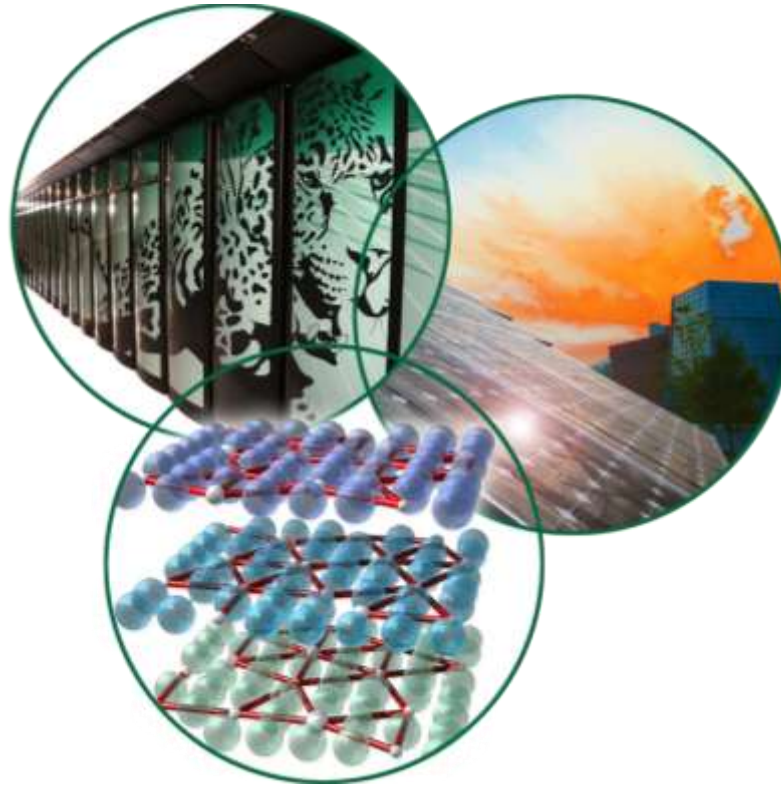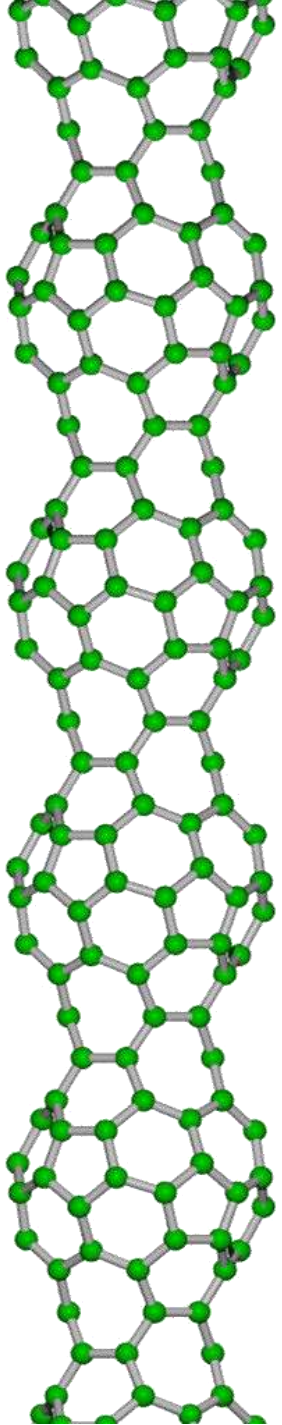# Energy Storage and Conversion: How can Theory, Modeling, and Simulation Help?

Bobby G. Sumpter
Nanomaterials Theory Institute
Center for Nanophase Materials Sciences
and
Computational Materials Science Group
Computer Science and Mathematics Division
Oak Ridge National Laboratory

1

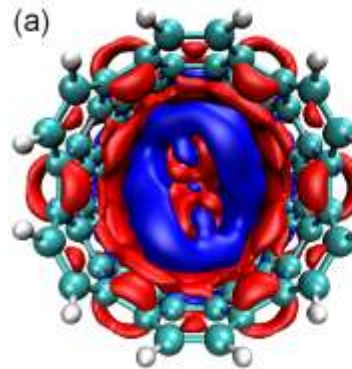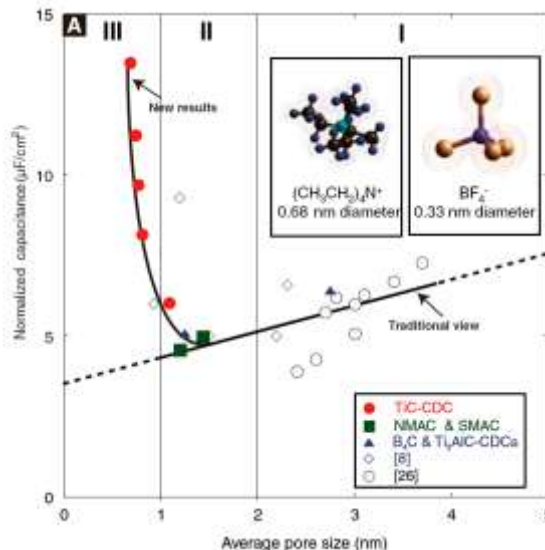# Funding and Collaborations

Computer Support:

- **NCCS/LCF**
- **ORNL CNMS& CSMD**
- **NERSC**

SciDAC
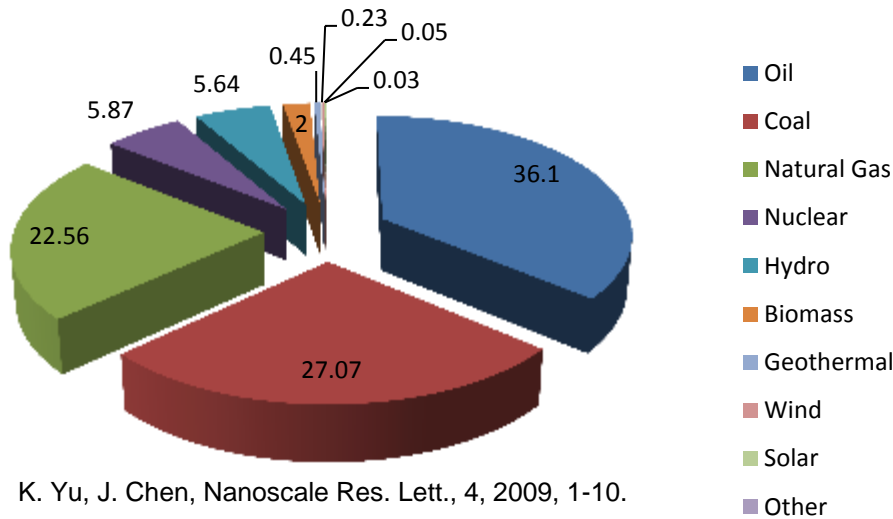Scientific Discovery through Advanced Computing

ENERGY APPITITE! *There is a projected doubling of world energy consumption within the next 50 years*

- **Desperate need for low- or even zero-emission sources of energy**

- **Energy based on electricity that can be generated from renewable sources, such as solar or wind, offers enormous potential for meeting future energy demands: *grand challenge***
  - **The use of electricity generated from these intermittent,**
  - **renewable sources requires efficient electrical energy storage.**

Energy conversion, storage, transmission
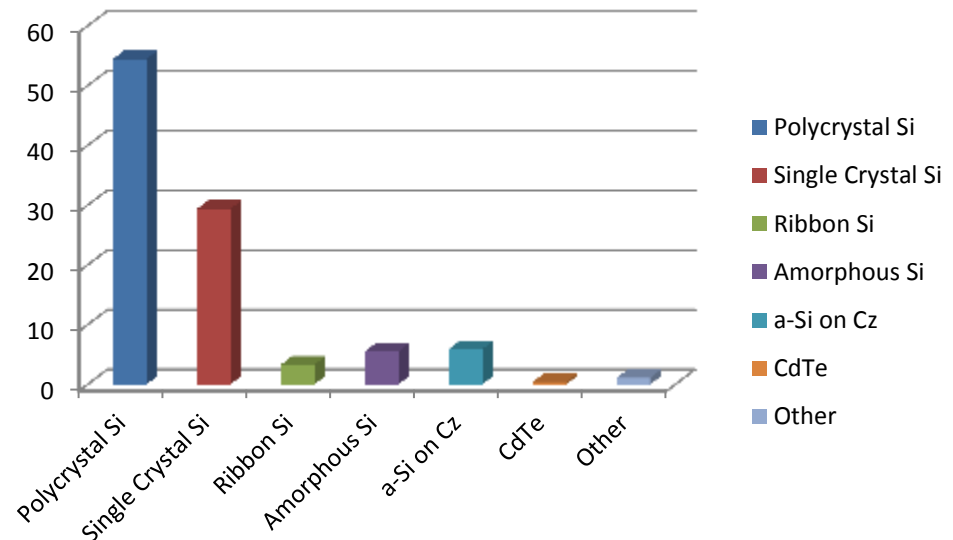
World Energy Consumption by Type

Pie chart legend: Oil, Coal, Natural Gas, Nuclear, Hydro, Biomass, Geothermal, Wind, Solar, Other

Values shown on pie: 36.1, 27.07, 22.56, 5.87, 5.64, 2, 0.45, 0.23, 0.05, 0.03

K. Yu, J. Chen, Nanoscale Res. Lett., 4, 2009, 1-10.

85.7% of worldwide energy consumption is from fossil fuels.

Type of Cell	Commercial Efficiency	Lab Efficiency
Wafer Silicon	**12%-18%**	**25%**
Film Silicon, c	**5%-6%**	**10%**
Film Silicon, a	**5%-8%**	**13%**
CdTe	**>9%**	**16.5%**
CIGS	**5-11%**	**19.5%**
Organic	**-**	**5.2%**
DSSC	**5-7%**	**11%**

Solar Energy Market, 2002

Bar chart legend: Polycrystal Si, Single Crystal Si, Ribbon Si, Amorphous Si, a-Si on Cz, CdTe, Other

A. Goetzberger, V.U. Hoffmann, *Photovoltaic Solar Energy Generation*, Springer

The Promise of Solar Energy
(interpreted via a technology that became common at the start of the 20th century)

Big, Fast, and Efficient??
(large area, low-cost, efficient)

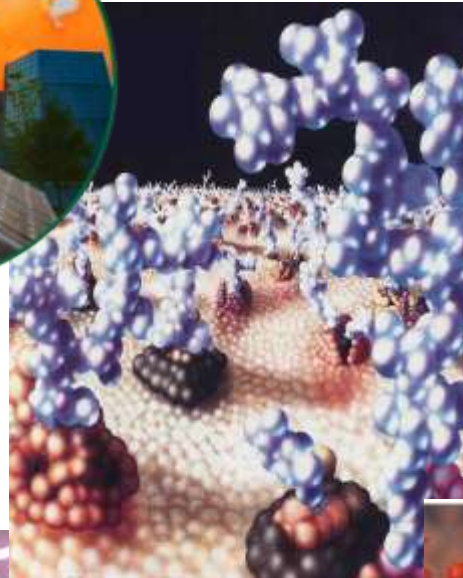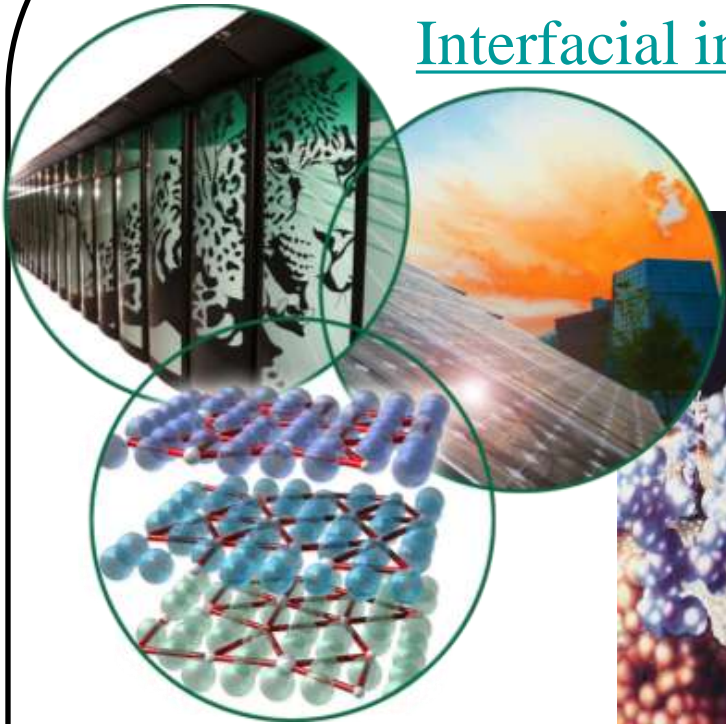Depends on economics and energy balance over life of device

$$\eta = V_{oc} \, j_{sc} \, FF$$

Focus on fundamental science using a system where interfaces and morphology are tunable
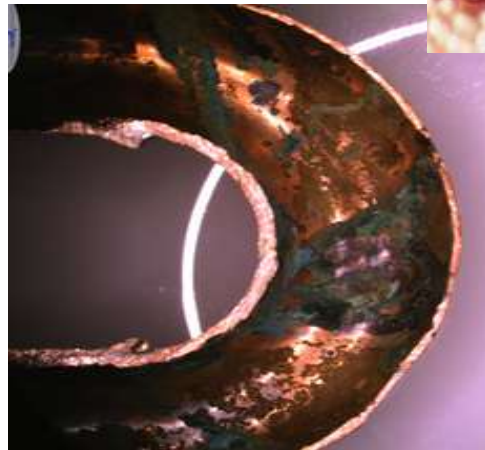
Importance of Fundamental Interactions

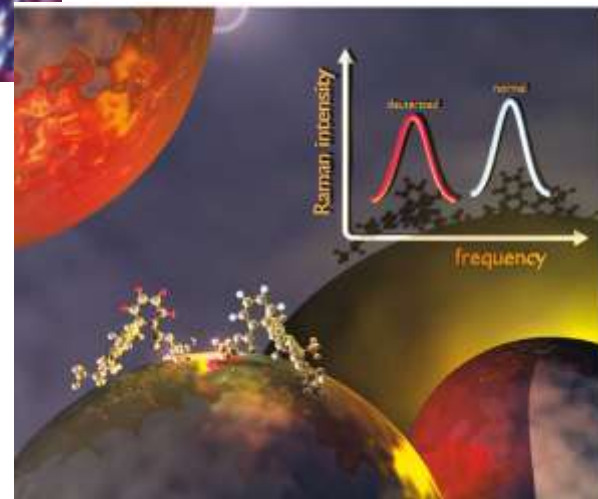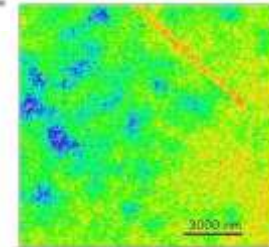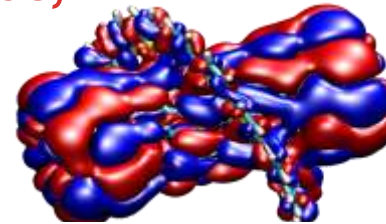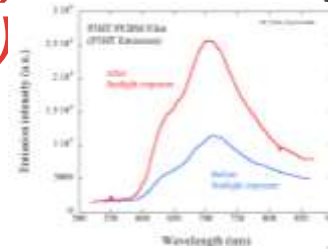Interfacial interactions are important to:
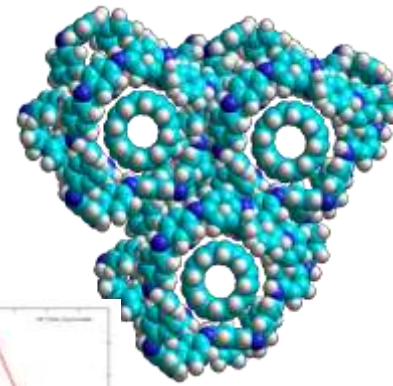

