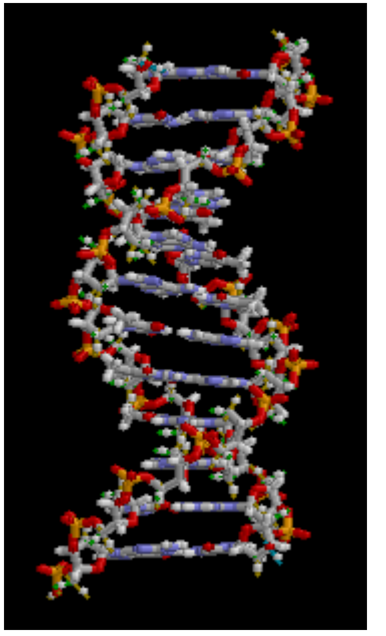
NGC2017

Section: Electronics Structure and Charge Transport; Chairs: Steffen Duhm and Evgeny Gousev; September 21, 1:30-2:00 pm



Generalized Charge Transfer (GCT) Model for Analysis of Transport Phenomena in Molecular and DNA stacks

Vladimir Burtman

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Prof. Anatoli Korkin, Arizona State University, USA

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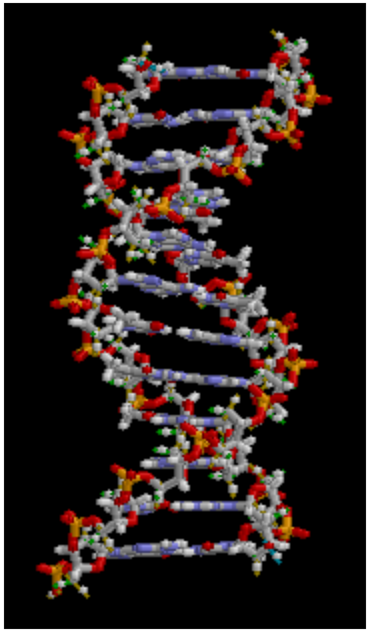
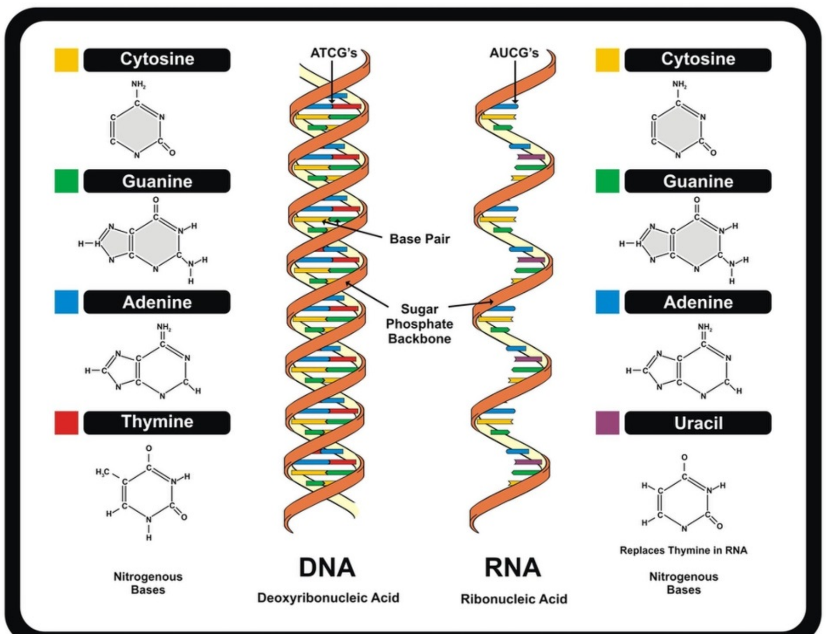


DNA: 60 years of history

DNA is made up of molecules called nucleotides. Each nucleotide contains a phosphate group, a sugar group and a nitrogen base. The four types of nitrogen bases are adenine (A), thymine (T), guanine (G) and cytosine (C). The order of these bases is what determines DNA's instructions, or genetic code. Similar to the way the order of letters in the alphabet can be used to form a word, the order of nitrogen bases in a DNA sequence forms genes, which in the language of the cell, tells cells how to make proteins.

The entire human genome contains about 3 billion bases and about 20,000 genes.



DNA discovery

DNA was first observed by a German biochemist named Frederich Miescher in 1869. But for many years, researchers did not realize the importance of this molecule. It was not until 1953 that James Watson, Francis Crick, Maurice Wilkins and Rosalind Franklin figured out the structure of DNA — a double helix — which they realized could carry biological information. Watson, Crick and Wilkins were awarded the Nobel Prize in Medicine in 1962 "for their discoveries concerning the molecular structure of nucleic acids and its significance for information transfer in living material."

1. Introduction: DNA-devices in Molecular Nanoelectronics Timeline

1953: James Watson, Francis Crick, Maurice Wilkins and Rosalind Franklin figured out the structure of DNA — a double helix

1960: R. Feynman (discussion of DNA with Schrodinger), “Plenty of Room at the Bottom”

1997: J.M. Tour, M. A. Reed Testing a “Single Molecule” Devices, *Science*

1999: Kelley DNA-mediated charge transport *Science*

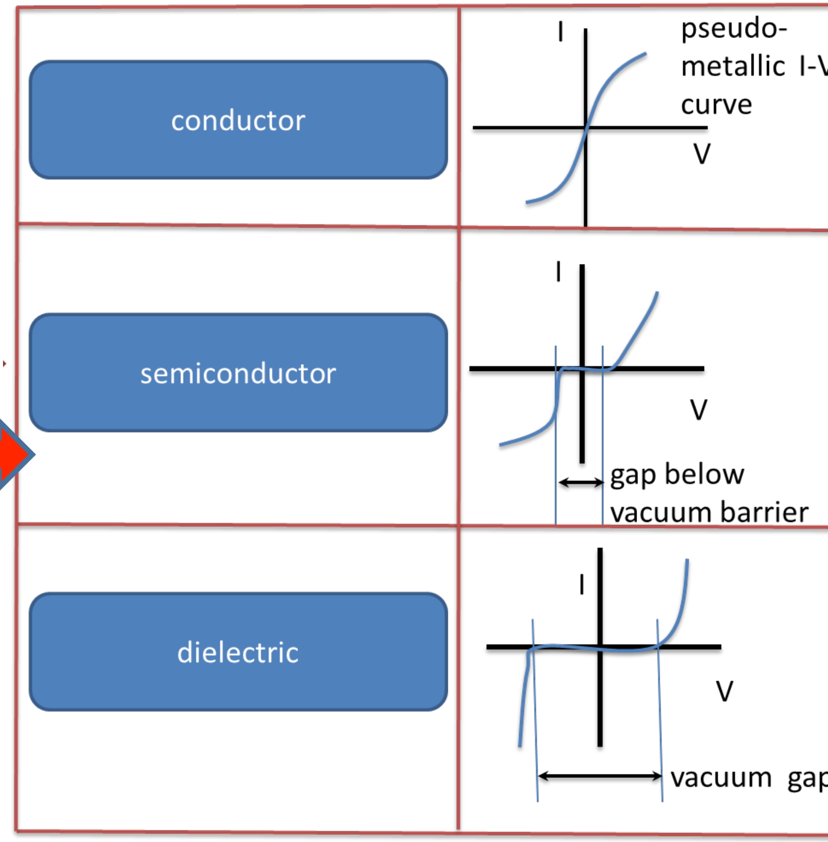
2016: DNA-solid transport: state of the art @ next slide

