PARIS 2014
JMC 14
CMD 25

CONDENSED MATTER IN PARIS 2014

CMD 25 - JMC 14
August 24th - 29th
2014

Université
PARIS DESCARTES

Conference program, keynote speakers presentations and abstracts

Société Française de Physique

Symposium MC36 - Monday 25th 11:30 -12:30	Room Belladonne
Symposium MC36 - Tuesday 26th 11:30 -12:30	Room Pelletier
Symposium MC36 - Thursday 28th 11:30 -12:30	Room Pelletier
Symposium MC36 - Thursday 28th 14:00 -16:30	Room Pelletier

Symposia

MC36 : Theory: Density functional theory and beyond: Theory and applications

Monday 25th 11:30 -12:30 – Room Belladonne

12:00-12:30 Charge transfer in organic and hybrid organic/inorganic systems from first principles
Patrick Rinke, Fritz Haber Institute of the Max Planck Society

Tuesday 26th 11:30 -12:30 – "Optical Properties and Charge Transfer" - Room Pelletier

11:30-12:00 Optical properties of MoS_2. Excitons beyond the bandgap
Alejandro Molina-Sanchez, University of Luxembourg
12:00-12:15 Interaction of tetrakis-Schiff base compounds with carbon nanostructures from DFT: implications for charge transfer.
Sergey Pyrlin, University of Minho
12:15-12:30 Towards a first-principles determination of effective Coulomb interactions in correlated electron materials: Role of intershell interactions
Priyanka Seth, Centre de Physique Théorique

Thursday 28th 11:30 -12:30 – "Time-Dependent Density Functional Theory" - Room Pelletier

11:30-12:00 Electron energy loss and inelastic x-ray scattering cross sections from time-dependent density-functional perturbation theory
Iurii Timrov, Scuola Internazionale Superiore di Studi Avanzati / International School for Advanced Studies
12:00-12:15 Time-Dependent Density Functional Theory for Quantum Electrodynamics
Walter Tarantino, Laboratoire des Solides Irradiés
12:15-12:30 *How to calculate Dynamical Structure Factors? From analysis to new methods*
Igor Reshetnyak, Laboratoire des Solides Irradiés, European Theoretical Spectroscopy Facility

Thursday 28th 14:00 -16:30 – Room Pelletier

14:00-14:30 The phonon-limited resistivity of graphene: electron-phonon interactions, screening and Boltzmann transport equation.
Thibault Sohier, Institut de minéralogie, de physique des matériaux et de cosmochimie
14:30-14:50 First-principles calculations of electron-phonon coupling in semiconductors
Jelena Sjakste, Laboratoire des Solides Irradiés, Ecole Polytechnique, CEA-DSM-IRAMIS CNRS

Interaction of tetrakis-Schiff base compounds with carbon nanostructures from DFT: implications for charge transfer.

Sergey V. Pyrlin[1]; Nicholas D.M. Hine[2]; Marta M.D. Ramos[2]; Martha V. Escárcega-Bobadilla[3,4], Gustavo A. Zelada-Guillén[4].

1. *Group of Computational and Theoretical Physics, Center of Physics and Department of Physics, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal;*
2. *Cavendish Laboratory, University of Cambridge, JJ Thomson Avenue, Cambridge CB3 0HE, United Kingdom;*
3. *Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007 - Tarragona, Spain;*
4. *Polymaterials AG. Innovapark 20, 87600 Kaufbeuren, Germany.*

