

MODERN TRENDS IN ELECTRON TRANSFER CHEMISTRY: FROM MOLECULAR ELECTRONICS TO DEVICES

Meeting Conveners:

Dr. Jyotishman Dasgupta (TIFR, Mumbai)

Dr. Ravindra Venkatramani (TIFR, Mumbai)

Dates: 28th and 29th January 2016

Venue:

**International Center for Theoretical Sciences
Bangalore, INDIA**



Scientific Program

Day 1: 28th January

Breakfast at Guest house

9:00 am: Introductory words by Director, ICTS.

SESSION CHAIR: Ravindra Venkatramani

9:30 -10:00 am: Bhaskaran Muralidharan, IIT Bombay

"Molecular thermoelectric heat engines and coolers"

10:00-10:30 am: Mahesh Hariharan, IISER Trivandrum

"Strategies to Reduce the Rate of Charge Recombination"

10:30 -11:00 am: Upendra Harbola, IISc Bangalore

"Spectroscopy of molecular junctions"

-----**11:00-11:15 am:** Tea Break-----

SESSION CHAIR: Jyotishman Dasgupta

11:15-11:45 am: Satish Patil

"Donor-Acceptor Based 'order in disorder' Conjugated Polymers"

11:45-12:15 pm: Ravindra Venkatramani

"Molecular Breadboard Circuits"

-----**12:30 - 2:30 pm:** Lunch + Poster session-----

SESSION CHAIR: Deepa Khushalani

2:30 -3:00 pm: Ayelet Vilan

"Molecularly Controlled Semiconductor Interfaces"

3:00 - 3:30 pm: Swapan Pati

"Quantum Dots and Molecular Electronics in Weak Coupling limit"

3:30 -- 4:00 pm: Jyotishman Dasgupta

“Charge Transfer Rates in Soluble P3HT:PCBM Nano-aggregates Predict the Solvent Dependent BHJ Film Morphology”

Free time before the public talk

4:30 - 5:30 pm: ICTS Public Lecture by Latha Venkataraman

5:30 - 6:00 pm: Post lecture get-together Tea

6:00-8:00 pm: Data blitz by all poster attendees

-----**Dinner at 8:00 pm**-----

Day 2: 29th January

Breakfast at Guest house

9:00 am: Planning for future meetings: Discussion lead by Jyotishman Dasgupta

10:00 am: Morning poster session

12:00 noon: Vote of thanks to ICTS

-----**Lunch and depart**-----

ORAL PRESENTATIONS

ICTS Public Lecture

Scaling of Electronic Devices: From the Vacuum Tube to a Single-Molecule Diode

Latha Venkatraman

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Most electronic devices made today use transistors as their smallest functional building blocks. Since their invention in the 1940s, their size has shrunk from the macroscopic scale to the current day transistor which has a characteristic dimension under twenty nanometers. Further miniaturization requires new basic understanding of electronic transport, as well as innovative mechanisms for controlling electron transfer at these reduced, nanometer, dimensions. The ultimate miniaturization of devices will likely involve structures at the atomic scale, thus devices created using single-molecule elements will provide a basic test bed for probing fundamental science of nanometer sized circuits. In this talk, I will review measurement techniques used create single-molecule circuits and then present our results illustrating how a diode with a high on/off ratio can be created.

Molecular Thermoelectric Heat Engines and Coolers

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Molecular charge transport may also be coupled to heat transport with the application of a temperature gradient [1]. This regime of *thermoelectric* transport

thus opens up newer functionalities such as molecular heat engines and coolers. The object of my talk is to thus draw attention to thermoelectric transport across molecular junctions. I will first introduce the Landauer picture of a molecular thermoelectric and how it aids in understanding molecular heat engines [1]. I will also discuss the related thermodynamics of thermoelectric transport across molecular systems, including the possibility of achieving the Carnot efficiency [2]. While pedagogically presenting some of our recent work [3-6], I will discuss in detail the implications of a typical linear response analysis and why it is insufficient. Finally, an outlook on junction and molecular cooling [6-7] will be presented.

[1] P. Reddy et. al., Science, 315, 1568 (2007).

[2] G. D. Mahan and J. O. Sofo, PNAS, 93, 7486, (1996).

[3] B. Muralidharan and M. Grifoni, Phys. Rev. B, 85, 155423, (2012).

[4] A. Agarwal and B. Muralidharan, Appl. Phys. Lett., 105,013104, (2014).

[5] B. Muralidharan and M. Grifoni, Phys. Rev. B, 88, 045402, (2013).

