAN** 3:20PM-3:55PM **BREAK**	3:10PM-3:45PM **BREAK** 3:45PM-4:05PM
4:00PM	3:55PM-4:15PM **DYER**	**WERNER** 4:05PM-4:40PM	3:55PM-4:15PM **SUBOTNIK**	**SPANO** 4:05PM-4:40PM
4:30PM	4:15PM-4:50PM	**BATHE**	4:15PM-4:50PM	**BITTNER**
5:00PM	**KRYLOV** 4:50PM-5:25PM	4:40PM-5:15PM **VELIZHANIN** 5:15PM-5:35PM	**MYERS** 4:50PM-5:25PM **NELSON**	4:40PM-5:15PM **WILHELM** 5:15PM-5:35PM
5:30PM	**CURUCHET** 5:25PM-6:00PM		5:25PM-5:45PM	**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 **Zhigang Shuai** (Tsinghua)

“Boosting OLEDs Efficiency through Theoretical Understanding and Computational Study”

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 **Jennifer Hollingsworth** (LANL)

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

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 **James Werner** (LANL)
"Time-Resolved Three Dimensional Single Molecule Tracking"

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-Donega** (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 **Johannes Gierschner** (Madrid Institute Adv. Studies)
"Controlled Light Emission in Organic Single Crystals for Optoelectronic Applications"

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 **Thomas Myers** (LANL)
"Explosive Chromophores for Photo-Thermal and Photo-Chemical Laser Initiation"

05:25pm – 05:45pm **Tammie Nelson** (LANL)
"Modeling Photochemistry with Surface Hopping"

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 **David Nesbitt** (JILA)

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

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 **Andrew 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 Vardeny[1]
Uyen N. V. Huynh[1], Yaxin Zhai[1], and Sumit Mazumdar[2]

[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 (^{1}TT) 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.

E-mail: val@physics.utah.edu

** 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. Mazumdar[1]
Karan Aryanpour[1], Tirthankar Dutta[1], Souratosh Khan[1], Uyen N. V. Huynh[2], Z. Valy Vardeny[2]

[1]Department of Physics, University of Arizona, Tucson, Arizona 85721
[2]Department of Physics, University of Utah, Salt Lake City, Utah 84112

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 Eg of these materials. Multiple recent experimental observations indicate that small Eg 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.

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 electroluminscence; (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.

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.

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.

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.

Monday, June 13 **12:05pm-12:40pm**

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

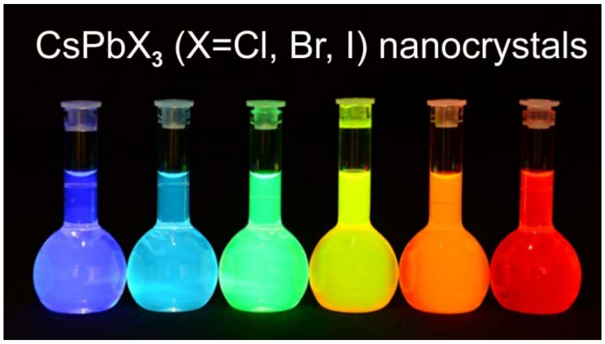
M. Kovalenko

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-synthestic 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±1 μJ cm-2 and high values of modal net gain of at least 450±30 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.



[1] L. Protesescu *et al*. Nano Letters **2015**, *15*, 3692–3696
[2] G. Nedelcu *et al.* Nano Letters **2015**, 15, 5635–5640
[3] S. Yakunin *et al.* Nature Communications **2015**, 9, 8056.

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 TiO_2 sensitized with organic molecules, water, semiconductor quantum dots, graphene and hybrid organic-inorganic perovskites, GaN/water interface, carbon nanotube bundles, mixtures of C_{60} 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.

Monday, June 13 **2:45pm-3:20pm**

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.

Excitation Energy Transfer and Vibronic Couplings in Multichromophores

Lyudmila Slipchenko[1]
Ben Nebgen[2]

[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.