Heterogeneous Catalysis
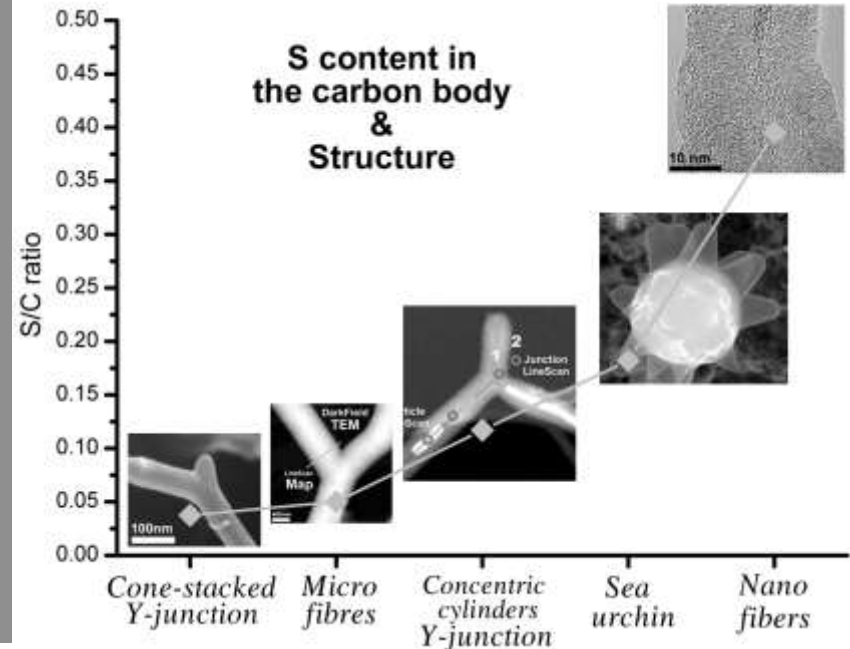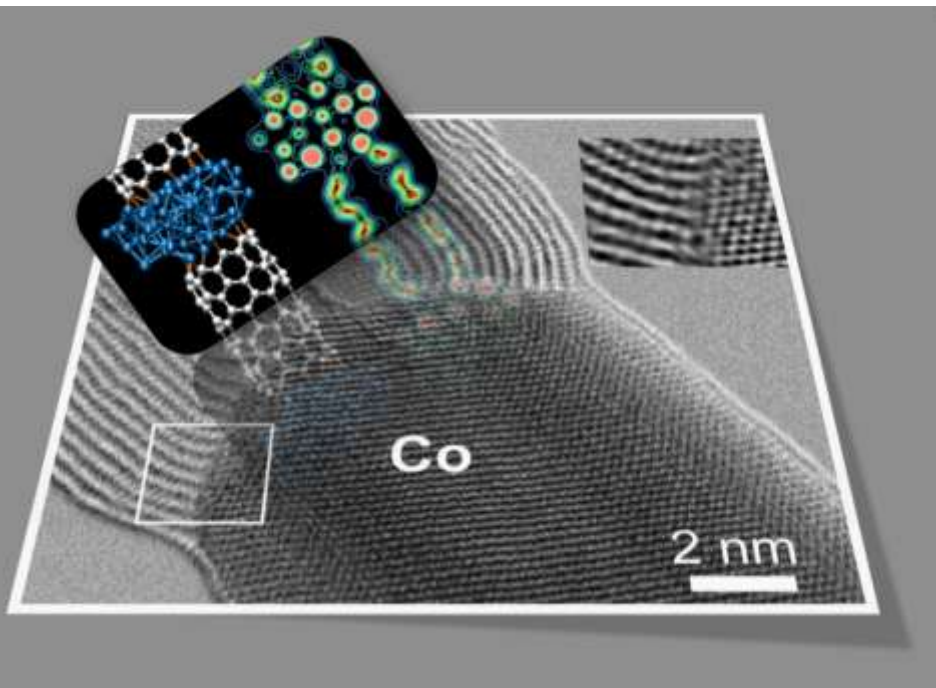
Adhesion

Corrosion

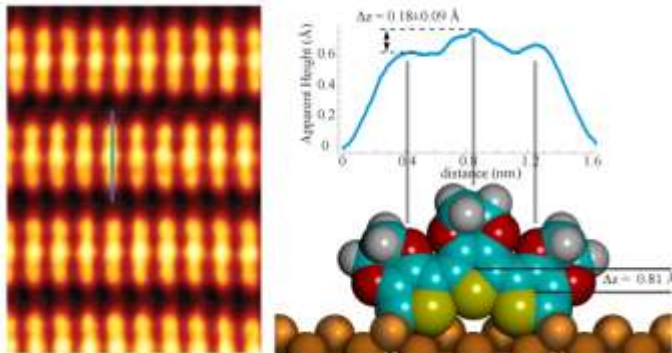Sensors

Some Research Topics

- Nanoscale self-assembly and organization:

  - *Surface confinement (gas deposition/storage)*
  - *Heterojunction interfaces (network assembly)*
  - *Tuning/controlling nanostructure (E-storage, composites, electronics, catalysis)*
  - *Polymer nanocomposites (solid electrolytes, photovoltaics)*
  - Nano-bio interactions (conjugate materials)

S content in the carbon body & Structure

Co

2 nm

S/C ratio

| Cone-stacked Y-junction | Micro fibres | Concentric cylinders Y-junction | Sea urchin | Nano fibers |

$$H\psi\left(r_1, r_2 \dots r_n\right) = E\psi\left(r_1, r_2 \dots r_n\right)$$

Computational nanoscience is a branch/intersection of chemistry, physics, biology and materials science that uses principles of computer science and mathematics and the results of theoretical physics and chemistry to assist in solving materials problems.

i.e., Fundamental equations are incorporated into efficient computer programs, to calculate the structures and properties of molecules and solids. While its results normally complement the information obtained by experiments, it can in some cases predict unobserved and emergent phenomena.

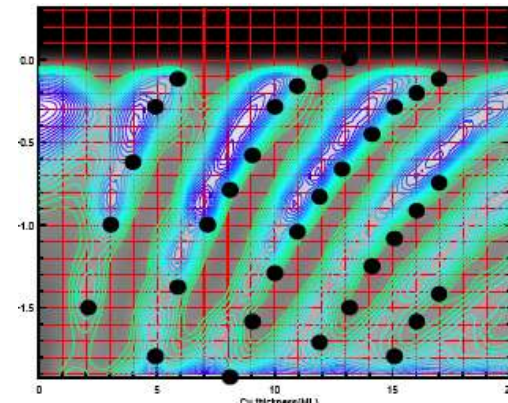$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_0}$$

$$\nabla \cdot \mathbf{B} = 0$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{J} + \mu_0 \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t}$$
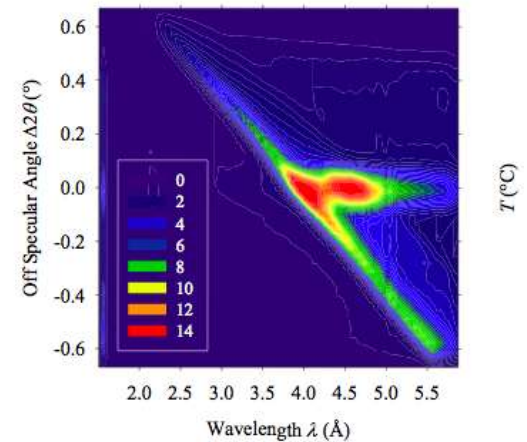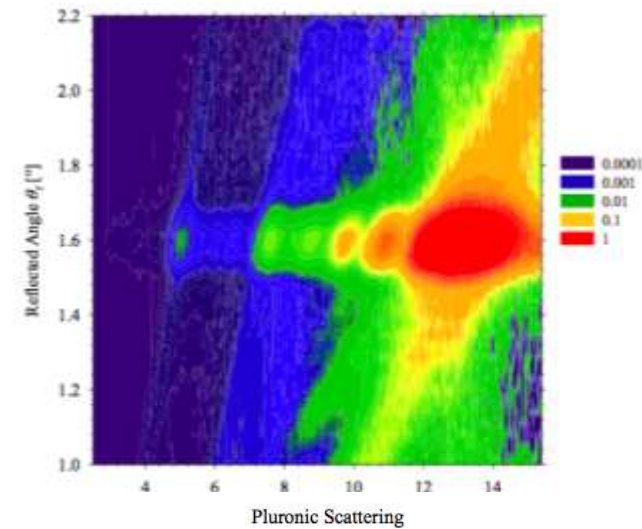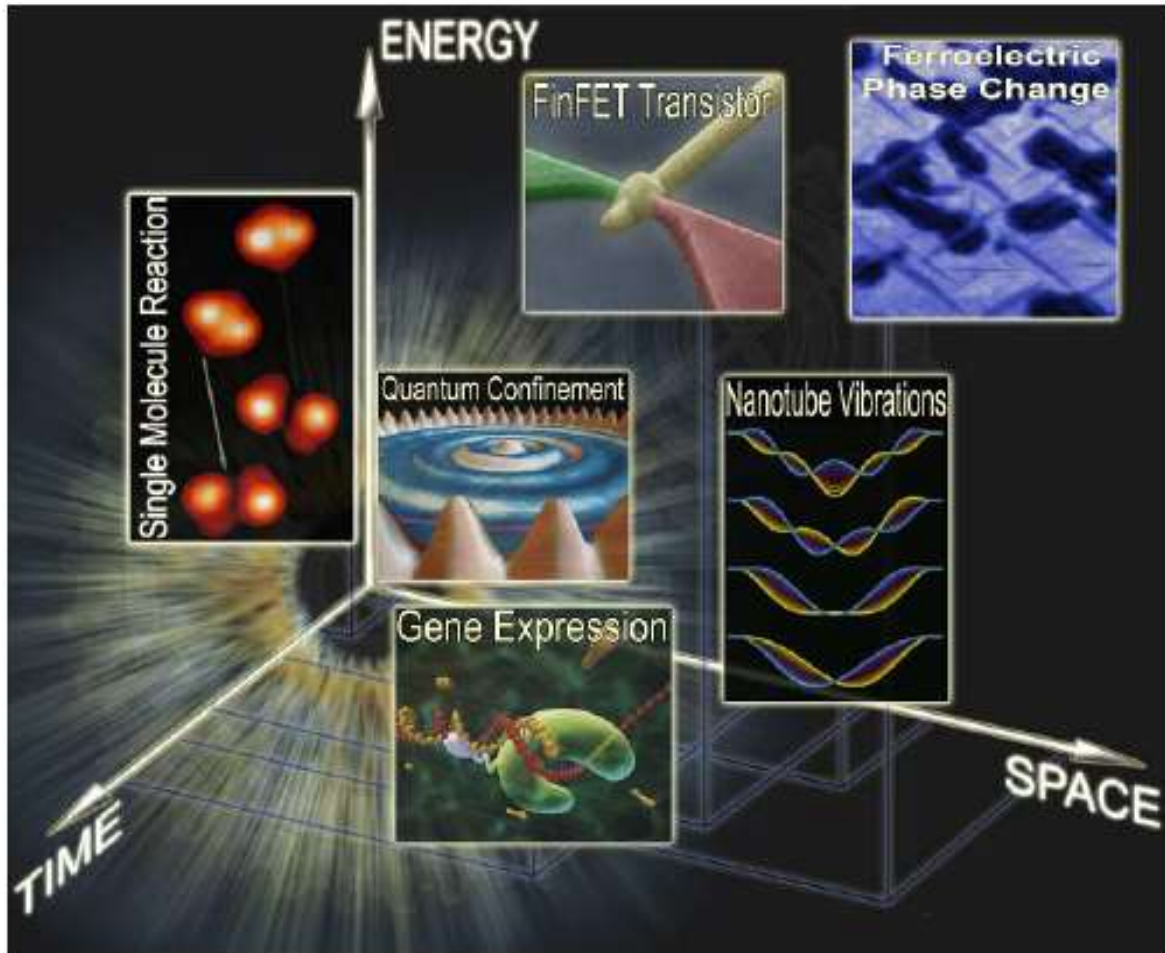
$$F = -\frac{\partial E}{\partial r}$$

$$F = m\ddot{r}$$

Seeing is the beginning of understanding

The power of science to describe and explain the universe around us begins with observation, leading through hypothesis and experiment/simulation to physical laws and theoretical models.