[6] A. Singha, S. D. Mahanti and B. Muralidharan, AIP Advances, 5, 107210, (2015).

[7] W. Lee et. al., Nature, 498, 209, (2013).

Strategies to Reduce the Rate of Charge Recombination

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Modulating excitons generated as a result of photoinduced electron transfer in crowded environments is vital for the development of photo-functional materials.¹ The hetero-junctions (HJs) in organic photovoltaics are termed as “transport highways” for the charge carriers to the respective electrodes.² Careful design and organization of molecular architectures at the HJs in organic solar cells dictates the fate of excitons generated. Molecular organization relies on interplay between various inter/intra molecular interactions such as multi-pole electrostatic interactions, dispersion and inductive effects, π - π interactions, hydrogen bonding etc. which determines electronic and optical properties associated with these materials. Myriads of models have been proposed in enhancing the survival times of the excitons generated at the HJs. Mullen and co-workers³ substantiated that compromise and dominance of various inter- and intra-molecular interactions operating in donor (D)-acceptor (A) self-assembled systems could generate segregated D-D/A-A stacks,⁴ D-A interdigitating alternate stacks etc. Aida and co-workers⁵

demonstrated the photochemical generation of spatially separated charge carriers through co-axial nanotubular arrangement of D and A. Wasielewski et al.⁶ extended the survival time of charge separated states through self-assembled D-A tetramers, trefoils, dimers and hydrogen bonded foldamers. Recent report from our group⁷ [demonstrated the importance of supramolecular vesicular scaffold in reducing the rate of charge recombination of the charge separated states.](#)⁸ Recently, we succeeded in synthesizing nonparallel D-A stacks wherein the D-A pair undergo self-assembly in CHCl₃ to form spherical aggregates that facilitated in sustaining the charge transfer intermediates for longer timescales through D-A stacks.⁹

1. G. S. Engel, T. R. Calhoun, E. L. Read, T.-K. Ahn, T. Mancal, Y.-C. Cheng, R. E. Blankenship and G. R. Fleming, *Nature*, 2007, **446**, 782-786.
2. M. Wang and F. Wudl, *J. Mater. Chem.*, 2012, **22**, 24297-24314.
3. L. F. Dössel, V. Kamm, I. A. Howard, F. Laquai, W. Pisula, X. Feng, C. Li, M. Takase, T. Kudernac, S. De Feyter and K. Müllen, *J. Am. Chem. Soc.*, 2012, **134**, 5876-5886.
4. G. Sforzini, E. Orentas, A. Bolag, N. Sakai and S. Matile, *J. Am. Chem. Soc.*, 2013, **135**, 12082.
5. Y. Yamamoto, T. Fukushima, Y. Suna, N. Ishii, A. Saeki, S. Seki, S. Tagawa, M. Taniguchi, T. Kawai and T. Aida, *Science*, 2006, **314**, 1761-1764.
6. V. L. Gunderson, A. L. Smeigh, C. H. Kim, D. T. Co and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2012, **134**, 4363-4372.
7. (a) R. T. Cheriya, J. Joy, A. P. Alex, A. Shaji and M. Hariharan, *J. Phys. Chem. C*, 2012, **116**, 12489-12498; (b) R. T. Cheriya, K. Nagarajan and M. Hariharan, *J. Phys. Chem. C*, 2013, **117**, 3240-3248.
8. R. T. Cheriya, A. R. Mallia and M. Hariharan, *Energy Environ. Sci.*, 2014, **7**, 1661-1669.
9. A. R. Mallia, P. S. Salini and M. Hariharan, *J. Am. Chem. Soc.*, 2015, 15604-15607

Spectroscopy of Molecular Junctions

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Understanding optical signals from current-carrying single molecular systems is of fundamental interest with potential applications to sensors and optoelectronic devices [1]. Time-resolved optical measurements in open junctions could provide information about neutral and various charged states of the molecule and their relaxation due to interactions with the surrounding. We will discuss a diagrammatic Liouville space approach to calculate time-

and frequency-resolved signals from a molecular junction [2,3]. Both photon and electronic (current) detections will be compared. After the junction reaches a steady state, characterized by a constant electron flux, it is driven by a sequence of temporally well-separated optical pulses. The photon and electron signals are expressed in terms of molecular correlation functions and expanded in molecular eigenstates, obtained from standard quantum chemistry calculations. We apply this formulation to compute signals from a junction made of Benzene-1,4-dithiol molecule.

[1] D. R. Ward et al., Nano Lett. 8, 919 (2008).