Ultrafast Energy Flow in Protein Structures

R. Brian Dyer

Emory University

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

University of Southern California, Los Angeles, USA

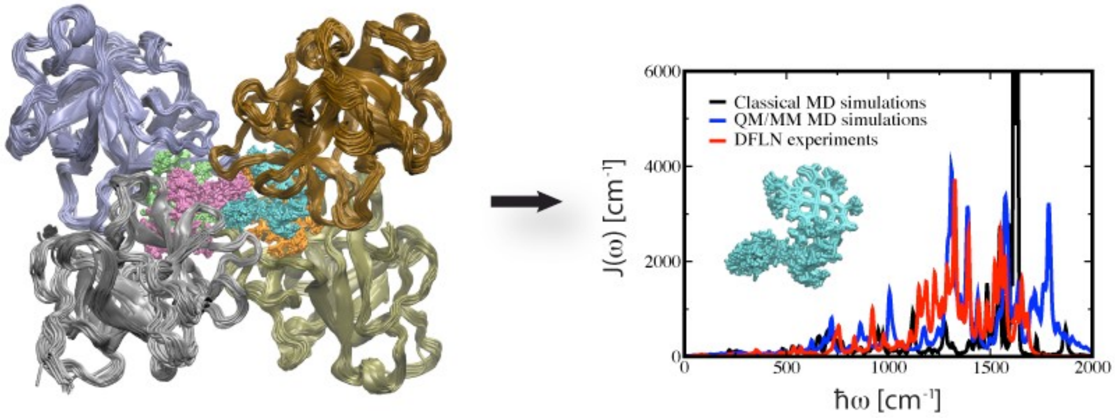
Non-linear spectroscopies have revolutionized many areas of material and life sciences. For example, techniques based on two-photon absorption (2PA) enable 3D and super-resolution imaging, nanosurgery, and targeted cell deactivation. This lecture will discuss 2PA spectra of several prototypical molecules (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

Carles Curutchet

Departament de Fisicoquímica, Facultat de Farmàcia, Universitat de Barcelona, Spain

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 bacteria[3] and the water-soluble chlorophyll binding protein (WSCP) of higher plants.[4]

[1] Curutchet et al. *J. Am. Chem. Soc.* 133, 3078 (2011).
[2] Viani et al. *J. Phys. Chem. Lett.* 4, 372 (2013); Viani et al. *Phys. Chem. Chem. Phys.* 16, 16302 (2014).
[3] Jurinovich et al. *ChemPhysChem* 15, 3194 (2014).
[4] Rosnik & Curutchet, *J. Chem. Theory Comput.* 2015, 11, 5826.

Optical Properties of Carbon Nanostructures

J.S. Lauret

Laboratoire Aimé Cotton, CNRS, Univ. Paris-Sud, ENS Cachan, Université Paris-Saclay

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].

[1] F. Vialla et al, Phys. Rev. Lett. 113, 057402 (2014)
[2] V. Ardizzone et al, Phys. Rev. B 91, 121410 (R) (2015)
[3] S. Zhao et al, in preparation

Photophysics of Localized Excitons in Cryogenic Carbon Nanotubes

A. Hoegele

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

Andrei Piryatinski

Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM

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 florescence 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.

[1] X. Ma, O.Roslyak, J. G. Duque, S. K. Doorn, A. Piryatinski, D. H. Dunlap, and H. Htoon. Influences of Exciton Diffusion and Exciton-Exciton Annihilation on Photon Emission Statistics of Carbon Nanotubes, Phys. Rev. Lett. 115 017401 (2015).
[2] O. Roslyak, C. Cherqui, D. H. Dunlap, and A. Piryatinski. Effect of Localized Surface-Plasmon Mode on Exciton Transport and Radiation Emission in Carbon Nanotubes, J. Phys. Chem. B 118 8070 (2014).
[3] O. Roslyak and A. Piryatinski. Effect of periodic potential on exciton states in semiconductor carbon nanotubes. Chem. Phys. (submitted). arXiv:1604.00079

Tuesday, June 14 **10:15am-10:35am**

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 (cs = 0.4 ps, CS = 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 (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 is S-PBN(b)-Ph4PDI-[(6,5) SWNT] and S-PBN-PZn-[(6,5) SWNT] superstructures, similar magnitude CS (CS = 0.4ps) and bi-exponential CR values (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

Tradition 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 basil planes. Among other potential application, these high-surface area nanographenes have an excellent cyclic durability and a much enhanced charge capacity as novel anode materials for LIBs. Moreover, 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 along and optimal d-spacing which allowing 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 C_{60} Polymerization

Jun Onoe

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

One-dimensional (1D) periodic uneven-structured C_{60} polymer (see Fig. 1), which has been synthesized by electron-beam (EB) irradiation of pristine C_{60} films, exhibits the electronic, optical, and phonon properties arising from 1D metal.[1–19] Since the 1D C_{60} 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 C_{60} polymer can be expected to show novel properties different from those of the nanocarbon allotropes. Indeed, it is interesting to note that the 1D C_{60} 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 Tomononaga-Luttinger Liquid states,[15,16] we will present the shape effects of □electron conjugation on the electron-phonon coupling strength for nanocarbon allotropes[17] and the anomaly in the resistivity of the 1D C_{60} 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 C_{60} film with almost the same-size space.[20] This topic will be also presented.