Theory, Modeling, Simulation, and Experiment at the Nanoscale

Chemistry
Organic, inorganic, analytical biochemistry

Materials Science

Ceramics, Nanoclusters, Conducting polymers, Composites, oxides, metals

Supramolecular chemistry

physical

Biosciences

Proteins,Nucleic acids, DNA,Compartments, organelles
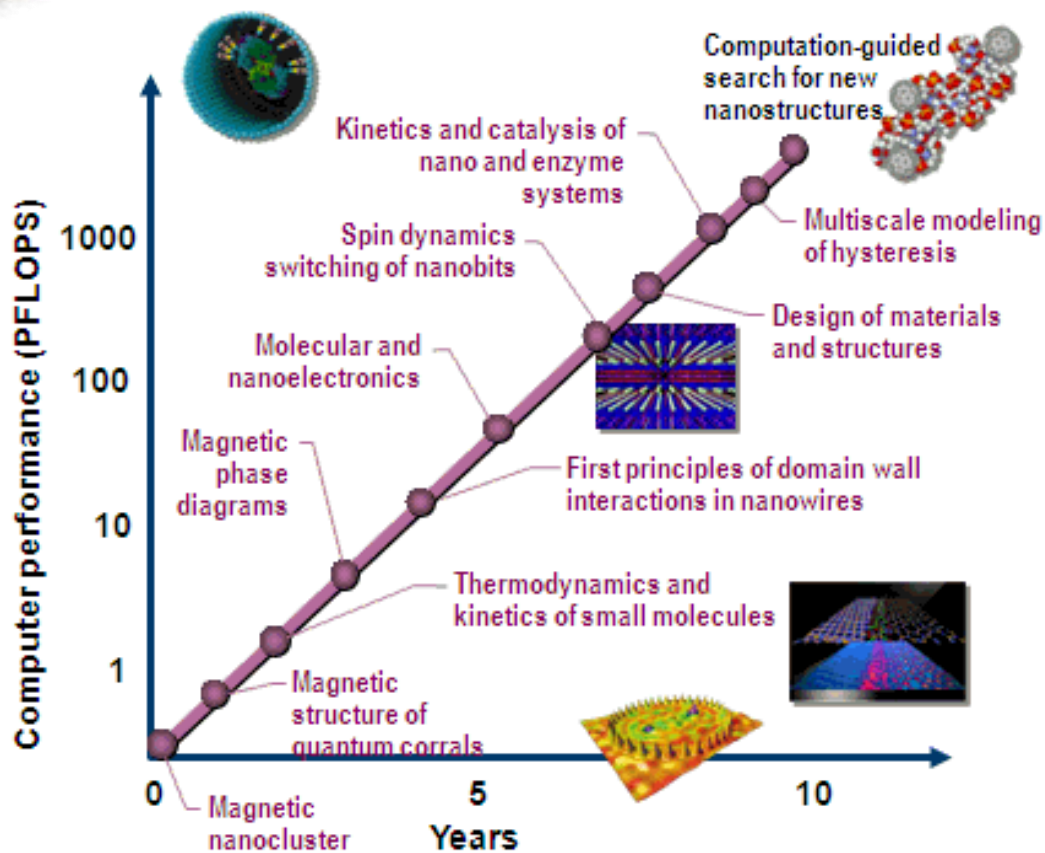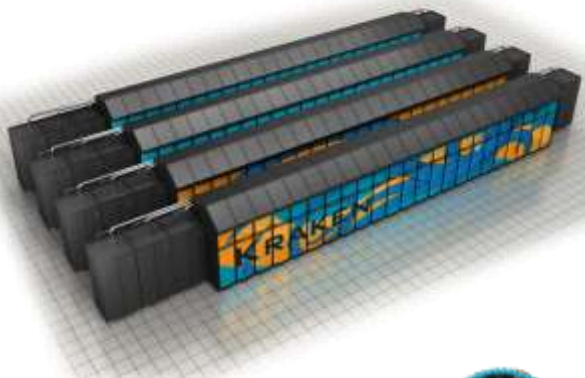
Physics
Solid state Condensed matter

Future Devices
Sensing, manipulation, Catalysis, Molecular (nano) electronics and optics, Molecular medicine, prosthetics, energy conversion and storage materials
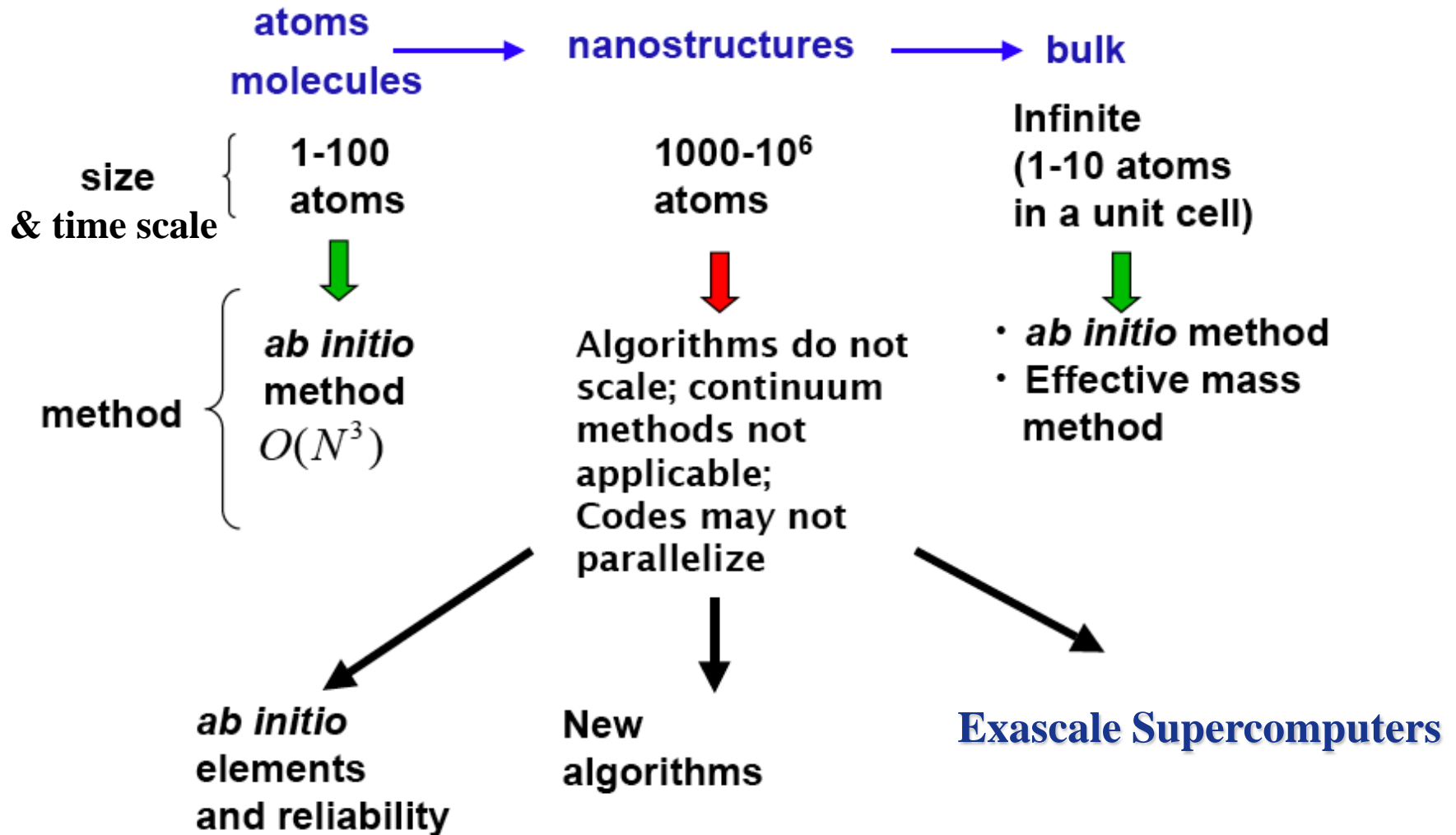
Understanding of the physics and chemistry

# 1000x performance increase in last 5 years, projected 1000x in next 10

Challenge for computational nanoscience

atoms molecules $\rightarrow$ nanostructures $\rightarrow$ bulk

size & time scale

- **1-100 atoms**
- **1000-10⁶ atoms** — **1000-10^6 atoms**
- **Infinite (1-10 atoms in a unit cell)**

method

ab initio method $O(N^3)$

Algorithms do not scale; continuum methods not applicable; Codes may not parallelize

- *ab initio* method
- Effective mass method

ab initio elements and reliability

New algorithms

Exascale Supercomputers

Calculations based on many-body theory: CC and QMC

- Outstanding 1.39 PetaFLOP/s sustained double-precision performance using the freely distributed *NWChem* electronic structure code (Apra et al., (2009))

- Performance result obtained on the full Cray XT5 machine at 60% peak FP, fully exploiting the aggregate CPU, RAM and network resources

- Self healing diffusion quantum Monte Carlo

CCSD(T) / cc-pVTZ (-f) energy
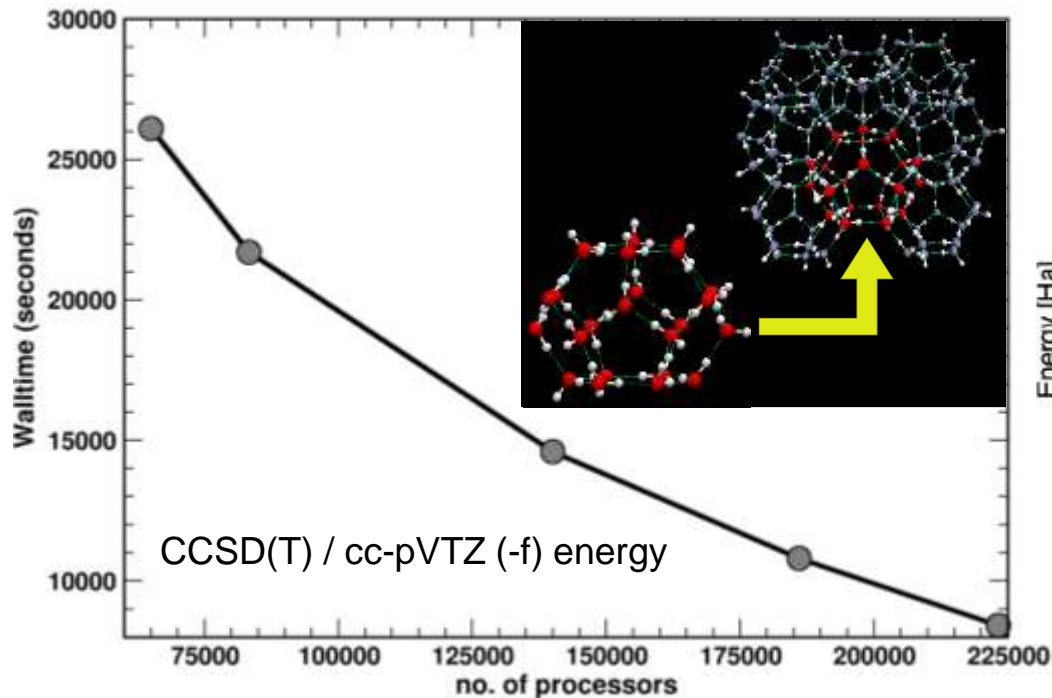
Picture: The tetrakaidecahedron $(H_2O)_{24}$ water cluster, building block of the structure I (sI) hydrate lattice

PRL104, 193001 (2010)
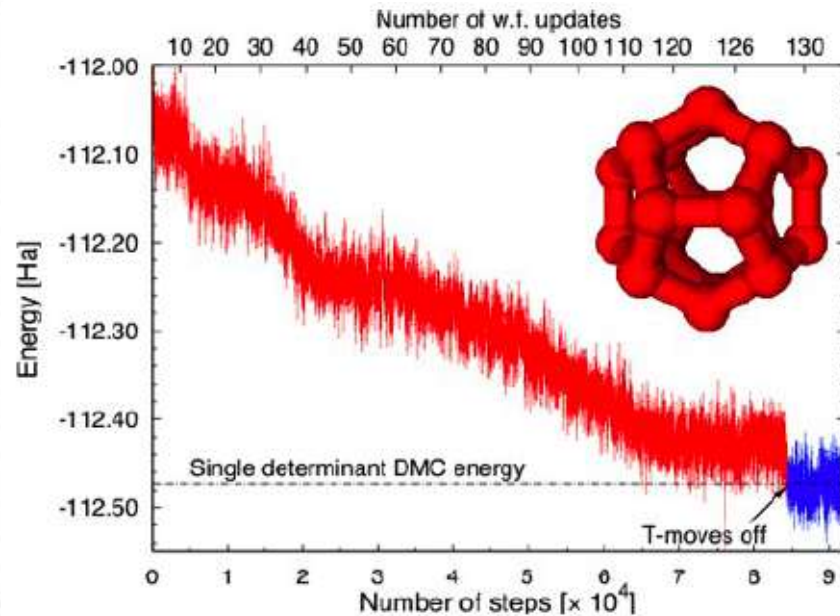
Computational Methods

- **Atomic-scale methods provide information on the structure, dynamics, and thermodynamics of the system.**
  - **Molecular dynamics (MD), mechanics (MM), Monte Carlo (MC)**
  - **Large-scale normal-mode analysis (NMA)**

- ***Ab Initio* (MB and DFT-MD) methods used to compute electronic and molecular structure, and to obtain interaction potentials, activation energies for transitions, and electronic spectra as input into MD, kinetic MC, course grain approaches.**
  - **NWChem, CPMD, MPQC, SAPT, VASP, SIESTA, QMC,** new Wavelet based methods
  - **Green function transport**

- **Mesoscale methods**
  - **SCFT, CDFT, Course grained models, analytical**

- **Heuristic methods provide complementary ways to perform efficient optimization and modeling based on experimental or simulation data**
  - **Computational neural networks, evolutionary algorithms**
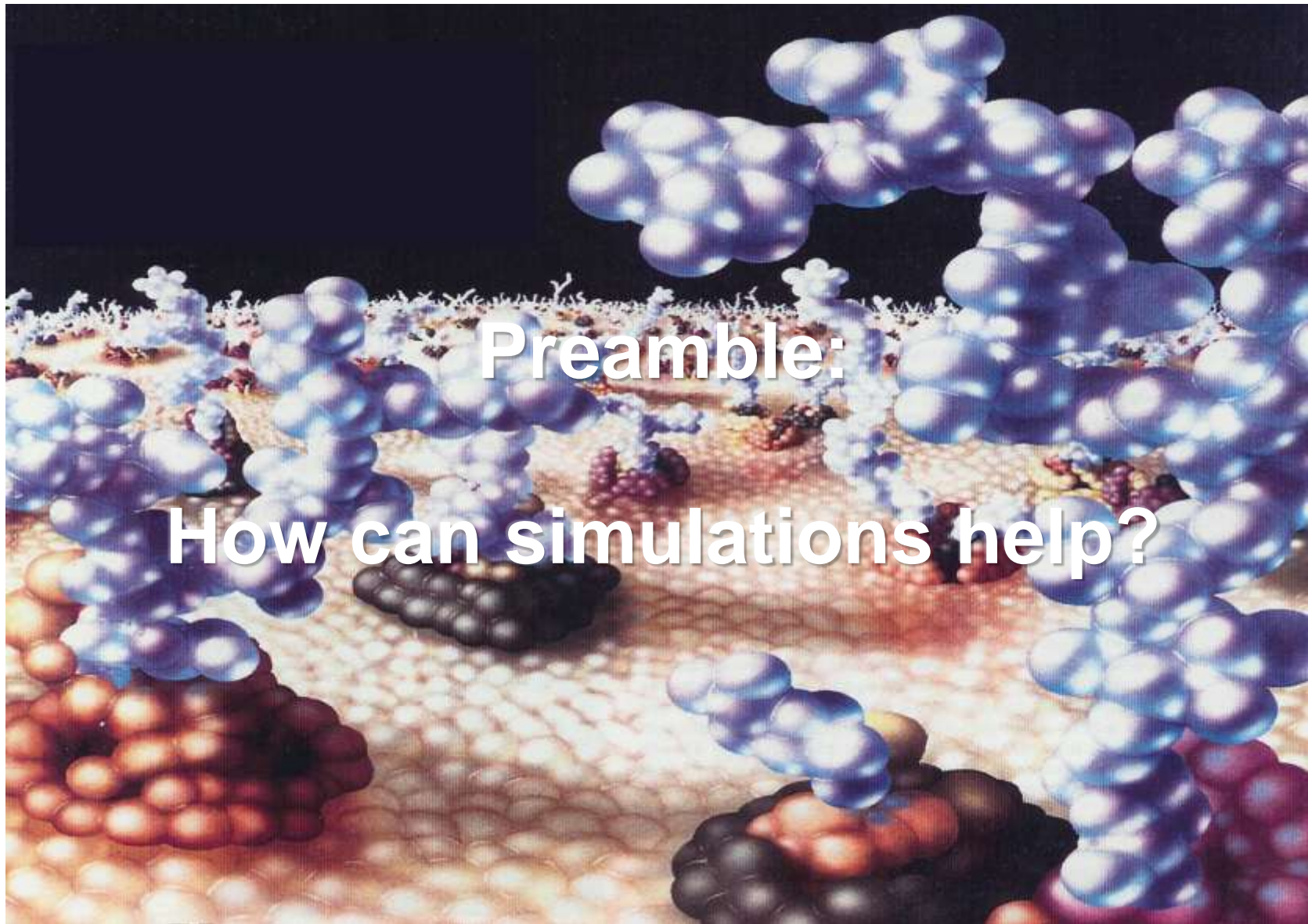
Preamble:

How can simulations help?