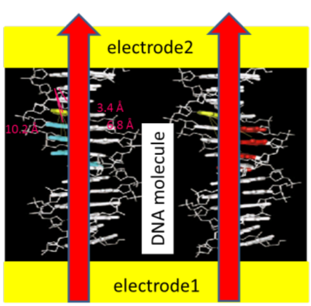
1. Introduction: Transport studies in solid state DNA molecular devices @2016

From: J.M.A Vivancos, J. Hihath, I. Diez-Perez, Biomolecular Electronics, in Molecular Electronics (ed Ioan Baldea), 2016 Pan Stanford Publishing, chapter8, pp. 281-313

Table 8.1 Conductance properties of DNA in different experimental environments

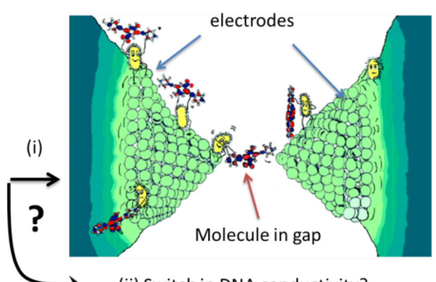
Year	Author	Properties	Sample type	No. of strands	Method	Ref.
1998	Braun et al.	Insulator	λ-DNA	Many	Thiolated contacts	[129]
1999	Fink & Shönen-berger	Metallic	λ-DNA	Bundles	LEEPS–Tungsten tip TEM grid	[130]
2000	Dekker et al.	Semiconductor	30 base pair Poly(GC)	One	Field trapping	[131]
2000	Cai et al.	Metallic	Poly(GC) Poly(AT)	Networks/ Bundles	AFM on Mica	[12
2000	de Pablo et al.	Insulator	λ-DNA	Several	Gold deposited on Top–AFM	[132]
2001	Dekker et al.	Insulator	50–200 nm mixed and poly(G:C)	Few	Thiol-bonded to EBL defined electrodes	[119]
2001	Rakitin et al.	Metallic	M-DNA	Bundles	Vacuum across electrodes	[133]
2001	Yoo et al.	Semiconductor	Poly(AT)–μm	One	FET Strands	[121]
2001	Yoo et al.	Semiconductor	Poly(GC)–μm	One	FET Strands	[121]
2001	Kasumov et al.	Metallic	λ-DNA non-specific contact	Few	Re/C contacted	[134]
2003	Shigematsu et al.	Non-crystalline hopping mech.	λ-DNA with CNT contacts	One	Triple probe conducting AFM	[135]
2004	Xu et al.	Hopping/Tunneling sequence dependence	8–14 base pairs strands	One	STM-BJ	[50]





Kelley, Science 1999

(i) Measurement artifacts?



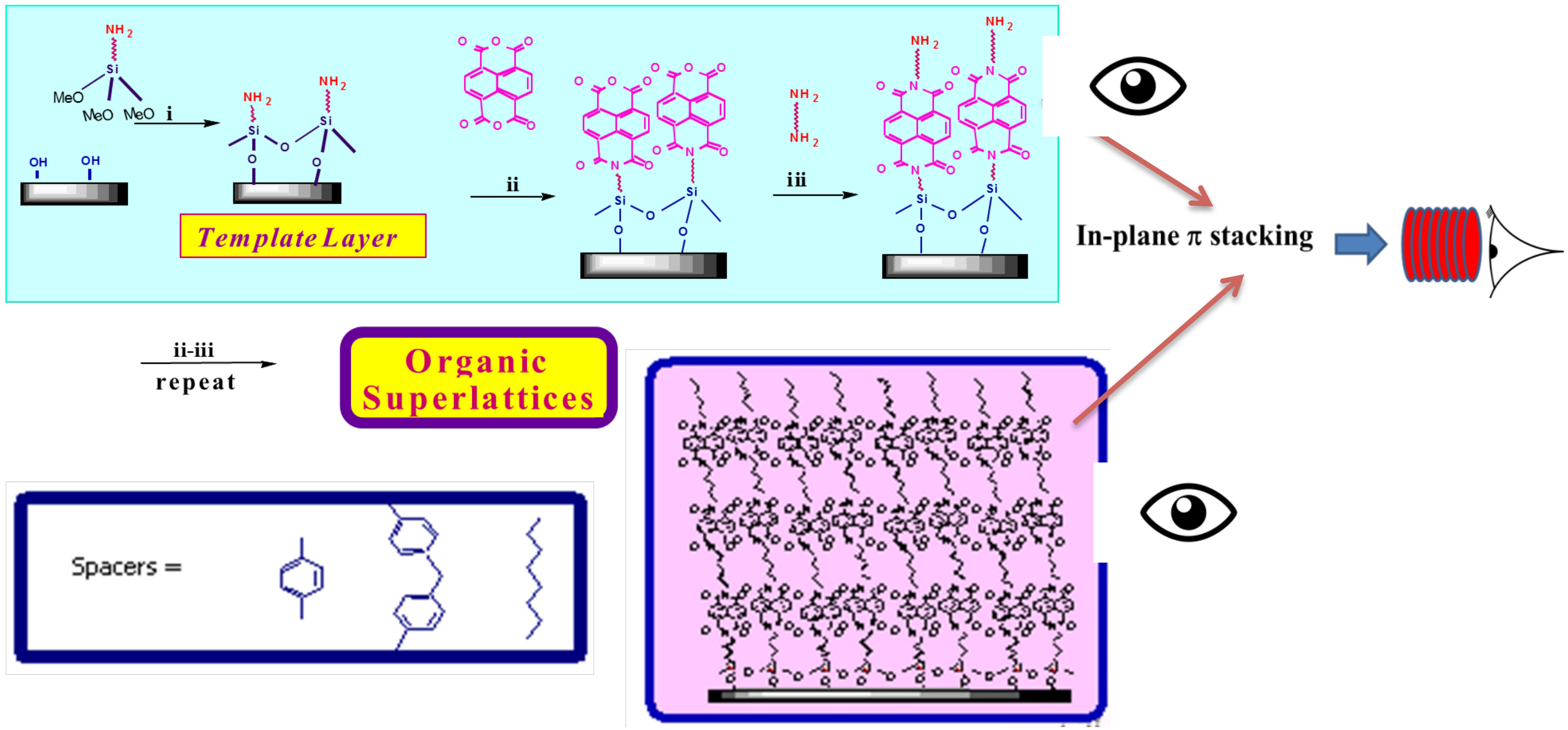
(ii) Switch in DNA conductivity?