We believe that the 1D periodic uneven-structured C_{60} 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.

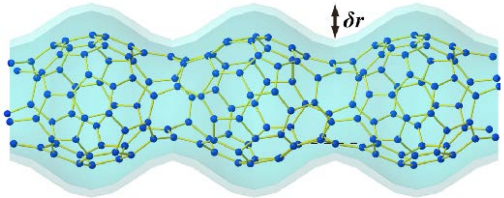


FIG. 1. Schematic illustration of 1D periodic uneven-structured C_{60} polymer.

[1] *APL* **82**, 595 (2003), [2] *APL* **85**, 2741 (2004), [3] *PRB* **72**, 155416 (2005), [4] *JPCB* **110**, 22374 (2006), [5] *PRB* **74**, 195426 (2006), [6] *PRB* **75**, 233410 (2007), [7] *APL* **92**, 094102 (2008), [8] *JAP* **104**, 103706 (2008), [9] *J. Phys. D*: *Appl. Phys.***45**, 485302 (2012), [10] *Diamond & Relat. Mater.* **33**, 12 (2013), [11] *JAP* **108**, 033514 (2010), [12] *APL* **97**, 241911 (2010), [13] *J. Phys.*: *Condens. Matter* **24**, 175405 (2012), [14] *APL* **104**, 113301 (2014), [15] *Europhys. Lett.* **97**, 27001 (2012), [16] *PRB* **79**, 201401 (R) (2009), [17] *PRB* **90**, 155435 (2014), [18] *Carbon* **81**, 842 (2015) [19] *Carbon* **96**, 316 (2016), [20] submitted.

Visualizing Single Molecule Absorption at the Nanometer Scale

Lea Nienhaus

Massachusetts Institute of Technology, Department of Chemistry

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

Ming Zheng

Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland

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.

ming.zheng@nist.gov

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

Sergey Varganov

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.

Tuesday, June 14 **3:10pm-3:45pm**

Studies of Natural and Artificial Photosynthesis

Victor S. Batista

Yale University, Department of Chemistry & Energy Sciences Institute

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.

[1] Biochemistry **55**: 981–984 (2016) The S3 State of the O2-Evolving Complex of Photosystem II: Insights from QM/MM, EXAFS and Femtosecond X-ray Diffraction, Mikhail Askerka, Jimin Wang, David J. Vinyard, Gary W. Brudvig, and Victor S. Batista.

[2] Biochemistry **54**: 1713-1716 (2015) Analysis of the Radiation-Damage-Free X-ray Structure of Photosystem II in Light of EXAFS and QM/MM Data, Mikhail Askerka, Jimin Wang, Gary W. Brudvig, and Victor S. Batista.

[3] Biochemistry **53**: 6860–6862 (2014) Structural Changes of the Oxygen-Evolving Complex of Photosystem II induced by the S1 to S2 Transition: A Combined XRD and QM/MM Study, Mikhail Askerka, Jimin Wang, Gary W. Brudvig, and Victor S. Batista.

[4] ACS Catalysis **5**: 2317-2323 (2015) Triplet Oxygen Evolution Catalyzed by a Biomimetic Oxomanganese Complex: Functional Role of the Carboxylate Buffer. Ivan Rivalta, Ke R. Yang, Gary W. Brudvig, and Victor S. Batista.

[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.

[6] ACS Catalysis **5**: 2317-2323 (2015) Photoinduced Water Oxidation at the Aqueous GaN$(10\bar{1}0)$ Interface: Deprotonation Kinetics of the First Proton-Coupled Electron-Transfer Step, Mehmed Z. Ertem, Neerav Kharche, Victor S. Batista, Mark S. Hybertsen, John C. Tully and James T. Muckerman.