Using computational methods to explore structure-function relations at the nanoscale

Understand, predict, and ultimately control matter and energy at the electronic, atomic, and molecular levels: foundations for new energy technologies

Electronic transport processes on the nanoscale
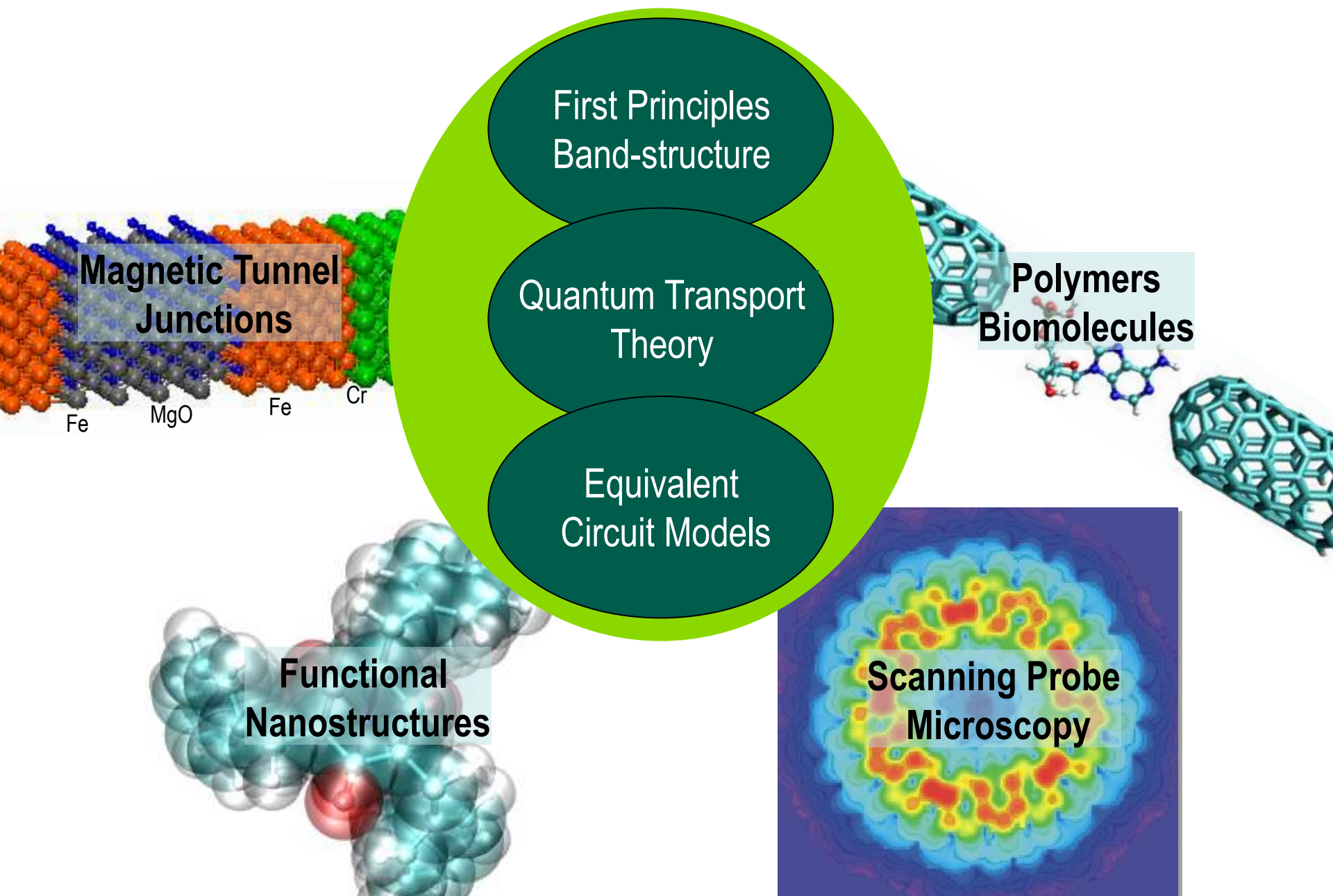
Example: Nanoscale structure and transport properties-efficient nanoelectronics?

(a) Energy (meV) vs Angle (degrees) — parallel, perpendicular

(b) Conductance (G_0) vs Energy (eV) — Pristine, Parallel, Perpendicular

(c) Current vs Voltage (V) — Parallel, Perpendicular
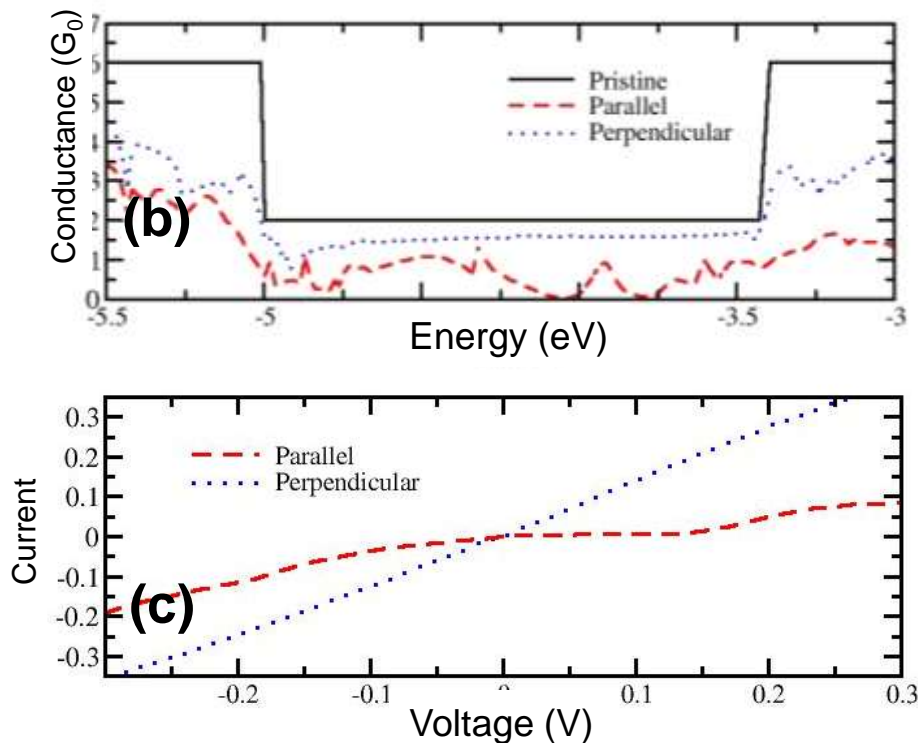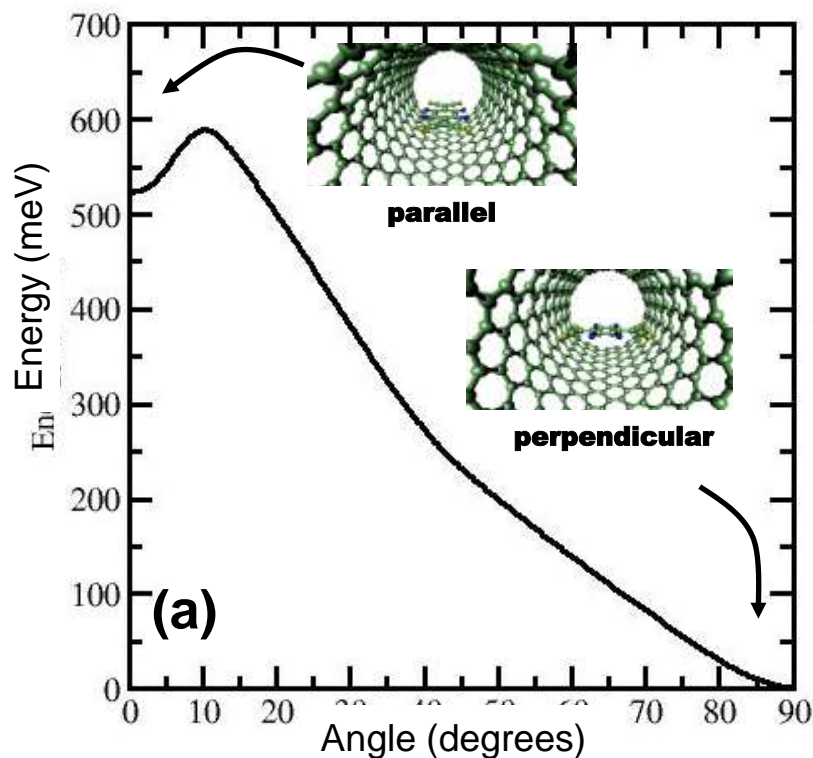
• **Electronic structure of a carbon nanotubes can be manipulated by physisorption of organic molecules: encapsulation or on the outer wall**

• **Charge transfer processes induced by encapsulated organic molecules can lead to efficient n- and p-type doping of a single-walled carbon nanotube**

•**Orientational effects ⟶ intrinsic electronic gating**

Meunier, Sumpter, et al JCP **123**, 024705 (2005); PRL **98**, 056401 (2007); IJQC **106** 3334 (2006) ; Nanotech **18**, 424032 (2007).

Summary

- Molecules can be combined with nano-materials used in various ways for the design of new electronic devices

- *Devices can be understood, modeled and designed using high level theoretical methods and analysis tools... Computationally demanding but computers don't eliminate the need for careful thinking...*

- The understanding of molecular electronics calls for a mixture of expertise from *quantum chemistry* (molecular part) to *solid state physics* (electronics part),...

Simple question – simple answer?:
Can Mo form 1D atomic chains in NTs?

Yes, but…
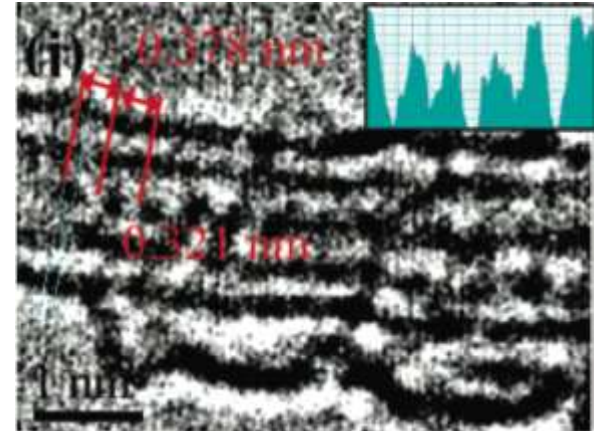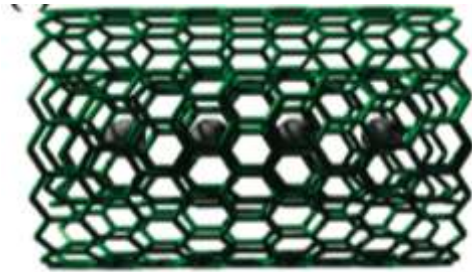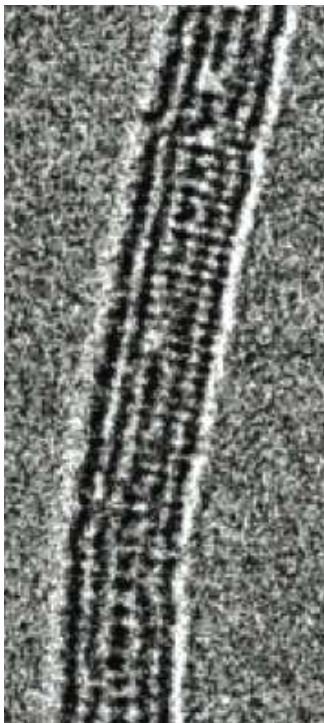
"The interatomic distance measured between Mo atoms […] ranged from 0.32 to 0.38, slightly larger than in Mo crystal (0.315 nm)"

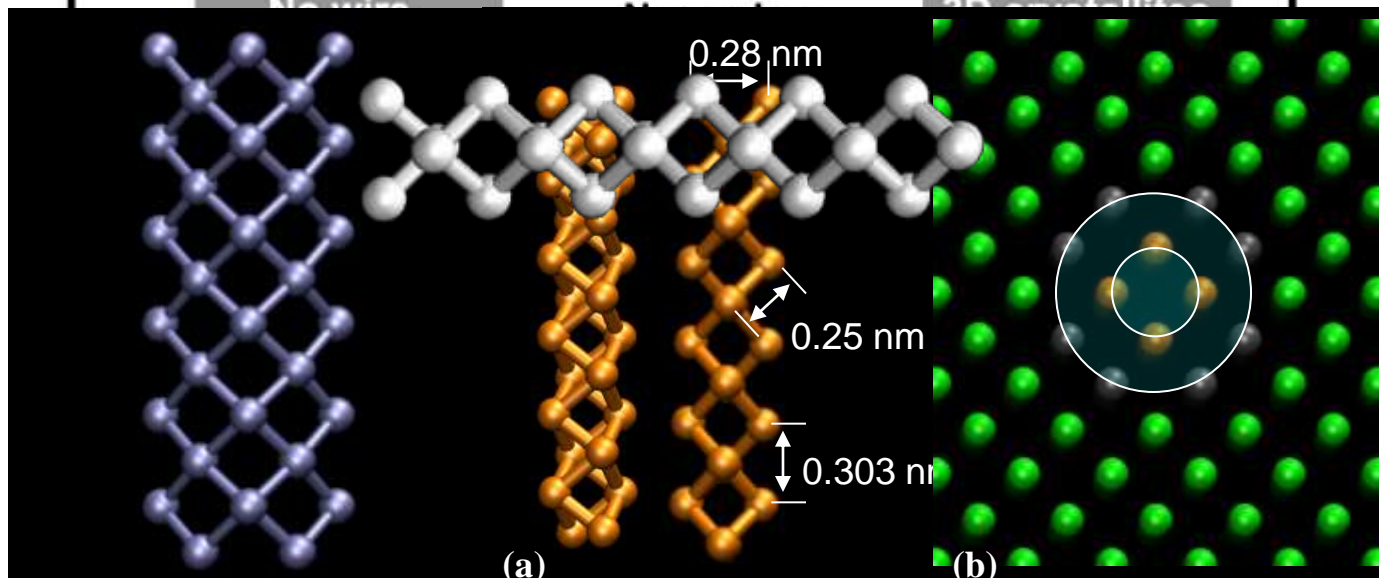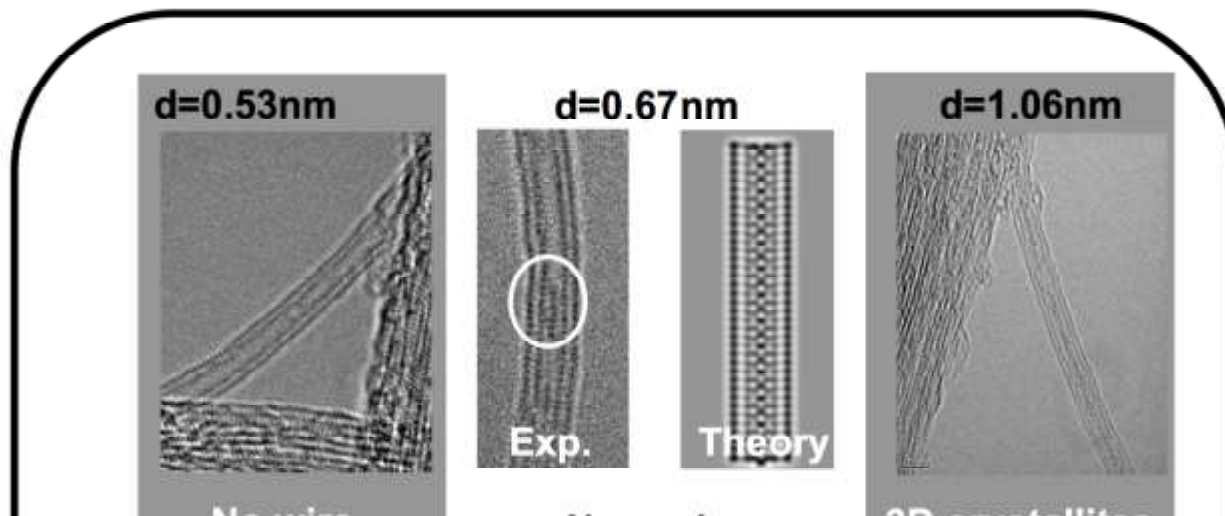**Nano Letters, 8 (1), 237 (2008)**
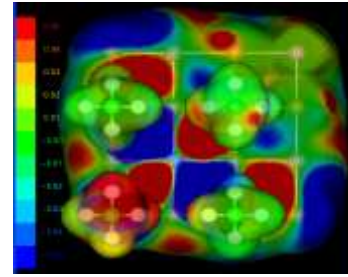
Mo element
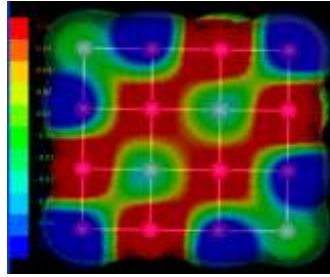
BCC (a=0.31 nm)