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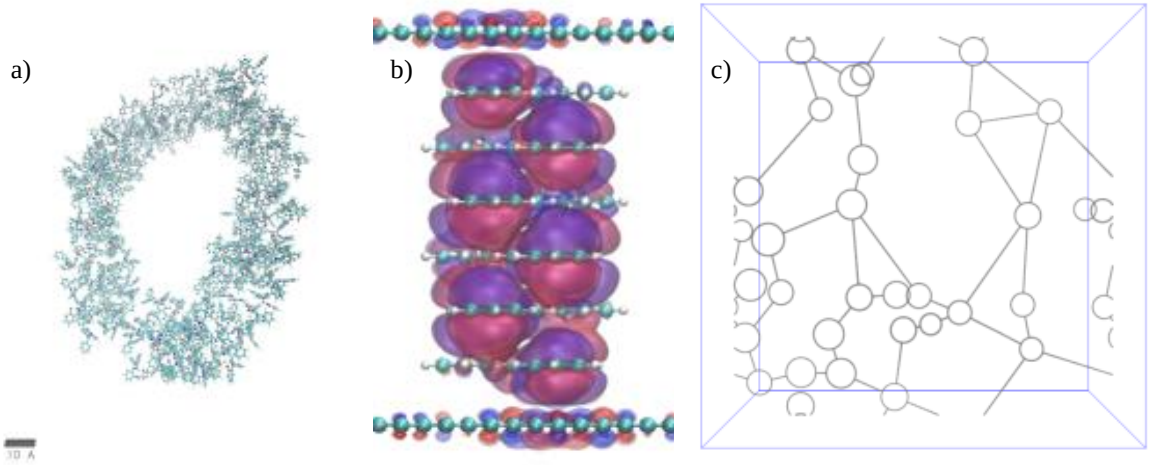
Development of polymer composites by addition of nano-sized inclusions to matrix attracts increasing attention in the last decades as a potential way to prepare functional materials, the properties of which could be fine-tuned by varying the nanoadditives' concentration and alignment inside polymer. Carbon nanotubes (CNTs) and graphene nanoribbons (GNRs) are widely used as highly promising additives when high mechanical strength and good electrical conductivity are desired [1]. However their poor interaction with surrounding matrix and tendency to form agglomerates lead to decline of material properties' improvement with increasing concentration [2]. To tackle this problem surface functionalization is applied. However, as chemical bonding interrupts continuous sp2-bonded outer layer, the electrical properties could be severely damaged by grafting of functional groups. For this reason, there is a high demand for non-bonding functional molecules.

This work is focused on the interaction between CNT/GNR and tetrakis-Schiff base compounds. As it was shown previously [3], the later can form continuous networks of interconnected micrometer sized rings and rods with rim thickness of a few nanometers both on the surface and in the bulk of polymer. It was also noticed, that CNTs could be incorporated into these molecular networks and aligned along the rings and rods. Here we report the investigation of the interaction between tetrakis-Schiff bases and the surface of carbon nanotubes and graphene nanoribbons by means of density functional theory and molecular dynamics and its influence on the composite electrical properties studied by meso-scale Monte Carlo modeling.

Using the ONETEP [4] and SIESTA [5] density functional packages the relaxed structures of molecular complexes, consisting of CNT/GNR fragment and tetrakis-Schiff base molecule, were obtained both with and without van der Waals correction and the orientation dependant interaction energy were studied. A special attention is devoted to the frontier orbitals of the molecular complexes. It is shown, that HOMO and LUMO orbitals of the neighboring molecules and CNT/GNR surface level can overlap in the proximity of frontier orbitals of CNT/GNR thus facilitating charge transfer. For single base tetrakis-Schiff molecules with flat geometry a ballistic conduction channel appears for stacked molecular wire. For wedge-like double base molecules, forming the mentioned above ring-rod networks, with smaller overlap of frontier

orbitals and more complex mutual arrangement, the electron hopping model is proposed to investigate the effect of this peculiar interaction on the entire composite electric properties.

Final impact of CNT/GNR incorporation into self-assembled rings-and-rods molecular networks on the percolation threshold and conductivity of polymer composite is assessed by evaluation of resistivity of a model sample with molecular network, simulated with Monte Carlo method using the experimental data on rings distribution, sizes and connectivity. The resistivity of CNTs uniformly distributed, agglomerated and arranged in ring-rod network is compared.



Left to right: Molecular ring, self-assembled from dual tetrakis-Schiff base compounds by MD simulation; a stack of single base tetrakis-Schiff base compounds sandwiched between two GNRs; MC simulated network of rings and rods in plane.

Acknowledgments: The work was supported by European Community's Seventh Framework Programm through the Marie Curie Initial Training Network "CONTACT" for the tailored supply-chain development of CNT-filled composites with improved mechanical and electrical properties (FP7-PEOPLE-ITN-2008-238363) http://www.contactproject.eu/ and Portuguese Foundation for Science and Technology (FCT) through the PhD grant SFRH/BD/88995/2012. The Center of Physics of University of Minho research is sponsored by FEDER funds through the program COMPETE- Programa Operacional Factores de Competitividade and by national funds through FCT-Fundação para a Ciência e a Tecnologia, under the project PEst-C-FIS/UI607/2011-2012.