[7] J. Catalysis 310: 37-44 (2014) Photoelectrochemical Oxidation of a Turn-On Fluorescent Probe Mediated by a Surface Mn(II) Catalyst Covalently Attached to TiO$_2$ Nanoparticles, Alec C. Durrell,Gonghu Li, Matthieu Koepf, Karin J. Young, Christian F. A. Negre, Laura J. Allen, W. R. McNamara, H. Song, Victor S. Batista, R. H. Crabtree and Gary W. Brudvig.

[8] *ACS Catalysis* **5**: 7104-7113 (2015) Mechanism of Manganese-Catalyzed Oxygen Evolution from Experimental and Theoretical Analyses of ^{18}O Kinetic Isotope Effects, Sahr Khan, Ke Yang, M. Zahid Ertem, Victor S. Batista and Gary W. Brudvig.

Time-Resolved Three Dimensional Single Molecule Tracking

James Werner

Center for Integrated Nanotechnologies (CINT)
Los Alamos National Laboratory, Los Alamos, NM

Programming Synthetic Nanoscale Excitonic Circuits using DNA

Mark Bathe

Principal Investigator, Laboratory for Computational Biology & Biophysics (http://lcbb.mit.edu)
Associate Professor, Department of Biological Engineering, MIT
Associate Member, Broad Institute of MIT & Harvard
Member, MIT Centers for Environmental Health Sciences, Excitonics, Neurobiological Engineering

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.

[1] Designer nanoscale DNA assemblies programmed from the top down. Veneziano, R., Ratanalert, S., Zhang, K., Zhang, F., Yan, H., Chiu, W., Bathe, M. *Science*, DOI: 10.1126/science.aaf4388 (2016).

[2] Programmed coherent coupling in a DNA-based excitonic circuit. Boulais, E., Sawaya, N., Veneziano, R., Andreoni, A., Lin, S., Woodbury, N., Yan, H., Aspuru-Guzik, A., Bathe, M. *Submitted* (2016).

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

Kirill A. Velizhanin
Avadh Saxena

Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM

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

Gergely T. Zimanyi[1]
Luman Qu[1], Marton Voros[2]

[1]Physics Department, UC Davis
[2]Argonne National Laboratories

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 surfaceassociated 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 metalenriched 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 CuInE2 (E = S, Se), are attracting increasing attention as alternative for the well-known heavy metal based NCs (CdE and PbE, E = 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 CuInE2 NCs and hetero-NCs with sizes, shapes and hetero-architectures that are not attainable by direct synthesis protocols (e.g. wurtzite CuInS2 bifrustum NCs, CuInE2 nanorods and multipods, CuInSe2/CuInS2 dot core/rod shell nanorods and concentric core/shell QDs, CuInTe2/CuInSe2 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 CuInS2 based core/shell QDs. The origin of the optical properties of CuInS2 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].

[1] W. van der Stam, A. C. Berends, C. de Mello Donega, ChemPhysChem 2016, 17, 559-581.
[2] W. van der Stam et al., Chem. Mater. 2015, 27, 621-628.
[3] W. van der Stam et al., ACS Nano 2015, 9, 11430 - 11438.
[4] K. E. Knowles, et al., J. Am. Chem. Soc. 2015, 137, 13138 - 13147.
[5] W. D. Rice, et al., J. Phys. Chem. Lett. 2014, 5, 4105 - 4109.

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

Nikolay S. Makarov[1]
Hunter McDaniel[2], Addis Fuhr[1], Victor I. Klimov[1]

[1]*Center for Advanced Solar Photophysics, Chemistry Division, Los Alamos National Laboratory*
[2]*UbiQD*

Nanocrystals (or quantum dots) of ternary I-III-VI2 semiconductors such as CuInSexS2-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 CuInSexS2-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 CuInSexS2-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.

[1] Meinardi et al. Nature Nanotech., 10, 878-885 (2015).
[2] McDaniel et al. Nature Comm., 4, 3887 (2013).
[3] Zhang et al. Chem. Mater., 26, 1204-1212 (2014).
[4] Speranskaya et al. Langmuir, 30, 7567-7575 (2014).
[5] Rice et al. J. Phys. Chem. Lett., 5, 4105-4109 (2011).

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

Samuel D. Stranks

[1]Research Laboratory of Electronics, Massachusetts Institute of Technology
[2]Cavendish Laboratory, University of Cambridge

Organic-inorganic perovskites such as CH3NH3PbI3 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 hetereogenity 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 CH3NH3PbI3 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.

Wednesday, June 15 **2:10pm-2:45pm**

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.