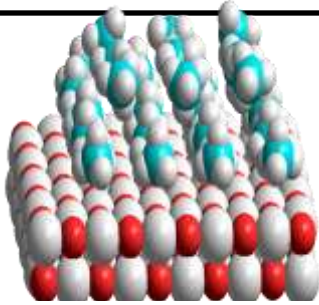**Electron configuration: [Kr] $4d^5 5s^1$**

In fact, the answer is not so simple…

(a)   (b)

How do interfacial interactions (surface-adsorbate) influence the structure/dynamics of methane?

Fundamental structure and orientation of CH_4

Stag-Rot-Rot. Rotating a methane in 15 deg increments

1st layer CH_4

2nd layer CH_4

3rd layer CH_4

10 meV, C_3V rotation
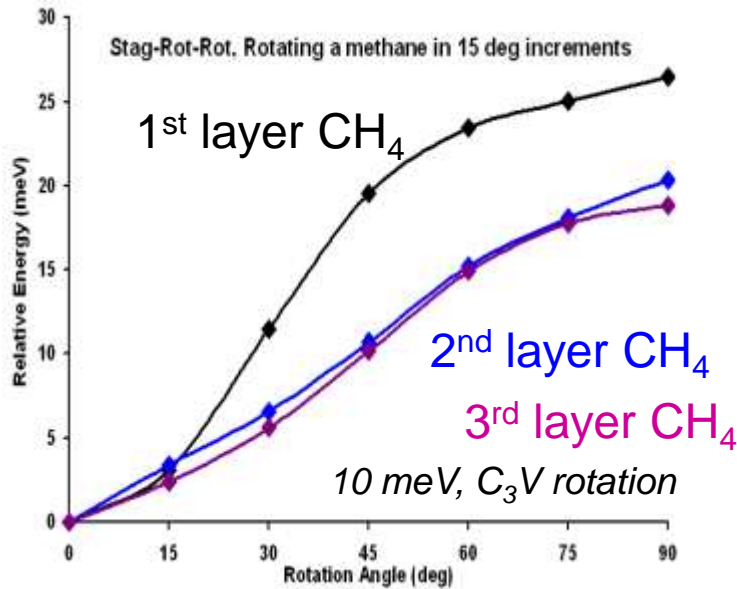
Barriers to rotation as larger numbers of layers are adsorbed

Calculated INS of CH4 Monolayer on MgO(100)

Peaks appear here as layer growth occurs

Expt

"Fingerprint" region
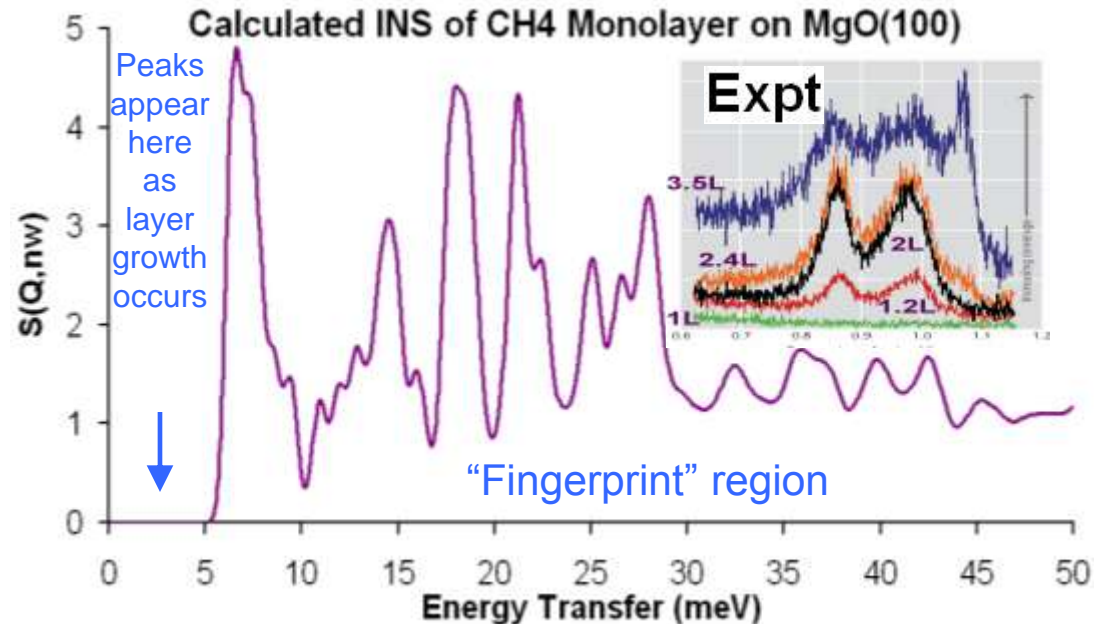
Surface-adsorbate interactions dictate 1st layer orientation; adsorbate-adsorbate 3rd

References: Phys. Rev. B. **73**, 195313 (2006); J. Phys. Chem. C. **111**, 966 (2007)

World Energy Consumption by Type

0.23
0.05
0.45
0.03
5.64
5.87
2
22.56
36.1
27.07

- Oil
- Coal
- Natural Gas
- Nuclear
- Hydro
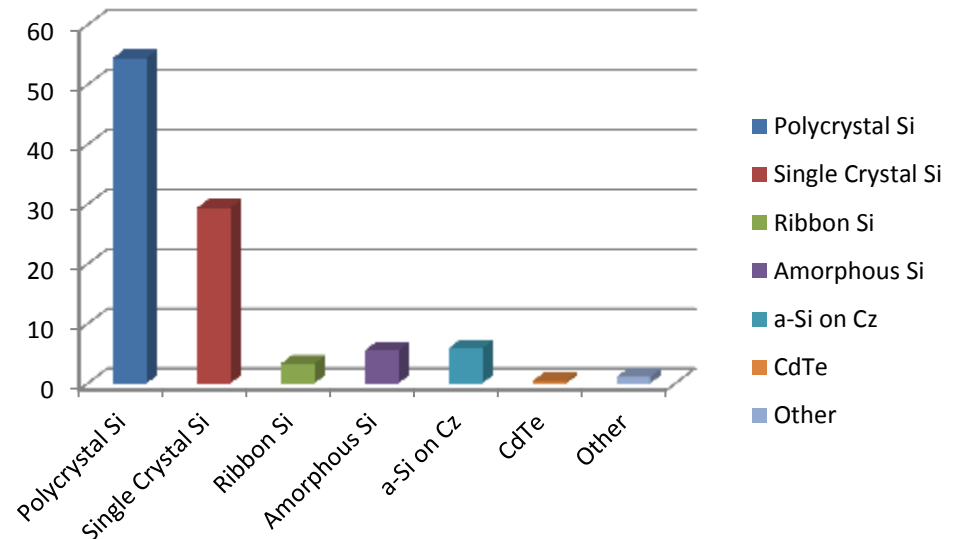- Biomass
- Geothermal
- Wind
- Solar
- Other

K. Yu, J. Chen, Nanoscale Res. Lett., 4, 2009, 1-10.

85.7% of worldwide energy consumption is from fossil fuels.

Type of Cell	Commercial Efficiency	Lab Efficiency
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DSSC	**5-7%**	**11%**

Solar Energy Market, 2002

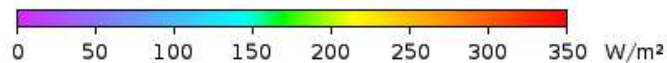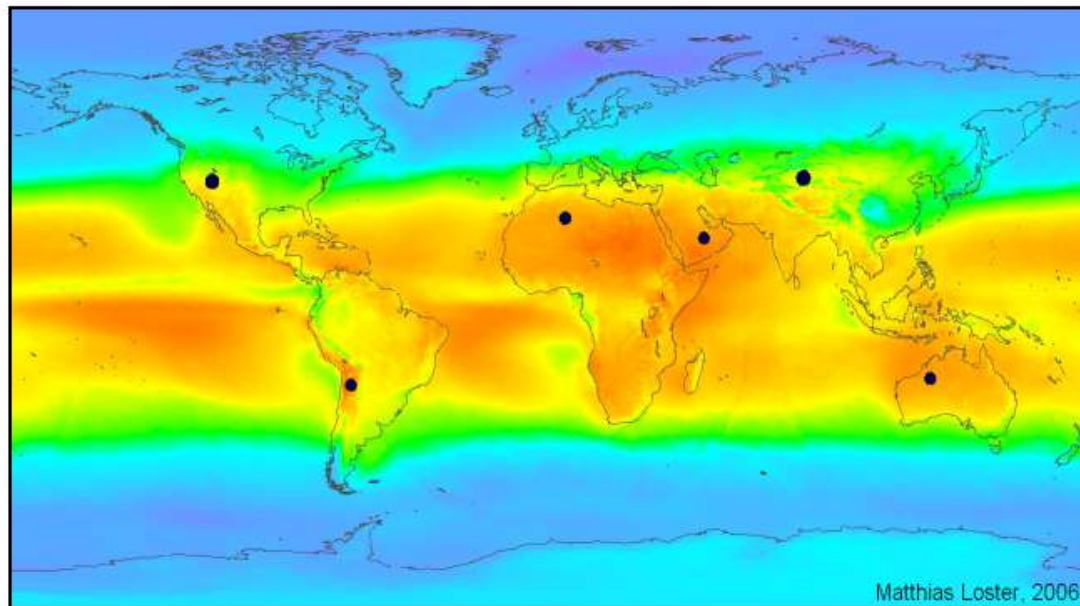- Polycrystal Si
- Single Crystal Si
- Ribbon Si
- Amorphous Si
- a-Si on Cz
- CdTe
- Other

A. Goetzberger, V.U. Hoffmann, *Photovoltaic Solar Energy Generation*, Springer
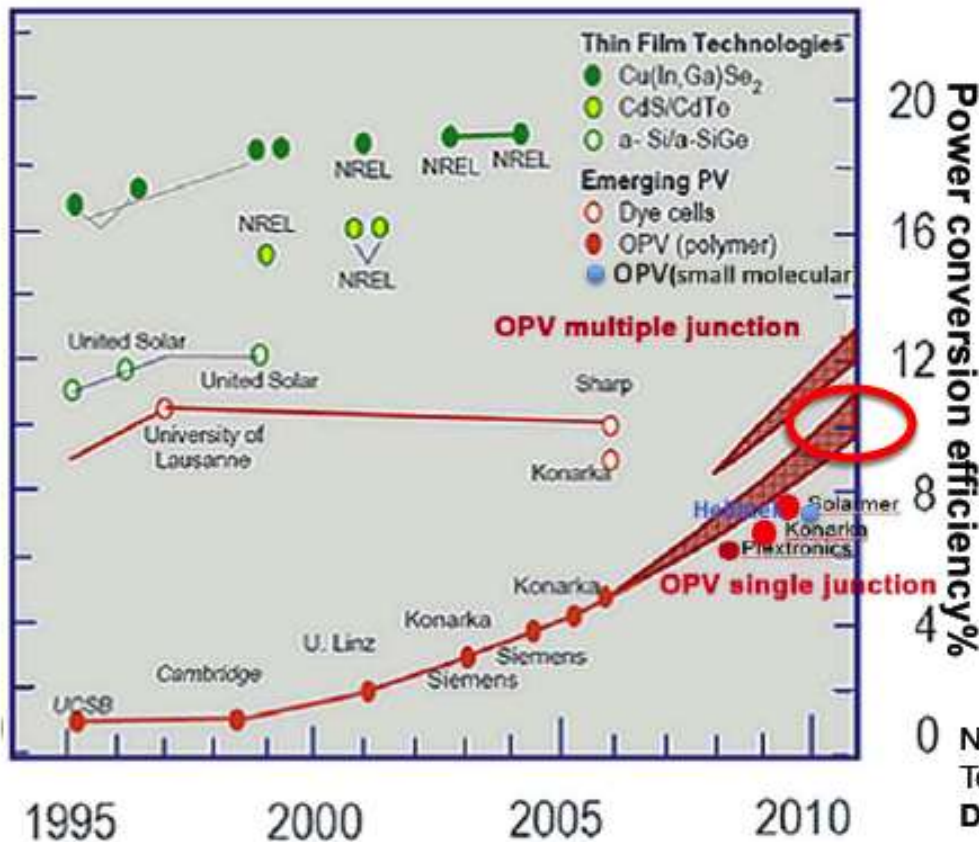
Yearly Solar fluxes & Human Energy Consumption

Solar	3,850,000 EJ
Wind	2,250 EJ
Biomass	3,000 E
Primary energy use (2005)	487 EJ
Electricity (2005)	56.7 EJ

Matthias Loster, 2006

0   50   100   150   200   250   300   350 W/m²

Σ● = 18 TWe

Inorganic and Organic Photovoltaic Progress:
What efficiency do OPV's need to reach?