[1] Spitalsky Z., Tasis D., Papagelis K., Galiotis C., "Carbon nanotube-polymer composites: Chemistry, processing, mechanical and electrical properties," Prog. in Polymer Sci. **35**, 357-401 (2010).
[2] Matveeva, A. Y., Tiusanen, J. M., Pyrlin, S. V., Van Hattum, F. W. J. "Investigation of the mechanical properties of injection moulded CNT reinforced thermoplastic polymer parts". Paper presented at the International SAMPE Technical Conference, 1714-1725 (2013).
[3] Escárcega-Bobadilla M.V., Zelada-Guillén G.A., Pyrlin S.V., Wegrzyn M. et al. "Nanorings and rods interconnected by self-assembly mimicking an artificial network of neurons," Nature Communications **4**, Art. 2648. doi:10.1038/ncomms3648 (2013).
[4] Skylaris, C.-K., Haynes, P. D., Mostofi, A. A., Payne, M. C., "Introducing ONETEP: Linear-scaling density functional simulations on parallel computers," Journal of Chemical Physics **122(8),** 084119 (2005).
[5] Soler, J. M., Artacho, E., Gale, J. D., García, A., Junquera, J., Ordejón, P., Sánchez-Portal, D. "The SIESTA method for ab initio order-N materials simulation," Journal of Physics Condensed Matter **14(11)**, 2745-2779 (2002).

Self-assembling tetrakis-Schiff base compounds for CNT reinforced composites: *combined MD, DFT & charge transfer study*

Sergey V. Pyrlin[1]; Nicholas D.M. Hine[2]; Marta M.D. Ramos[2]; Martha V. Escárcega-Bobadilla[3,4], Gustavo A. Zelada-Guillén[4].

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CONTACT

ITN "CONTACT": http://www.contactproject.eu/

The research aim of ITN "CONTACT" is the tailored industrial supply-chain development of CNT-filled polymer composites with improved mechanical and electrical properties

acciona Infrastructure

PROMOLDING creating polymer solutions

BAYER

mta ttk

i3N INSTITUTE FOR NANOSTRUCTURES, NANOMODELLING AND NANOFABRICATION

polyMATERIALS creative polymer technologies

AIMPLAS INSTITUTO TECNOLÓGICO DEL PLÁSTICO

OxfordMaterials

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Imperial College London

TAMPEREEN TEKNILLINEN YLIOPISTO

EISENHUTH

SEVENTH FRAMEWORK PROGRAMME

This project has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 238363

i3N Universidade do Minho Imperial College London

Outline:

1. Introduction to CNT composites' problems:
   - *Why do we bother?*
   - *Why conventional way fails?*
   - *Any other way?*
2. Computer study of self-assembly in double base compounds:
   - *DFT&MD study of a single molecule and dimer*
   - *MD study of molecular ring self-assembly*
3. Charge transfer properties of Schiff-base compounds
   - *single molecule electronic structure*
   - *electron transfer in single tetkaris-Schiff base molecular system*
   - *double tetrakis-Schiff base systems [work in progress]*

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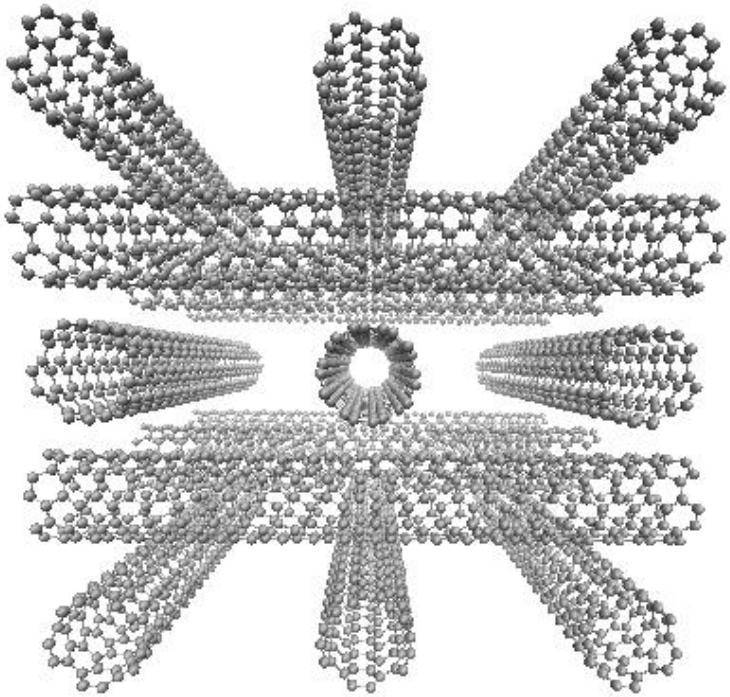
Introduction to CNT composites' problems: fantastic possibilities