Jorge M. Seminario
J. Am. Chem. Soc. 2001, *123*, 5616-5617

How to create molecular device with high charge mobility?

Molecular Layer Epitaxy

2. Molecular Layer Epitaxy (MLE) Derived π–stack, as a Model System for Analysis of Transport Phenomena in DNA devices



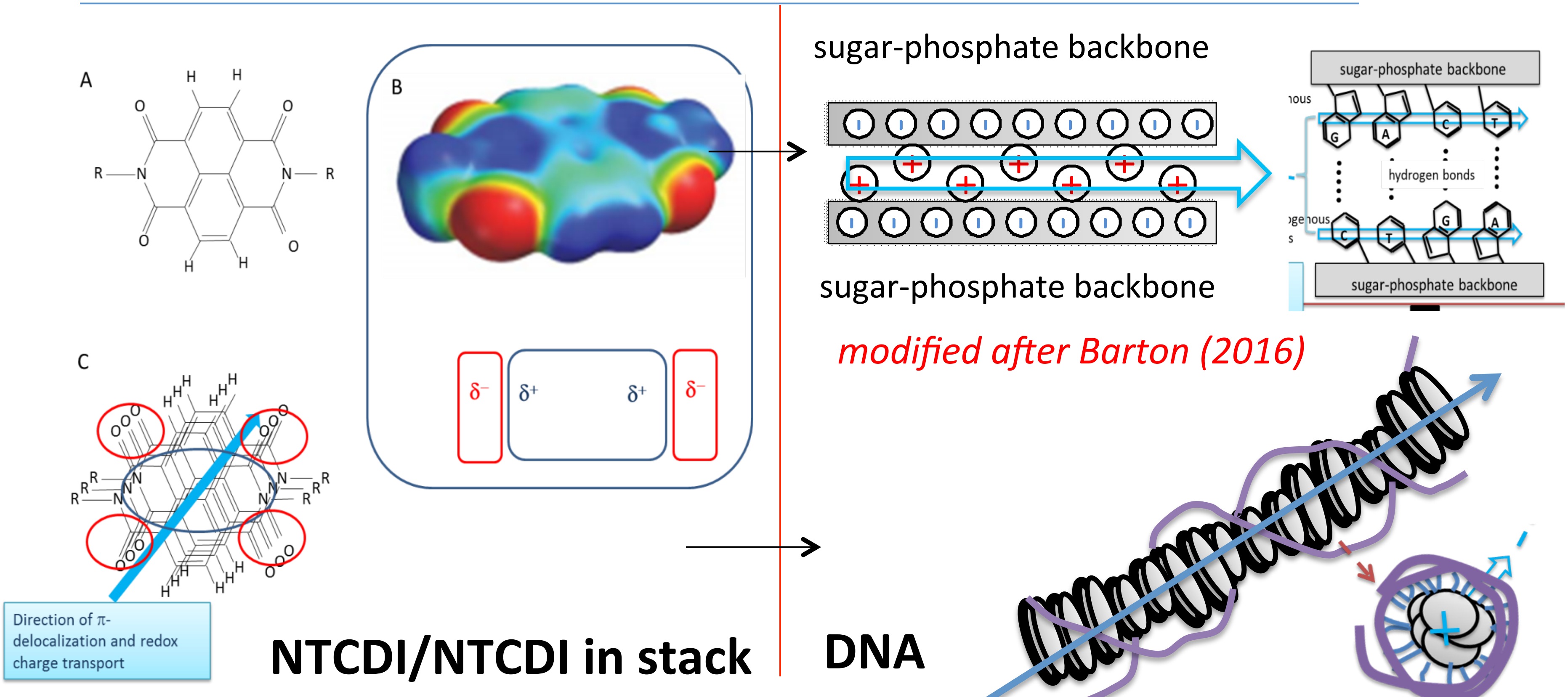
Example of surface chemistry, which yields rich p-aggregation system in naphthalene tetracarboxyl diimide (NTCDI) structure. The upper panel shows the assembly of NTCDI molecules mounted on covalent imide bonds in organic structure, which lead to formation of organic suprelattices and hetero-structures. The bottom left panel show the variety of ways in which NTCDI molecules can be connected within the same covalent bond. Eventually bottom right panel show the example of macroscopic ordering in NTCDI-contained structure with aliphatic spacers, which is shown as last molecular moiety in bottom-left section. The NTCDI molecules trend to form a molecular aggregates in orthogonal direction. This structure was accomplished by molecular layer epitaxy (MLE) method.

10:00 am – 10:30 am

Tatiana Kopylova, Tomsk State University, Tomsk, Russia, Molecular Layer Epitaxy Method for Molecular Nanoelectronics (September 22, Friday, Morning Fabrication of Nanostructured Materials and Devices I Chairs: Damir Islamov and Alexey Kovalgin)

3. Structural, Electrostatic and RedOx Similarity between π-aggregated Molecular Stack in MLE NTCDI and DNA

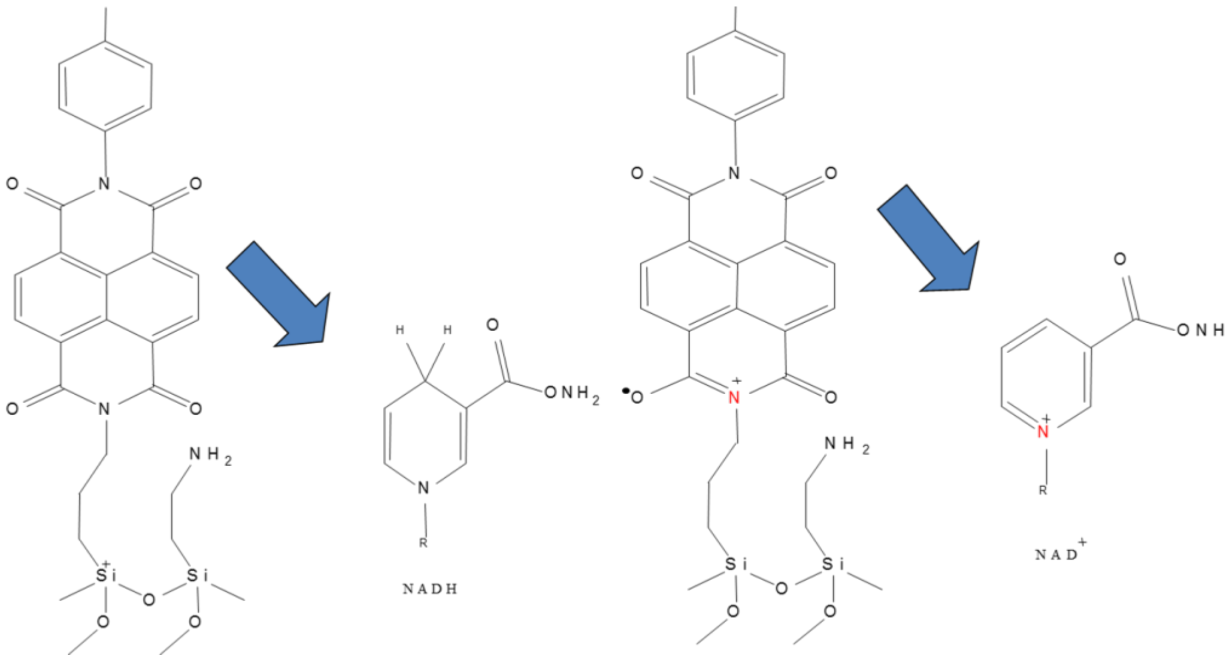
Packing and Electrostatics in NTCDA (left) and DNA (right)