PV	PCE%	Mobility cm^2/Vs
a-Si	12	1
Polymer	8.13	0.1
Crystlline organic nanowire	?	10

Commercialization of OPV viable at 10% power conversion efficiency

Next-Generation Organic Solar Cell Technology and Market Forecast, **Displaybank Co., Ltd, 2010**

Konarka

Why Organic PV

Heliatek
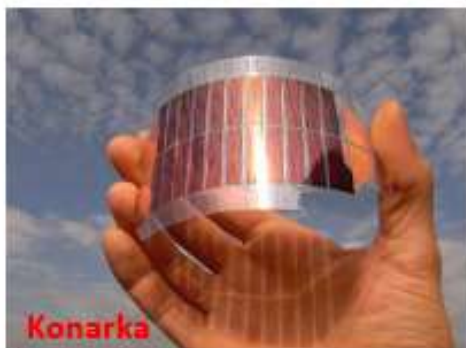
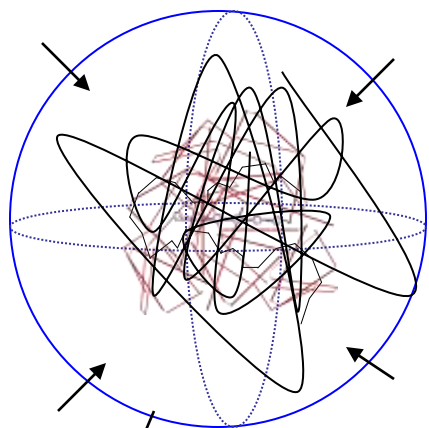|	Pros	Cons
Inorganic PV	High efficiency	High cost Materials shortage
Organic PV	Low cost, Large area Flexible, lightweight Low T processing Reel-to-reel printing	Low charge mobility Limited lifetime (3-5ys) Low efficiency

OPV is the most promising candidate for a next generation PV.
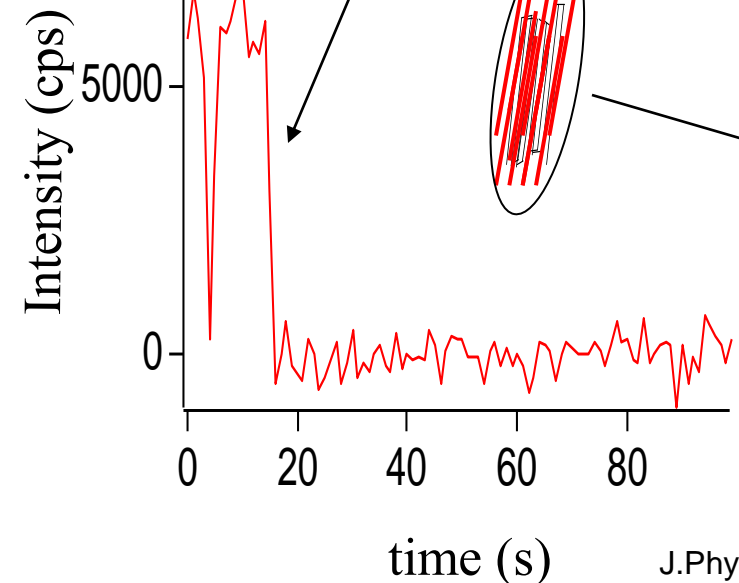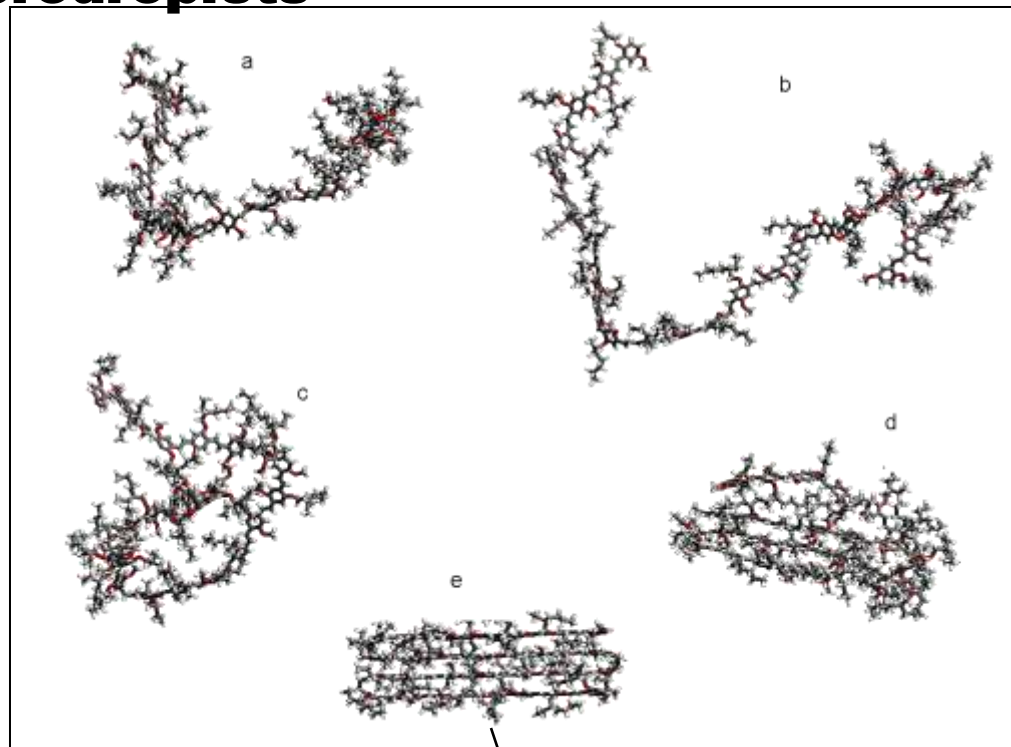*Efficiency must be improved, but cost and lifetime are very promising !*

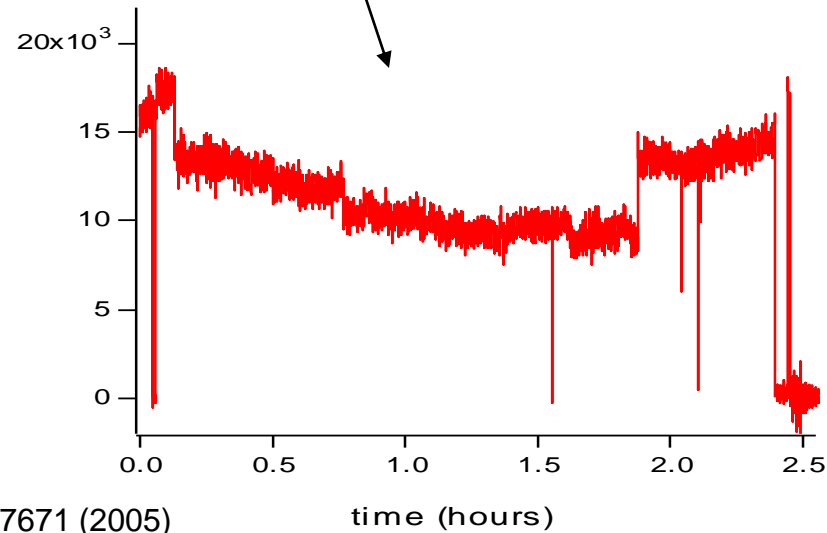# Single molecules of conjugated polymers isolated in microdroplets


??? ???

Intensity (cps)

5000

0

0   20   40   60   80

time (s)

Fluorescence Intensity
(cps/ 12 x12 pixel bin)

$20x10^3$

15

10

5

0

0.0   0.5   1.0   1.5   2.0   2.5

time (hours)

J.Phys. Chem. B. 109, 7671 (2005)

Photophysics

• Conjugated polymer (CP) ordering is critical for efficient photonic processes. Can this be controlled?

• Synthesis of CPs with controlled ordering and positions on a surface is difficult. How can this be optimized?

• CPs are easily oxidized compromising their long-term use: big problem for aging and reliability.


neutral   Charged (-1)   Charged (+1)
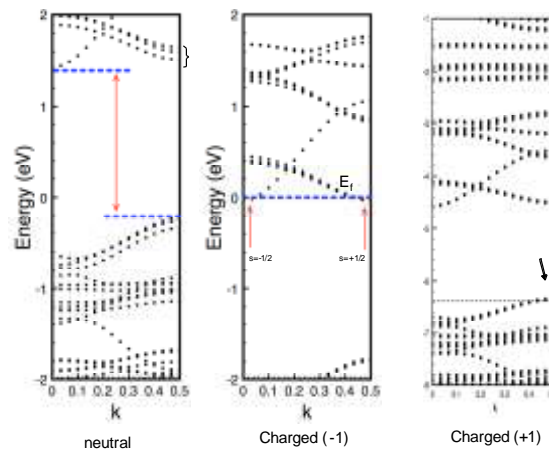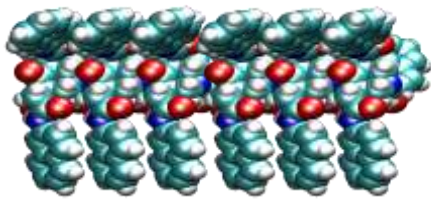
# How can we control long-range supramolecular ordering?

• Epitaxially confined arrays of conjugated polymeric materials

• Processing using controlled annealing, compatibilizers, substrate

• Alternative organic systems such as crystalline organic nanowires

• Nano-bio systems, hybrid composites
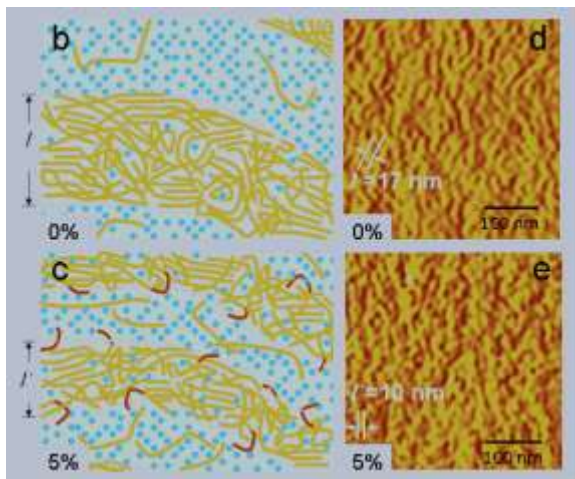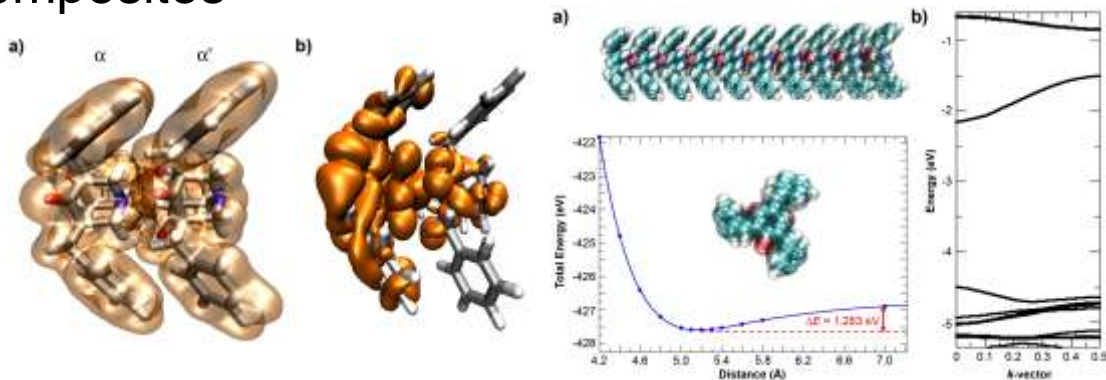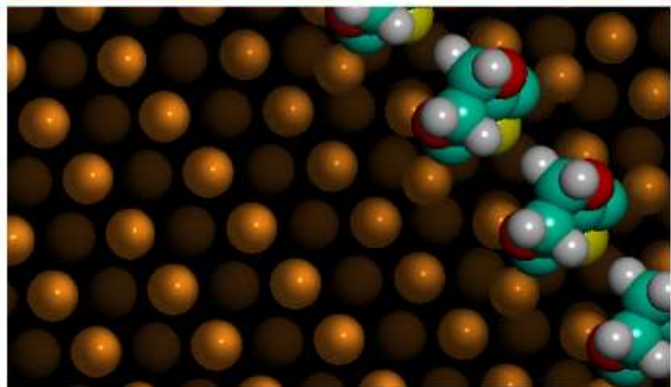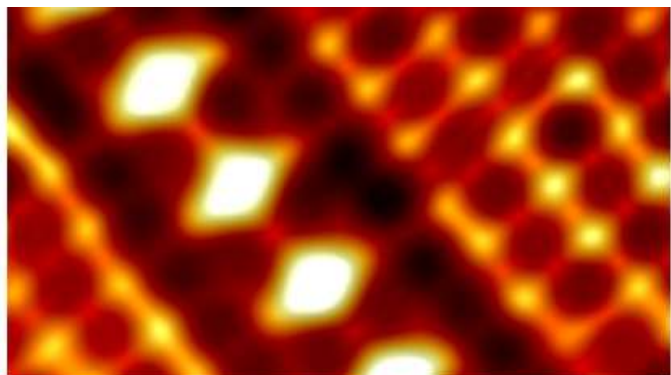
Epitaxially confined PEDOT: assembling aromatic building blocks into ordered structures that are mechanically robust and electronically interlinked

Scheme 1. Formation of epitaxially confined syn-PEDOT on Cu(110) surface.