[2] B. K. Agrawalla et al. J. Chem. Phys. 142, 212445 (2015).

[3] H. P. Goswami et al., J. Chem. Phys. 11, 4304 (2015).

Donor-acceptor based 'order in disorder' conjugated polymers

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A rapid improvement in performance of organic solar cells, light-emitting diodes and field-effect transistors largely originate from the successful development of new conjugated polymers. However, the fundamental question still remains related to the unequal mobility of hole and electron in π -conjugated polymers. A rational design of polymers is necessary to target n-type stable polymers, which can work in ambient processing conditions. Our laboratory employs a molecular engineering approach to develop high charge carrier n-type polymers for enhancing the performance of optoelectronic devices. In this talk, the integrated approach to materials design for enhanced electron mobility will be discussed. Specific emphasis will be placed on the guideline principle of the *donor-acceptor* approach to rationally design the low band-gap polymers with minimum defect, optimum energy levels and high electron mobility.

[1] M. A. Naik, N. Venkatramaiah, C. Kanimozhi, and S. Patil*, *J. Phy. Chem-C*, 2012, 116, 26128-26137

[2] C. Kanimozhi, N. Yaacobi-Gross, K. W. Chou, A. Amassian, T. D. Anthopoulos, S. Patil, *J. Am. Chem. Soc.* 2012, 134, 16532

Molecular Breadboard Circuits

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In conventional electrical and electronics engineering, solderless breadboard scaffolds are routinely used for quickly creating/ a range of electrical circuits of varied complexity. We will translate the concept of a breadboard circuit to the molecular scale through a theoretical analysis of the conductance and charge flow in a bis-terpyridine p-phenyl (TP1) molecular junction and experimental data from our collaborators.[1] The TP1 molecule forms one of the most complex molecular junctions studied to-date, with torsional rotational degrees of freedom between seven aromatic rings and as many as six anchoring possibilities to the metal electrodes. We show that 61 possible circuits can be created across the molecular breadboard, which are accessible within a Mechanically Controlled Break-Junction experiment. The circuits display quantum interference effects and exhibit conductance features spanning over 5-orders of magnitude.

[1] C. Seth, V. Kaliginedi, S. Suravarapu, D. Reber, W. Hong, T. Wandlowski, F. Lajolet, P. Broekmann, G. Royal, R. Venkatramani; *submitted*

Molecularly Controlled Semiconductor Interfaces

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Almost any modern electronic functionality occurs at interfaces: from p-n junctions to hetero-junctions, from lasers to sensors. The fact that these interfaces are predominantly inorganic has misled the community to overlook the critical contribution of interface chemistry to net electronic performance.^[1] By chemistry we mean that binding causes localized charge polarization (i.e., dipole) that can further induce huge potential barrier within

the semiconductor. Organic molecules, with their closed-shells, localized orbitals, hold strong polarization naturally. Therefore, inserting molecular monolayers into inorganic interfaces promotes basic understanding as well as providing an efficient applicative tuning of the electronic performance.^[2] Our study is focused on a model system of monolayers adsorbed on oxide-free, H-Si, covered with a metal, such as Hg or Pb. In these systems, a single substituent change leads to 8 orders of magnitude change in current across the junction,^[3] and even to a creation of a p-type region at the surface-region of n-doped Si ('population inversion').^[4] My talk will describe the fundamental relation between interfacial dipole and Si barrier height and its implication for molecular electronics, and organic electronics in general.

- [1] R. T. Tung, *Applied Physics Reviews* **2014**, *1*, 011304.
- [2] A. Vilan, O. Yaffe, A. Biller, A. Salomon, A. Kahn, D. Cahen, *Adv. Mater.* **2010**, *22*, 140.
- [3] A. Haj-Yahia, Yaffe, Bendikov, Cohen, Feldman, Vilan, Cahen, *Adv. Mater.* **2013**, *25*, 702.
- [4] O. Yaffe, L. Scheres, S. R. Puniredd, N. Stein, A. Biller, R. Har-Lavan, H. Shpaisman, H. Zuilhof, H. Haick, D. Cahen, A. Vilan, *Nano Letters* **2009**, *9*, 2390.