(A) Scheme showing electrostatics for aromatic interaction in NTCDI single molecule. (B) Cartoon present to describe qualitatively aromatic quadrupole moments in electron-deficient aromatics, 1,4,5,8-naphthalenetetracarboxlic diimide (NTCDI) that contain strongly electron withdrawing groups. The mode of stacking is emphasizing locations of electrostatic attraction or repulsion. The electrostatic potential surfaces for the representative aromatic units were plotted from DFT calculations. This presentation is adapted from ***Martinez and Iverson (2012).*** (C) Direction of p-stack and charge delocalization along the molecular stack. The electrostatic environment within this p-molecular stack can be considered similar to DNA electrostatics after: ***C. R. Martinez and B. L. Iverson, Rethinking the term "pi-stacking", Chem. Sci., 2012, 3, 2191-2201; 2012. DOI: 10.1039/c2sc20045g***

3. Structural, Electrostatic and RedOx Similarity between π-aggregated Molecular Stack in MLE NTCDI and DNA

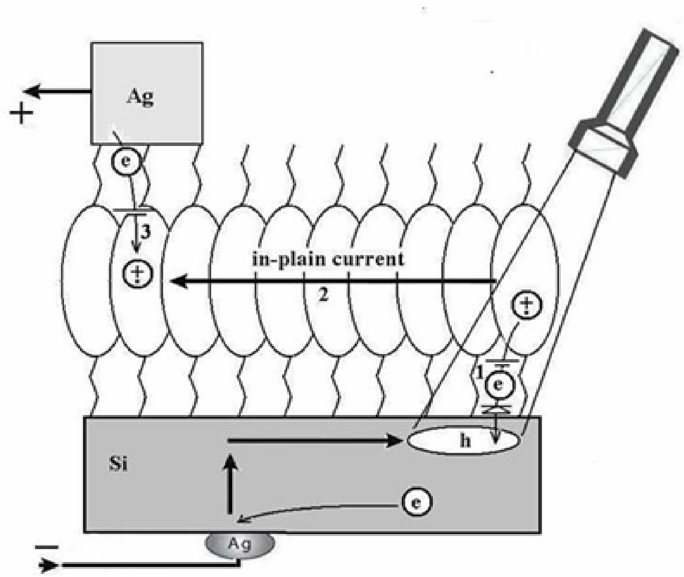
Redox Analogy of DNA Redox analog to NTCDI molecule



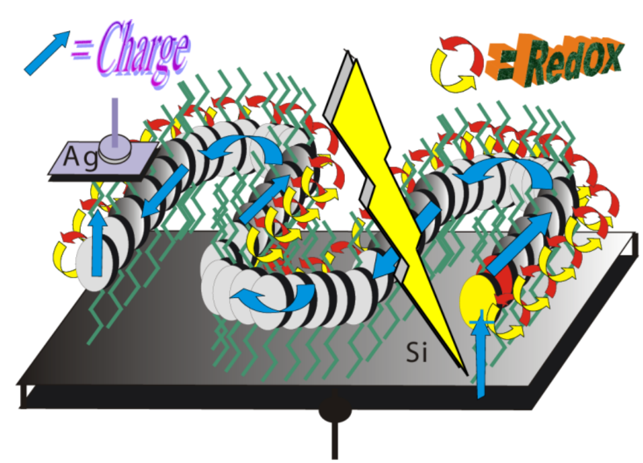
DNA Redox analog to NTCDI molecule. These radicals resemble those in protein and DNA molecules and combine essential structural motifs of the oxidized forms of two ubiquitous redox cofactors: NAD+ and semiquinone. These features ease oxidation of neutral molecules.

4. Experimental Results: Transport studies in NTCDI Molecular π-stack

Time-resolved photo-response in molecular π-stack



Operation of the SAM-PVC. Incident light creates holes (h) in the valence band of silicon. Upon ejection of electrons (reaction 1) from the immobilized molecules into the holes, cation radicals are formed. Cation radicals rapidly exchange with the neutral molecules (2); the positive charge travels through the film, resulting in the in-plain current. Reduction of cation radicals by silver (3) completes the photovoltaic element.



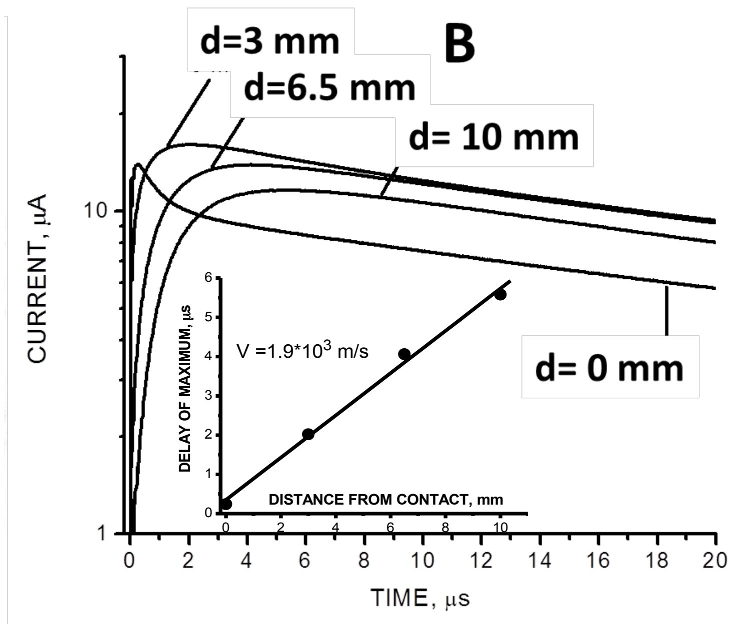
RedOx reactions

1. Si* + NTCDI $\longrightarrow$ (Si$^-$) + (NTCDI$^+$) : photo-oxidation
2. (NTCDI$^+$) + NTCDI $\longrightarrow$ NTCDI + (NTCDI$^+$) : dark self-exchange
3. (NTCDI$^+$) + Ag $\longrightarrow$ NTCDI + Ag+ : dark charge harvesting