Wednesday, June 15 **2:45pm-3:20pm**

Controlled Light Emission in Organic Single Crystals for Optoelectronic Applications

Johannes Gierschner

Madrid Institute for Advanced Studies, IMDEA Nanoscience, Madrid, Spain

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.

Wednesday, June 15 **3:20pm-3:55pm**

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 (Eg). Minimizing Eg 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 Eloss, where Eloss = Eg   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 Eg, giving rise to ECT   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.

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.

Modeling Photochemistry with Surface Hopping

Tammie Nelson

Los Alamos National Laboratory, Los Alamos, NM

A typical scenario of ‘simple’ photochemical dynamics occurring in energetic materials can be seen in Nitromethane (NM). NM is a high explosive (HE) that undergoes photolysis upon UV irradiation. The photochemical processes involved in NM decomposition could be applied to the design of novel photoactive HEs. Several pathways for the photodecomposition have been proposed over the years including NO_2 dissociation, methyl nitrite isomerization, and aci-ion formation. Our present non-adiabatic excited state molecular dynamics (NA-ESMD) capabilities based on surface hopping only allow dynamics of photophysics to be described. Our NA-ESMD simulations confirmed the previously measured excited state lifetime and total photolysis quantum yield in NM. However, the photochemical reactions cannot be described well with the current closed-shell approach. At best, our simulations identify intermediate species but *not the final photoproducts*; The subsequent dynamics of intermediates leading to additional bond breaking or recombination of fragments cannot be followed. Ultimately the system relaxes to the ground or excited states of fragments where the unknown initial conditions and probabilities of a specific product are entirely defined by photochemical reactions involving open-shell species.

Thursday, June 16 **8:30am-9:05am**

Unusual 2D Semiconductors and their Unexpected Properties*

David Tomanek

Physics and Astronomy Department, Michigan State University, East Lansing, MI 48824, USA

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 AsxP1-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.

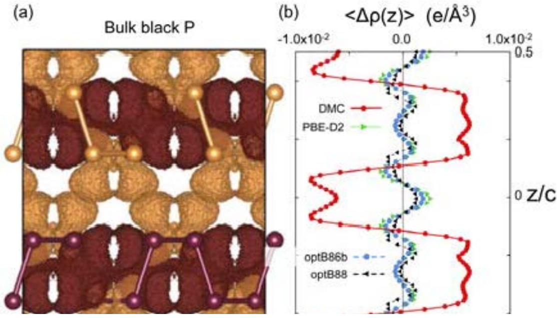


FIG 1 Calculated electron density difference representing the charge redistribution caused by assembling the bulk structure from isolated monolayers. (a) Diffusion Monte Carlo (DMC) isosurfaces bounding regions of excess electron density (dark brown) and electron deficiency (light brown), with respective values ±6.5×10^{-3} e/Å^3. (b) <Δρ(*z*)> 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.

[1] H. Liu *et al. ACS Nano* **8,** 4033 (2014).
[2] L. Shulenburger, A.D. Baczewski, Z. Zhu, J. Guan, and D. Tománek, Nano Lett. **15**, 8170 (2015).
[3] Zhen Zhu, Jie Guan, and David Tománek, Phys. Rev. B **91**, 161404(R) (2015).
[4] Zhen Zhu, Jie Guan, and David Tománek, Nano Lett. **15**, 6042 (2015).
[5] Zhen Zhu, Jie Guan, Dan Liu, and David Tománek, ACS Nano **9**, 8284 (2015).

Permanent Excimer Superstructures by Supramolecular Networking of Metal Quantum Clusters

S. Brovelli

Materials Science Department
Università degli Studi di Milano-Bicocca

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)

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

David J. Nesbitt

JILA, National Institute of Standards and Technology and University of Colorado,
Department of Chemistry and Biochemistry, University of Colorado
Boulder, CO 80309

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) x 10-6) comparable with experimental estimates (10-6-10-5) of conventional Auger ionization efficiencies out of biexcitonic states.

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 Cognet, 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 cm^3/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.

[1] W. Nie, H. Tsai, R. Asadpour, J.-C. Blancon, A. J. Neukirch, G. Gupta, J. J. Crochet, M. Chhowalla, S. Tretiak, M. A. Alam, H.-L. Wang, A. D. Mohite, Science 2015, 347, 522.
[2] Blancon, J.-C.; Nie, W.; Neukirch, A. J.; Gupta, G.; Tretiak, S.; Cognet, L.; Mohite, A. D.; Crochet, J. J. Adv. Funct. Mater. 2016, DOI: 10.1002/adfm.201505324.