Quantum Dots and Molecular Electronics in Weak Coupling limit

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In this era of miniaturized devices, we have been trying to develop various quantum theories to describe charge transfer, transport, optical and magnetic phenomena within a unified approach. Towards this end, I shall discuss our efforts to understand Negative differential Conductance (NDC), rectification and Coulomb blockade behaviors in molecules [1,2] and in coupled quantum dots [3,4], using Kinetic theory within quantum many body picture in the weak coupling limit. I shall touch upon the recent work on transport and thermoelectric calculations within Landauer-Buttiker formalism to obtain heat to voltage conversion efficiency in a spin-crossover molecule

based two-terminal junction [5]. I shall also discuss the new processes (Coherent Destruction of Tunneling (CDT) and Photon Assisted Tunneling (PAT) that occur in a coupled quantum dots device between two electrodes, when light is shined on the nano-junction [6].

1. D. Ghosh, P. Parida, S. K. Pati, Submitted (2016).
2. B. Muralidharan, A. W. Ghosh, S. K. Pati and S. Datta, *IEEE Nano Trans.* **6**, 536 (2007).
3. P. Parida, S. K. Pati and A. Painelli, *Phys. Rev. B* **83**, 165404 (2011).
4. P. Parida, S. Lakshmi and S. K. Pati, *J. Phys.: Cond. Matt.* **21**, 095301 (2009).
5. D. Ghosh, P. Parida and S. K. Pati, *Appl. Phys. Lett.*, **106**, 193105 - 193108 (2015)
6. P. Parida, T. Seidaman and S. K. Pati, Submitted (2016)

Charge Transfer Rates in Soluble P3HT:PCBM Nano-aggregates Predict the Solvent Dependent BHJ Film Morphology

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Device efficiency of bulk heterojunction (BHJ) solar cells is critically dependent on the nano-morphology of the solution-processed *polymer:fullerene* blend. Active control on blend morphology can only emanate from a detailed understanding of solution structures during the film casting process. We show that photoinduced charge transfer (CT) rates can be used to probe the effective length scale of the pre-formed solution structures arising from a mixture of poly(3-hexylthiophene-2,5-diyl) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) in three different organic solvents. Using the diffusive component of the charge transfer rate, we deduce ~ 3 -times larger functional nano-domain size in toluene than in chlorobenzene thereby correctly predicting the relative polymer nanofiber widths observed in annealed films. We thus provide the first experimental evidence for the postulated *polymer:fullerene:solvent* ternary phase that seeds the eventual morphology in spin-casted films.[1] Our work motivates the design of new chemical additives to tune the grain size of the evolving *polymer:fullerene* domains within the solution phase.

[1] P. Roy, A. Jha and J. Dasgupta, *Nanoscale* 2016, DOI: 10.1039/C5NR06445G

POSTER PRESENTATIONS

Sabyasachi Mukhopadhyaya, *Weizmann Institute of Science*

"Integrating Proteins into Electronics"

Kalaivanan Nagarajan, *IISER-Thiruvananthapuram*

"Activation of Triplet Excited State in Core-Twisted Perylenediimides"

Soham Maity, *IISc Bangalore*,

"Study on Charge Photogeneration in Diketopyrrolopyrrole Based Copolymers"

Hari Kumar Yadalam, *IISc Bangalore*

"Statistics of an adiabatic charge pump*"

Bitan De, *IIT Bombay*

"Nanocaloritronics of the Anderson-Hollstein molecular system"

Aniket Singha, *IIT Bombay*

"Nanoscale thermoelectric packaging and cooling"

Palas Roy, *TIFR Mumbai*

"Tracking Exciton Dynamics in Low-bandgap Conjugated Polymers using Femtosecond Stimulated Raman Spectroscopy"

Imon Mandal, *TIFR Mumbai*

"Unusual Absorption spectral Features of non-aromatic charged amino acids: Implications for tracking protein unfolding and aggregation."

Ankita Das, *TIFR Mumbai*

"Probing Dynamic Water Interaction with Molecular Nanocages Using Host-Guest Charge Transfer States"

Rahul Gera, *TIFR Mumbai*

"Probing Excited State Redox Reactions Inside Molecular Containers".

Charu Seth, *TIFR Mumbai*

"Bis-terpyridine based molecular junction as a breadboard"

Joel Cornelio, *TIFR Mumbai*

"Towards Understanding of the Conformational Equilibrium of FAD under Confinement"

K. Vijayalakshmi, *TIFR Mumbai*

"Ultrafast triplet generation in solution: Critical need of reactive triplet in mediating polycyclopene photoisomerization reaction"

Tushita Mukherjee, *IISc Bangalore*

"Effect of Chalcogens on Electronic and Photophysical Properties of Vinylene-Based Diketopyrrolopyrrole Copolymers"

Dibyajyoti Ghosh, *JNCASR Bangalore*

"Spin Crossover Molecule based Thermoelectric Junction"

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