4. Experimental Results: Transport studies in NTCDI Molecular π-stack

Kinetics and Redox role in photo-response

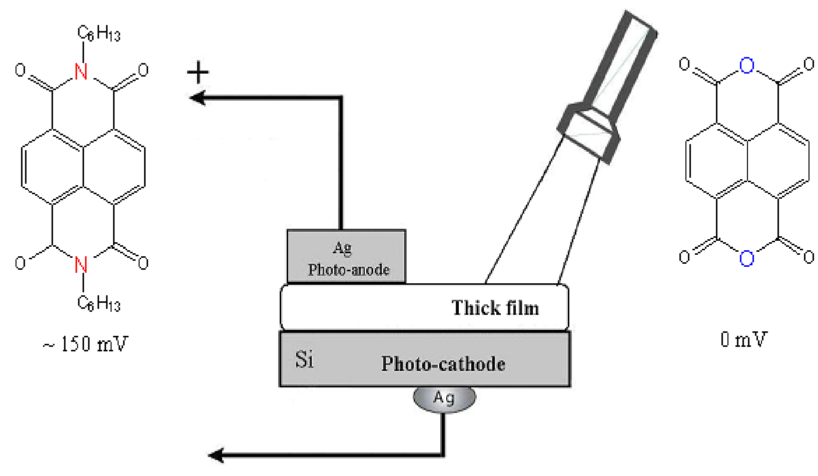
Velocity of electronic wave in MLE NTCDI π-aggregates



B) Kinetic of photoresponse at different d.

The dependency of the $T_{1/2}$ of the voltage rise on the distance l between the bright spot and the silver photoanode. The solid line approximates the points by a parabola $T_{1/2}=l^2/D$ with the parameter $D \sim 10^6\ cm^2/s$.

Role of RedOx in MLE NTCDI π-aggregates

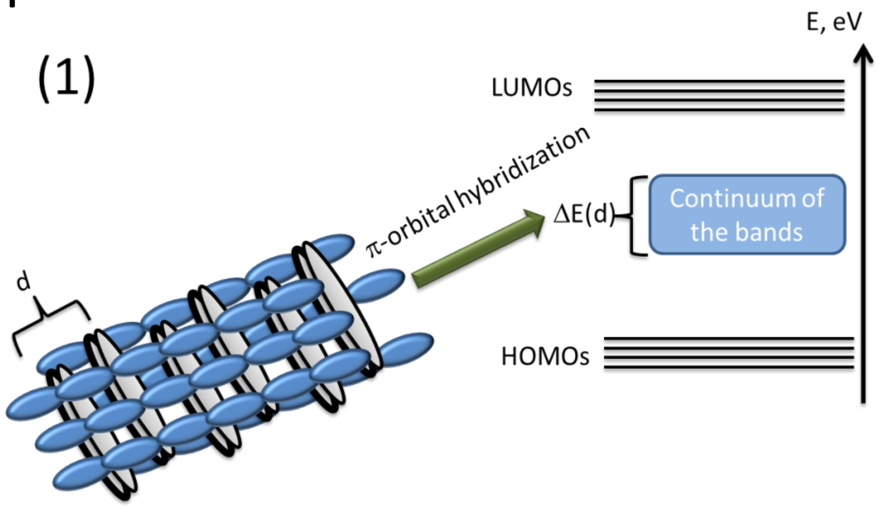


Light harvesting in thick films: molecular redox. Only film composed of C6-NTCDI-C6 molecule, which contains a nitrogen atom (red color on the left panel), was active in long-range harvesting. NTCDA molecule with unsubstantiated oxygen (blue color on the right panel) could not sustain any long-range redox transport. We took this fact as evidence of polaron transport in latent channel in SAM devices.

5. Discussion of Experimental results and Generalized Charge Transfer Model for Molecular π-stack

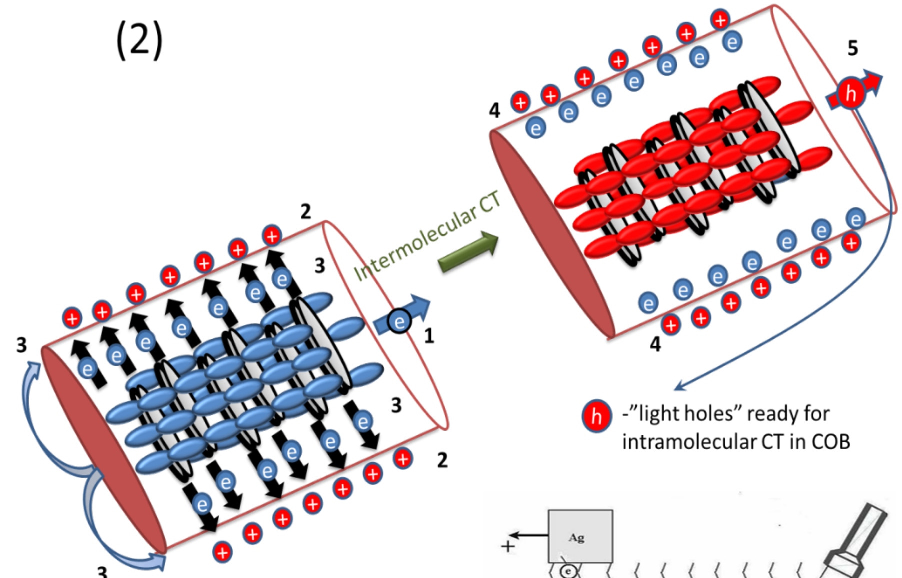
1. Formation of Continuum of Bands” (COB) or “states-in-the-gap”

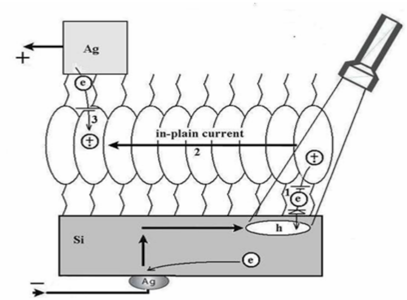
(1)



2. Role of intermolecular and intramolecular CT

(2)