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 resole 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 CH3NH3PbI3 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 CH3NH3PbI3, 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.

Dynamics of Electronic Excitations at Interfaces

Dmitri Kilin

Department of Chemistry and Biochemistry, North Dakota State University, Fargo, ND 58018
Email: Dmitri.Kilin@ndsu.edu

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]

[1] Han, Y., S. Tretiak, and D. Kilin, *Dynamics of charge transfer at Au/Si metal-semiconductor nano-interface.* Mol. Phys., 2014. **112**(3-4): p. 474-484.

[2] Huang, S., T.M. Inerbaev, and D. Kilin, *Excited state dynamics of Ru10 cluster interfacing anatase TiO2(101) Surface and liquid water.* Journal of Physical Chemistry Letters, 2014. **5** (16): p. 2823-2829.

[3] Junkman, D., et al., *Ab Initio Analysis of Charge Carrier Dynamics in Organic-Inorganic Lead Halide Perovskite Solar Cells.* Mater. Res. Soc. Symp. Proc., 2015. **1776**: p. DOI: 10.1557/opl.2015.782.

[4] Yao, G., et al., *Molecular dynamics in finding nonadiabatic coupling for β-NaYF4: Ce3+ nanocrystals.* Molecular Physics, 2014. **113**(3-4): p. 385-391.

[5] Kilina, S., D. Kilin, and S. Tretiak, *Light-Driven and Phonon-Assisted Dynamics in Organic and Semiconductor Nanostructures.* Chemical Reviews, 2015. **115**((12)): p. 5929–5978.

[6] Jensen, S.J., T.M. Inerbaev, and D.S. Kilin, *Spin Unrestricted Excited State Relaxation Study of Vanadium(IV)-Doped Anatase.* The Journal of Physical Chemistry C, 2016. **120**(11): p. 5890-5905.

[7] Vogel, D.J. and D.S. Kilin, *First-Principles Treatment of Photoluminescence in Semiconductors.* Journal of Physical Chemistry C, 2015. **119**(50): p. 27954-27964.

[8] Han, Y., et al., *Photofragmentation of the Gas-Phase Lanthanum Isopropylcyclopentadienyl Complex: Computational Modeling vs Experiment.* The Journal of Physical Chemistry A, 2015. **119**(44): p. 10838-10848.

Disorder in Organic Semiconductors Due to Fluctuations in Space Charge Density

David Dunlap[1]
Tzu-Cheng Wu[1], Susan Atlas[1], and Steve Valone[1], Andrei Piryatinski[2]

[1]Dept. of Physics and Astronomy, University of New Mexico
[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.

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

F. C. Spano

Department of Chemistry, Temple University, Philadelphia, PA 19122

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-aggregates[1] 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]

[1] M. Kasha, Radiation Research **20** (1), 55-70 (1963), [2] N. J. Hestand and F. C. Spano, J. Chem. Phys. **143** (24), 244707 (2015), [3] F. C. Spano and C. Silva, Ann. Rev. Phys. Chem. **65** (2014), [4] F. C. Spano, Acc. Chem. Res. **43** (3), 429-439 (2010), [5] F. Wurthner and M. Stolte, Chem. Comm. **47** (18), 5109-5115 (2011), [6] B. A. Jones, A. Facchetti, M. R. Wasielewski and T. J. Marks, J. Am. Chem. Soc. **129** (49), 15259-15278 (2007), [7] N. J. Hestand, R. Tempelaar, J. Knoester, T. L. C. Jansen and F. C. Spano, Phys. Rev. B **91** (19), 195315 (2015), [8] H. Yamagata, D. S. Maxwell, J. Fan, K. R. Kittilstved, A. L. Briseno, M. D. Barnes and F. C. Spano, J. Phys. Chem. C **118** (49), 28842-28854 (2014).

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

Eric Bittner

University of Houston

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

Philipp Wilhelm[1]
Jan Vogelsang[1], Georgiy Poluektov[2], Eva Sigmund[2], Stefan-S. Jester[2], Sigurd Höger[2], John M. Lupton[1]

[1]Universität Regensburg, Universitätsstraße 31, 93053 Regensburg, Germany
[2]Universität Bonn, Gerhard-Domagk-Straße. 1, 53121 Bonn, Germany

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.