X = I, Br
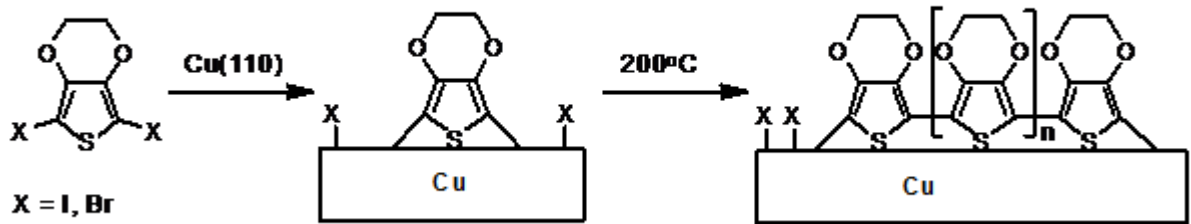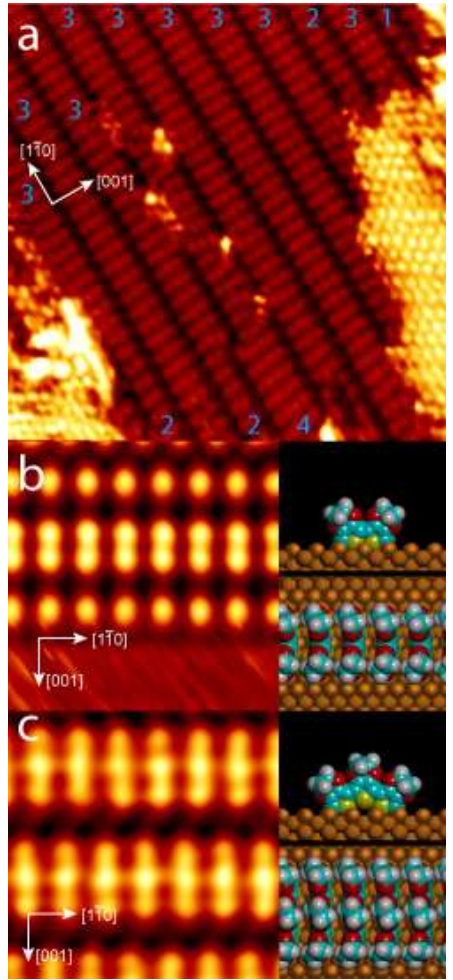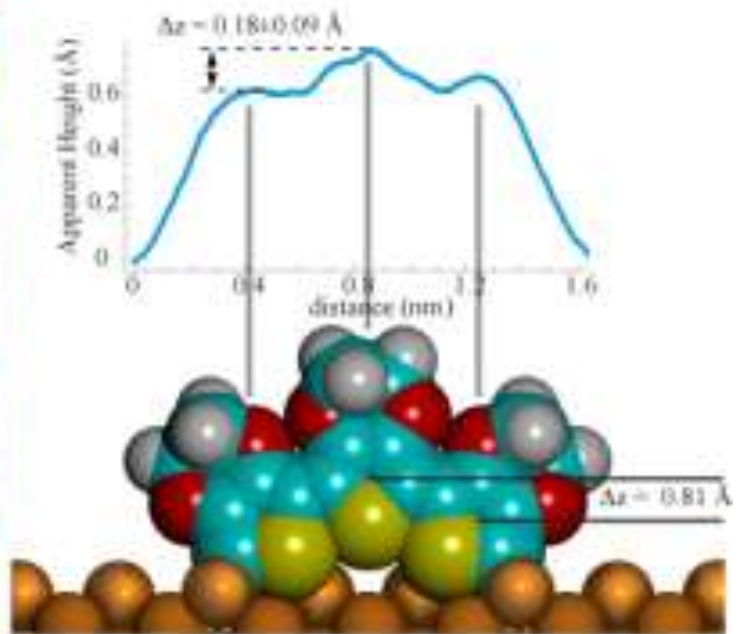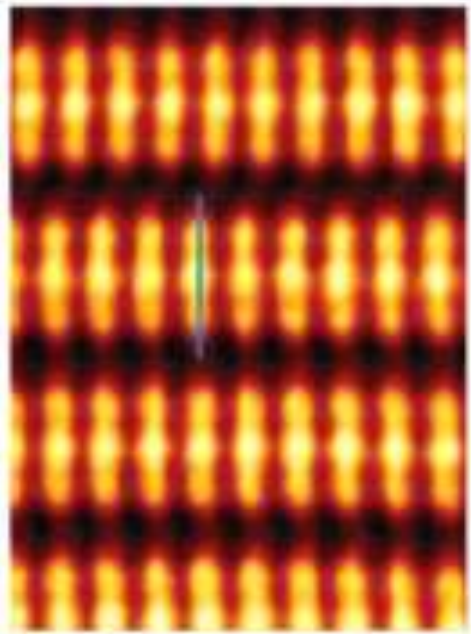
An ordered array of epitaxially confined poly-EDOT has been grown on the 110 facet of copper, using the surface simultaneously as a template and catalyst for polymerization.

Controlled Self-assembly and emergent properties
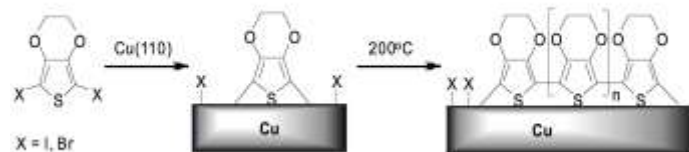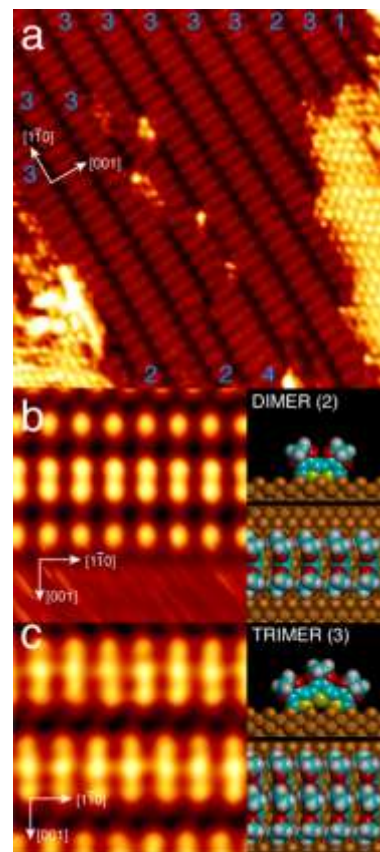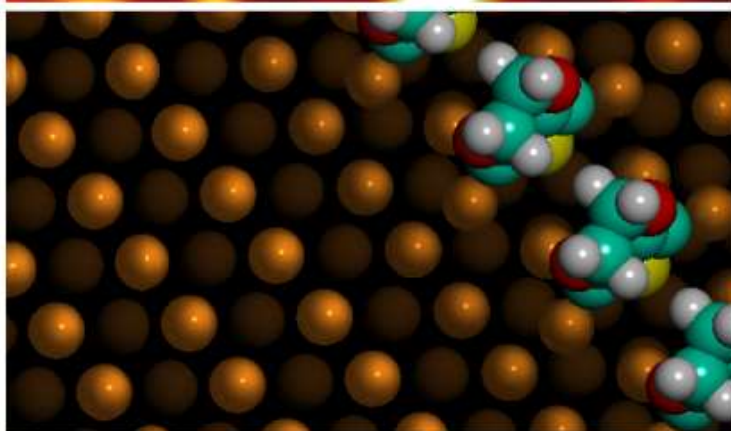

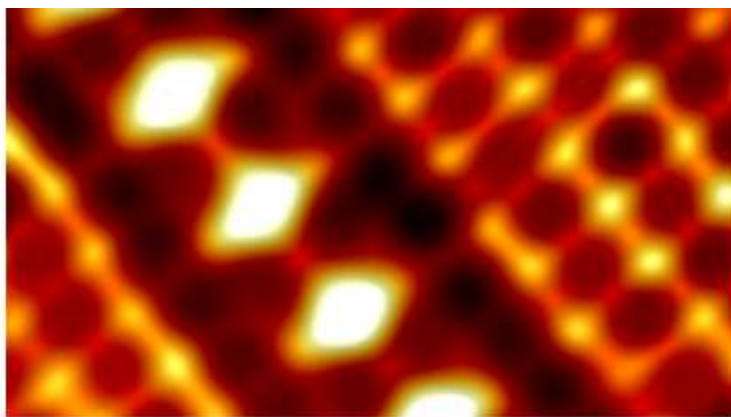Scheme 1. Formation of epitaxially confined *syn*-PEDOT on Cu(110) surface.
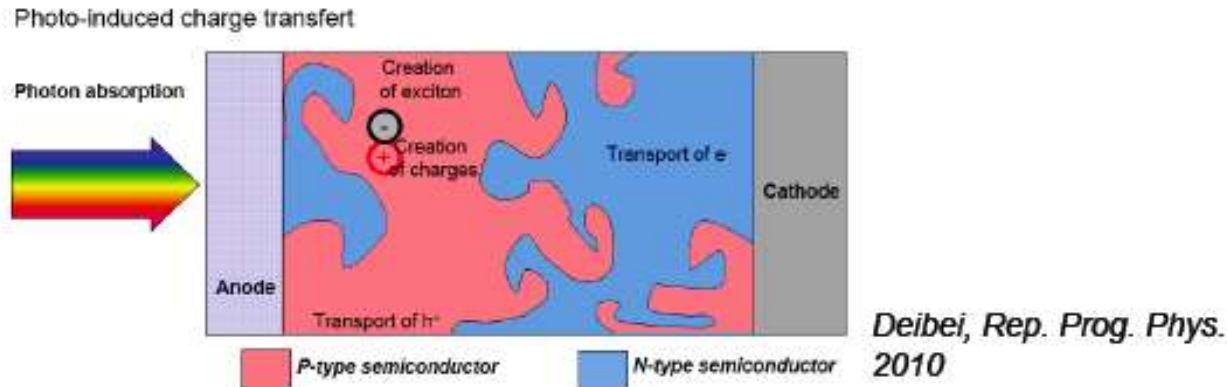
Using *in situ* STM imaging combined with first principles density functional theory calculations the surface-confined growth of ordered arrays of poly(3,4-ethylenedioxythiophene) (PEDOT) chains is demonstrated.

Current bottlenecks in OPV's

- ## Disordered heterojunction

Photo-induced charge transfert

Deibei, Rep. Prog. Phys. 2010

limited charge separation, high charge recombination, slow charge transport

- ## Strongly anisotropic charge transport

$\mu \sim 10^{-5}$ cm²/V.s
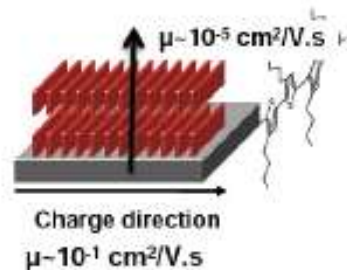
Charge direction
$\mu \sim 10^{-1}$ cm²/V.s
Sirringhaus, *Nature 1999*

most organic semiconductors prefer align their molecules perpendicular to the substrate, leading to inefficient charge transport in an OPV.

Disorder in donor-acceptor structures currently lead to critical barriers for exciton diffusion and charge transport – how can we overcome these?

Nanoscale Self-Assembly of Donar-σ-Acceptor Molecules
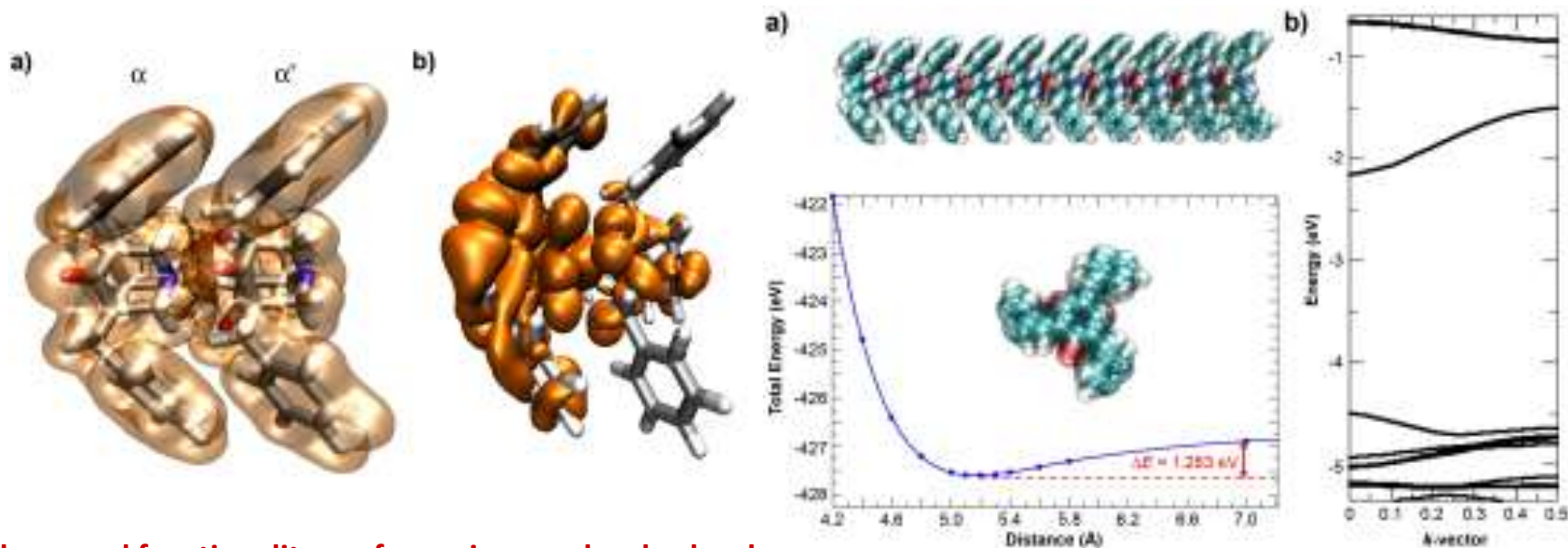
Shape and functionality confers unique molecular-level tunability in structure and function

➤Suitably functionalized molecules will self-assemble into well-defined solid-state architectures via non-covalent interactions.

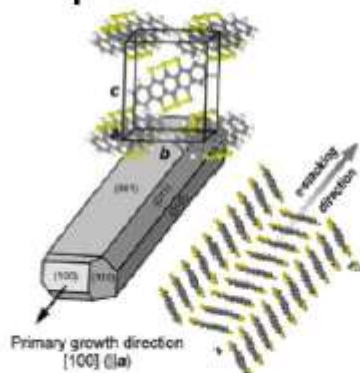➤Peripheral substituents can interact directly with the core and tune the electronic structure
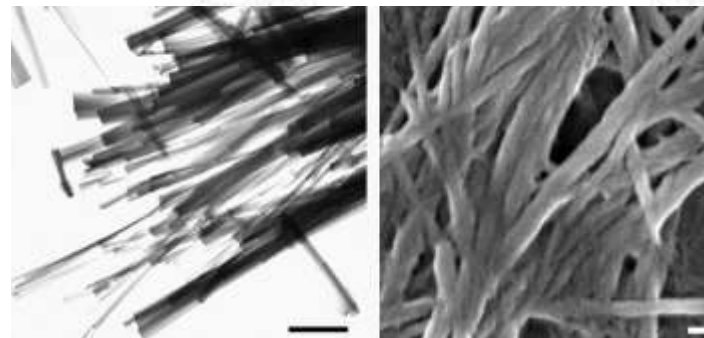
References: J. Phys. Chem. C 111, 18912 (2007); Int. J. Quan. Chem. 107, 2233 (2007); New J. Chem. 32, 1924 (2008); Org. Lett. 11, 4314 (2009)
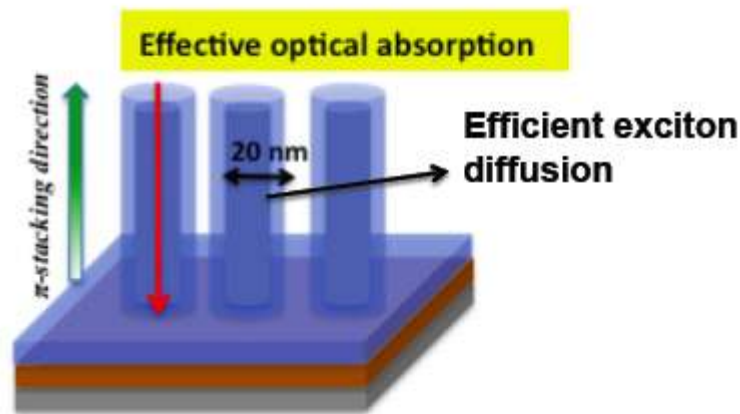
Advantage of Crystalline Organic Nanowires for OPVs
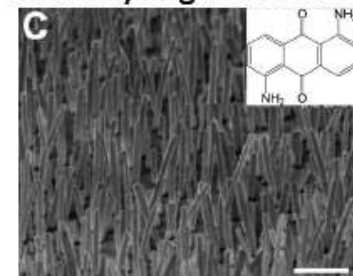
Highly efficient charge transport