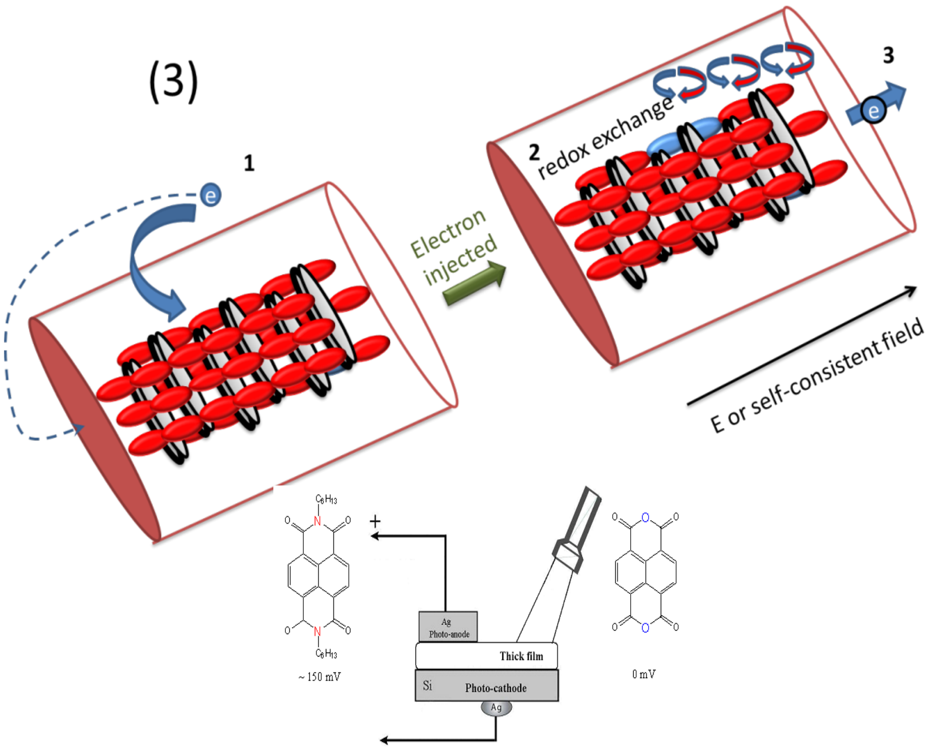
COB concept-Vladimir BURTMAN and Zeev Valy VARDENY, 2008, Design and Characterization of Novel Systems for Molecular Nanoscale Self-Assembly, Japanese Journal of Applied Physics, Vol. 47, No. 2, 2008, pp. 1165–1172

Dmitry Zaslavsky, Andrei Pakoulev, and Vladimir Burtman, Free-Energy-Driven Transfer of Charge in Dense Electrochemically Active Monomolecular Films 2004, JPCB, 108, 15815-15819.

5. Discussion of Experimental results and Generalized Charge Transfer Model for Molecular π-stack

3. Initiation of redox transport

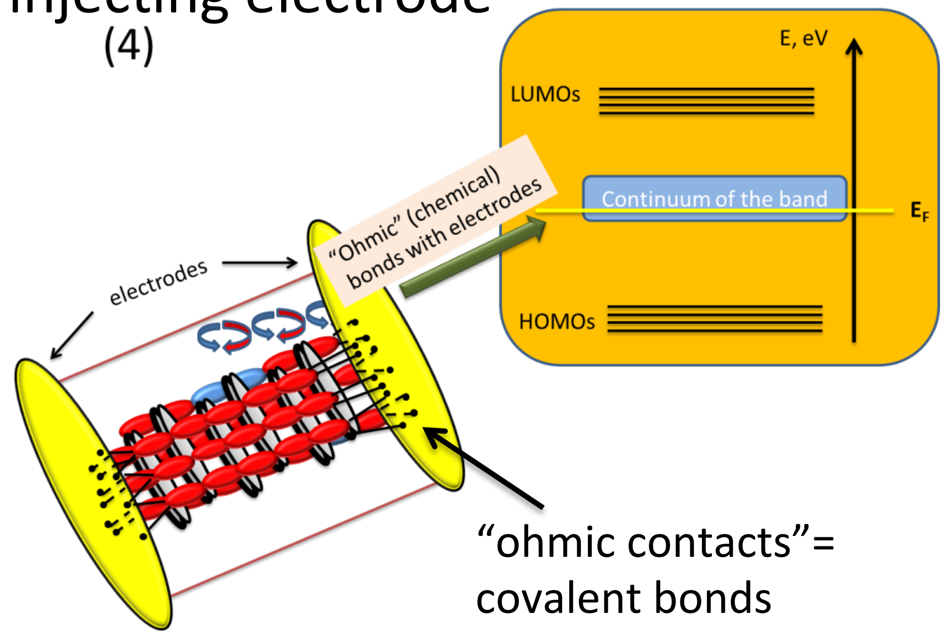
(3)



Dmitry Zaslavsky, Andrei Pakoulev, and Vladimir Burtman, Free-Energy-Driven Transfer of Charge in Dense Electrochemically Active Monomolecular Films 2004, JPCB, 108, 15815-15819.

4. Position of E_F vs COB: role of injecting electrode

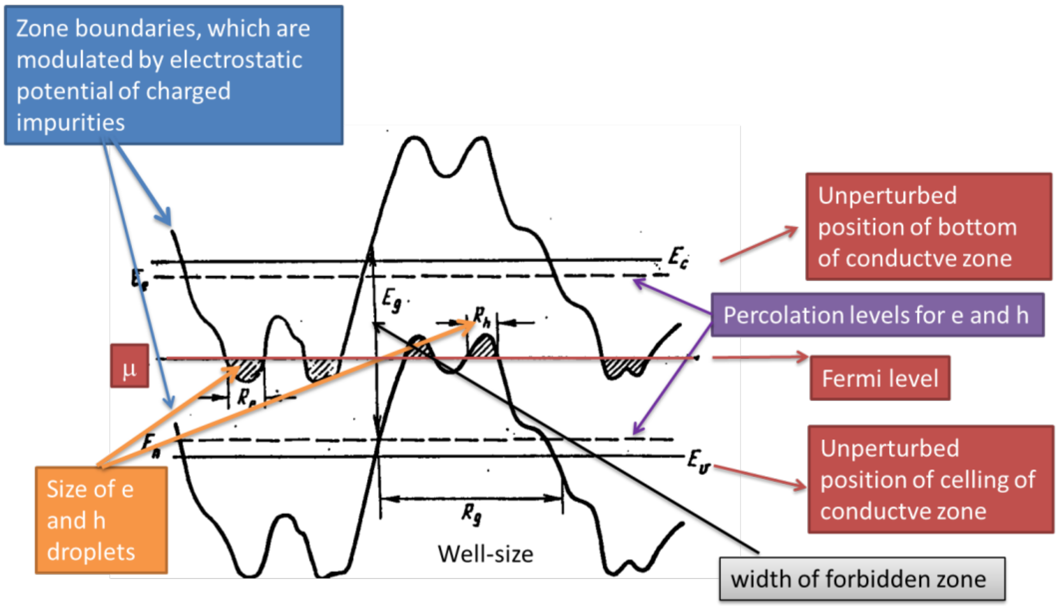
(4)



COB concept-Vladimir BURTMAN and Zeev Valy VARDENY, 2008, Design and Characterization of Novel Systems for Molecular Nanoscale Self-Assembly, Japanese Journal of Applied Physics, Vol. 47, No. 2, 2008, pp. 1165–1172

6. Theory: Notes on Model of Transport in Molecular Aromatic π-stack and Generalization on DNA case

Shklovsky-Efros Model of Fully Compensated Semiconductor



Screening in-gap Efros-Shklovsky potential (in COB) in π-aggregates

- **The number of electrons** in the wells is limited not only by **impurity** charge (here: number of π-electrons in monomer, dimer, trimer etc.) **but by Pauli principle** as well

-The large scale fluctuations that convert the intrinsic semiconductor to system, **which is similar to semi-metal**

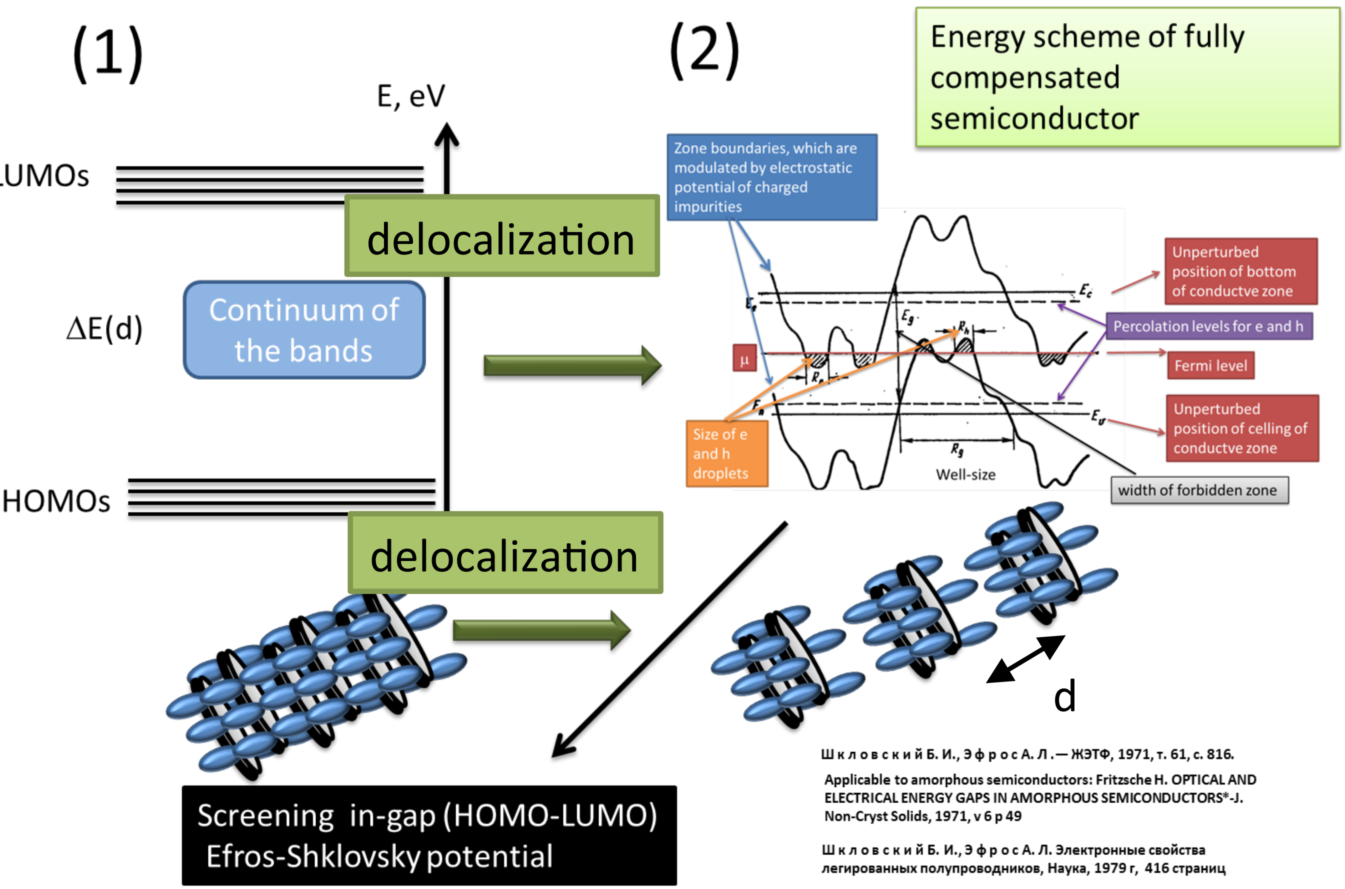
- There is a considerable density of electron states in forbidden zone. However the width of forbidden zone is close to Eg due to "smoothness" of "local potential"

Ш к л о в с к и й Б. И., Э ф р о с А. Л. Электронные свойства легированных полупроводников, Наука, 1979 г, 416 страниц

Applicable to amorphous semiconductors: Fritzsche H. OPTICAL AND ELECTRICAL ENERGY GAPS IN AMORPHOUS SEMICONDUCTORS*-J. Non-Cryst Solids, 1971, v 6 p 49

6. Theory: Notes on Model of Transport in Molecular Aromatic π-stack and Generalization on DNA case

Transition in molecular stack aggregate - to molecular dimer (COB to states DOS in the gap): Anderson's oscillations in Efros-Shklovsky model



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Applicable to amorphous semiconductors: Fritzsche H. OPTICAL AND ELECTRICAL ENERGY GAPS IN AMORPHOUS SEMICONDUCTORS*-J. Non-Cryst Solids, 1971, v 6 p 49

Ш к л о в с к и й Б. И., Э ф р о с А. Л. Электронные свойства легированных полупроводников, Наука, 1979 г, 416 страниц