Bao, Materials Today, 2008

Effective optical absorption

π-stacking direction

20 nm

Efficient exciton diffusion

Vertically aligned CONs

Zhao, JACS,2009

✓Low-temperature growth
✓Strong π-π interaction along NWs
✓Compatible with organic counterparts
✓Tunable bandgap
✓Directional charge transport

Xiao, Angew. Chem. 2007
Xiao, Adv. Mater. 2006
Xiao, Adv. Funct. Mater. 2008

1D self-assembly via π-π interactions induce efficient exciton diffusion and charge transport in CON's to address current bottlenecks in OPV's

Simulations of Block Copolymer and Polymer Nanocomposite Phase Structure, Stability, and Function for Energy Applications
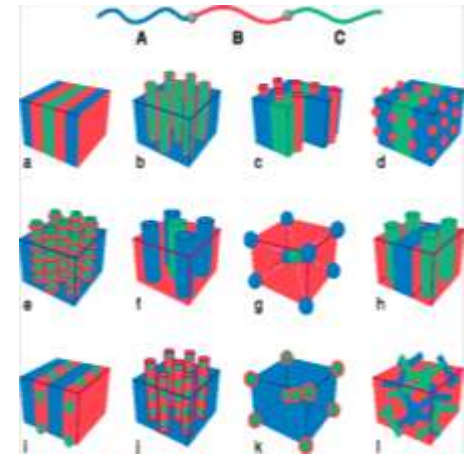
- **Energy challenges**
  - Develop high-performance polymer materials for critically important energy applications.
    - Efficient and inexpensive (i.e., third-generation) solar PV cells
    - High capacity, high power, and inexpensive electricity storage

- **Materials science challenges**
  - Understand and control the synthesis, morphology, stability, and properties of linear and nonlinear block copolymers.
    - How does molecular architecture influence polymer morphology and properties?
    - How can material's architecture and properties be manipulated by applied fields (shear, electric fields, confinement, etc.)?
  - Guidance is needed from theory, modeling, and simulation to design novel linear and nonlinear multiblock copolymer materials.

Triblock copolymers occupy a large, varied, and intricate phase space. At least 30 different morphologies are possible.

- **Computer science and mathematics challenges**
  - Coarse-graining and multiscale methods for simulation over multiple length and time scales
  - Efficient algorithms for sampling the density of states of continuous systems.
  - Scaling polymer codes to 10^5 to 10^6 processors
 - Effective use of multicore and accelerator co-processors

# Structure and Dynamics of Multicomponent polymeric materials
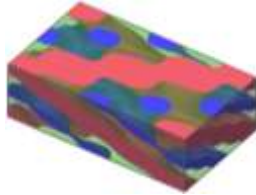
- How does molecular architecture influence polymer morphology and properties, and how can it be manipulated by orientational fields (shear, electric fields, confinement, substrate interactions, etc.)?

- What are the conformations of individual chain segments in the block copolymers and how are they affected by confinement and surface interactions?

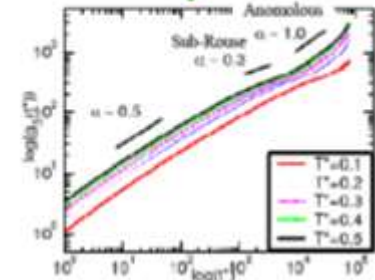**Nanophase Morphology via Simulations:** Phase Behavior and Diffusion in Homopolymer/Nanoparticle

Evolution of block copolymer morphology
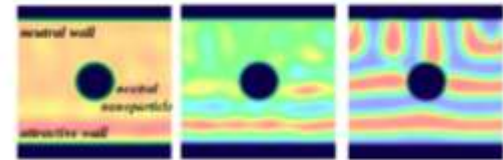
Equilibrium Phase Diagram
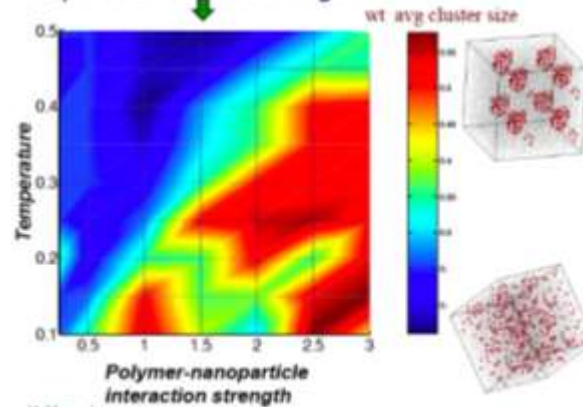
Dynamics: Anomolous diffusion in polymer-nanoparticle blends

*Reference: J. Chem. Phys. 130, 134910 (2009)*

Summary and Conclusions

• "Controlled" self-assembly can be useful for improving efficiency (properties, scaling, cost) of functional energy materials

- crystalline organic nanowires

- epitaxially confined arrays

- bulk morphology and domain size

- template structures
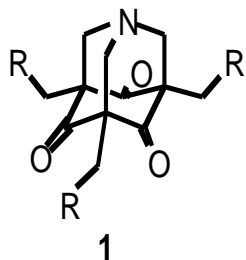
a R = Ph
b R = CONHPh
c R = CONHNaph (R^1 = H)
d R = CONHNaph (R^1 = n-$C_{12}H_{25}$)

Naph

1
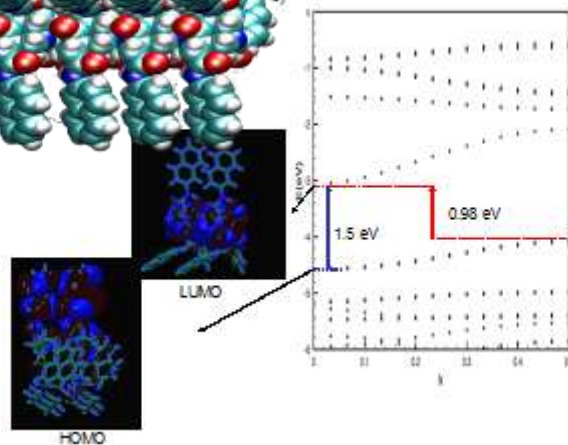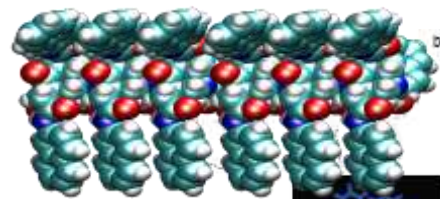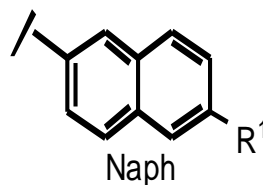
# Theory and modeling of Supercapacitors for Energy Storage

charging
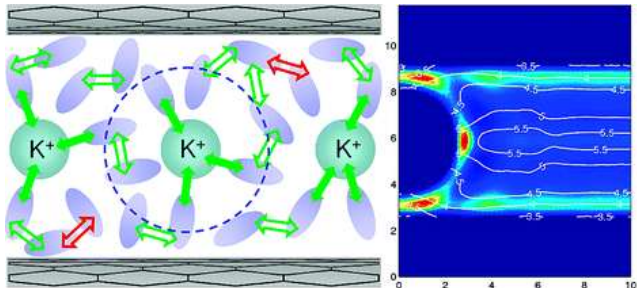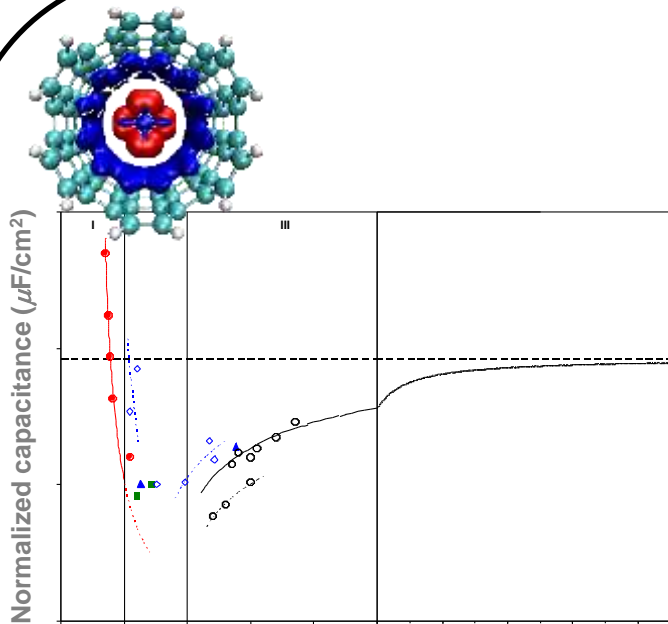
Supercapacitors are electrical energy storage devices that have large energy power and density. The density is tremendously improved by reducing pore sizes in the nanometer regimes. Computational studies allowed to show that partial desolvation is important, which allows to replace conventional model by a "wire-in-a-cylinder" model, which accounts for all the observed phenomena.
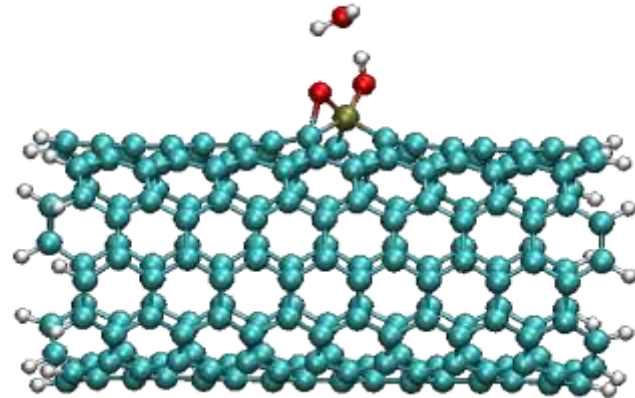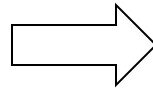
References: *Angew. Chem.* **120**, 3440 (2008) , *Chem. Eur. J.* **14**, 6614 (2008)
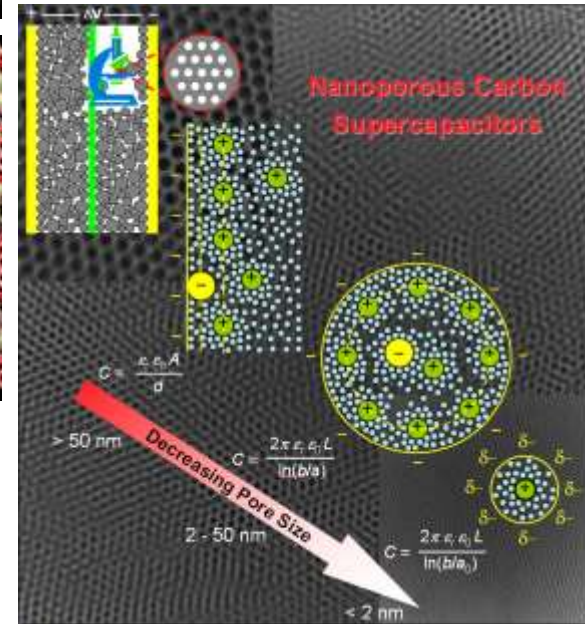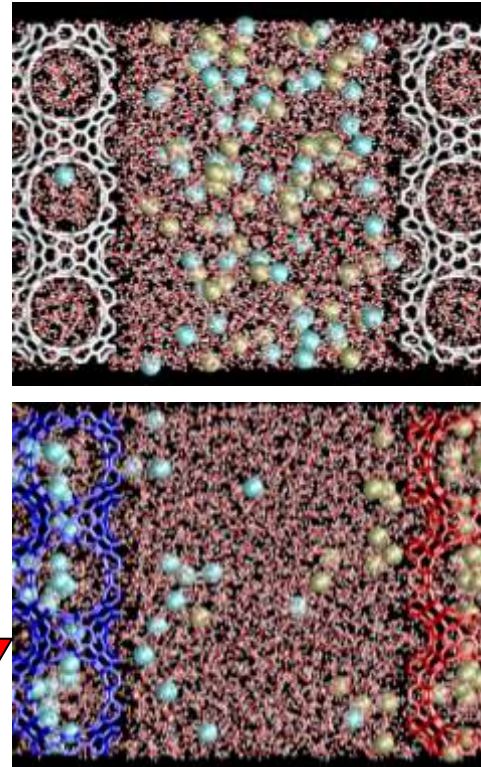
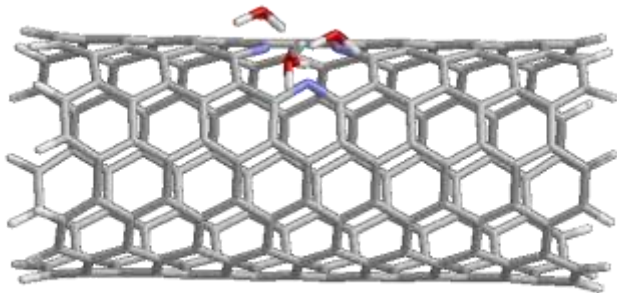# Pseudo-capacitance in carbon-based systems: realistic quantum mechanical treatment
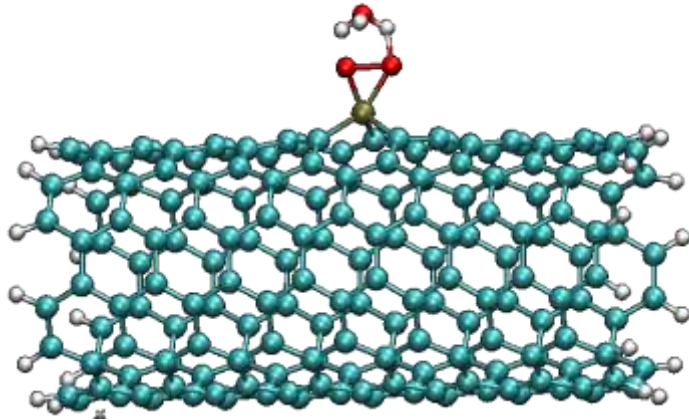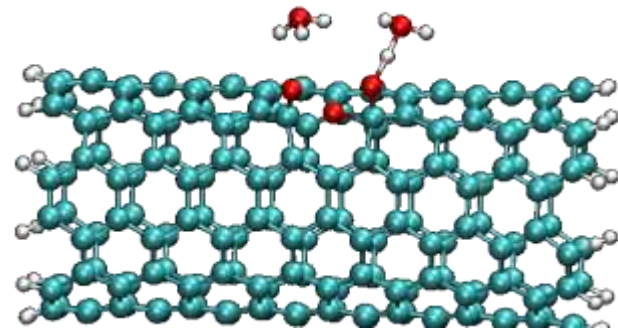

Oxidized P substituted CNT interacting with hydronium ion

Oxidized P substituted CNT during reduction by hydronium ion

Pyridine N defect with H3O

Quinone defect reduction

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