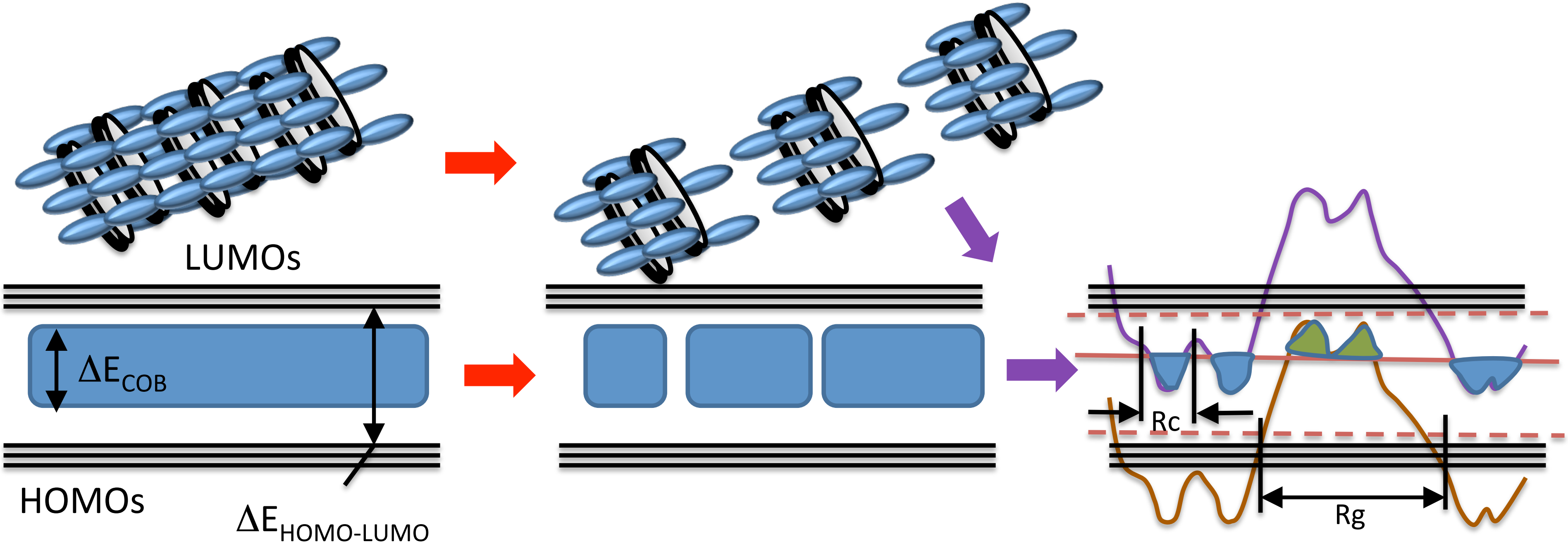
-induces electron screening barrier below spatial vacuum barrier

-therefore the σ(d) dependence can be sharper then for $\pi-\pi$ interplane tunneling

-effect is in delicate interplay between Anderson delocalization and Mott phenomena

6. Theory: Notes on Model of Transport in Molecular Aromatic π-stack and Generalization on DNA case

Molecular stack aggregate - to molecular dimer transition in Efros-Schklovsky model



percolation levels for e and h

Fermi energy, E_F

unperturbed positions of LUMOs and HOMOs

band boundaries, which are modified by electrostatic potential of clustered π-electrons

Rc - size of e and h “droplets” in π-stack

Rg - well size

delocalization

changes due to delocalization

6. Theory: Notes on Model of Transport in Molecular Aromatic π-stack and Generalization on DNA case

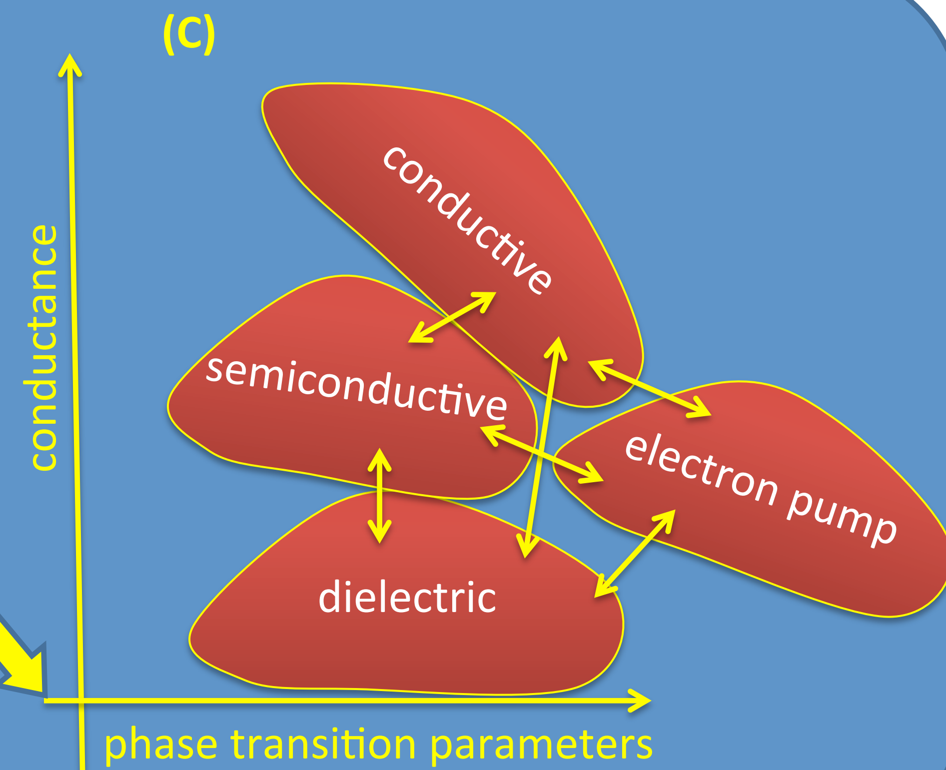
Phase Transitions in Molecular π-stack

(A) Phase transition phenomena:

1) Charge delocalization in π-staking
2) Strength of intermolecular CT
3) Redox
4) Proximity of contacts conductance to ohmic
5) Cooperative dynamics of polarization-CT phenomena
6) Dimensional transitions

(B) Phase transition parameters:

1) Molecular inter- and intra- dynamic
2) Temperature
3) Molecular electrostatics
4) Chemical environment
5) Charge excitations, redox and relaxations efficiency and dynamic



7. Conclusion

Model of CT in π-stack:

1. We introduce a new QM approach to transport in organics, including DNA and π-stack (relies on Anderson localization, Mott transitions and Efros-Shklovsky in-gap phenomena)

2. Addresses the question on how to achieve high charge mobility in organics

3. Explains phase transition in DNA and π-stack, explains how “molecular pump” is working

4. Explains enormous possibilities to manipulate mobility of charges in Molecular Nanoelectronics and Biology

5. DNA heterogeneity still has to be accounted

Thanks!

Do you like to know more on Molecular Layer Epitaxy Method?

10:00 am – 10:30 am	Tatiana Kopylova, Tomsk State University, Tomsk, Russia, Molecular Layer Epitaxy Method for Molecular Nanoelectronics (September 22, Friday, Morning Fabrication of Nanostructured Materials and Devices I Chairs: Damir Islamov and Alexey Kovalgin)