Z. Spitalsky et al. Prog. in Polymer Sci. 2010, vol. 35, p. 357-401
Young modulus & Tensile strength increase ***~10x*** by adding 1 vol%
Conductivity increase ***~16* orders of magnitude**
Percolation threshold **~0.003 wt%**



* Photographs from *www.baytubes.com*

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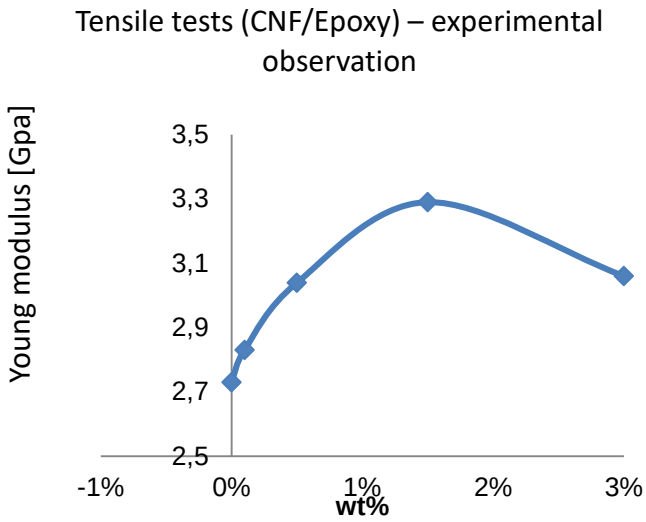
Introduction to CNT composites' problems: so why do we bother?

Anna Y. Matveeva, Ferrie W.J. van Hattum
I3N - Institute for Nanostructures, Nanomodelling and Nanofabrication, Portugal; www.i3n.org



More – is not better!

* Photographs from *www.baytubes.com*

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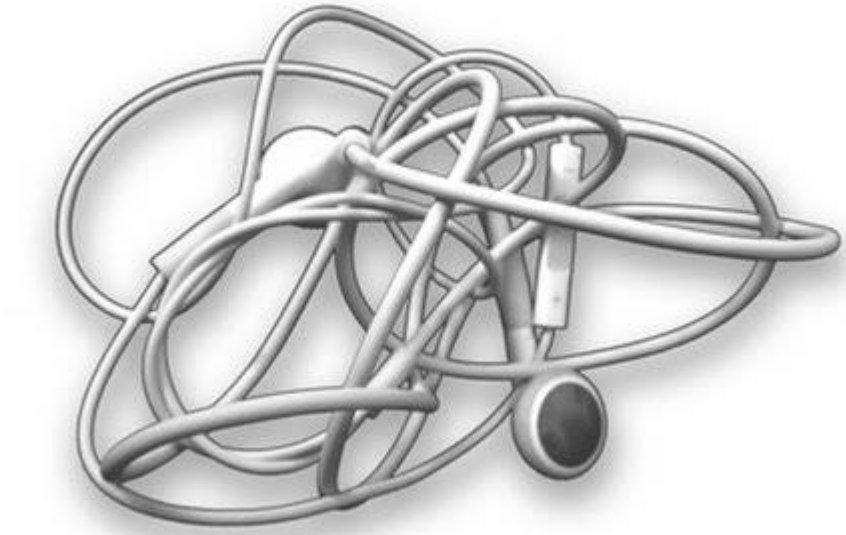
Introduction to CNT composites' problems: so why do we bother?

What happened to my nanotubes???



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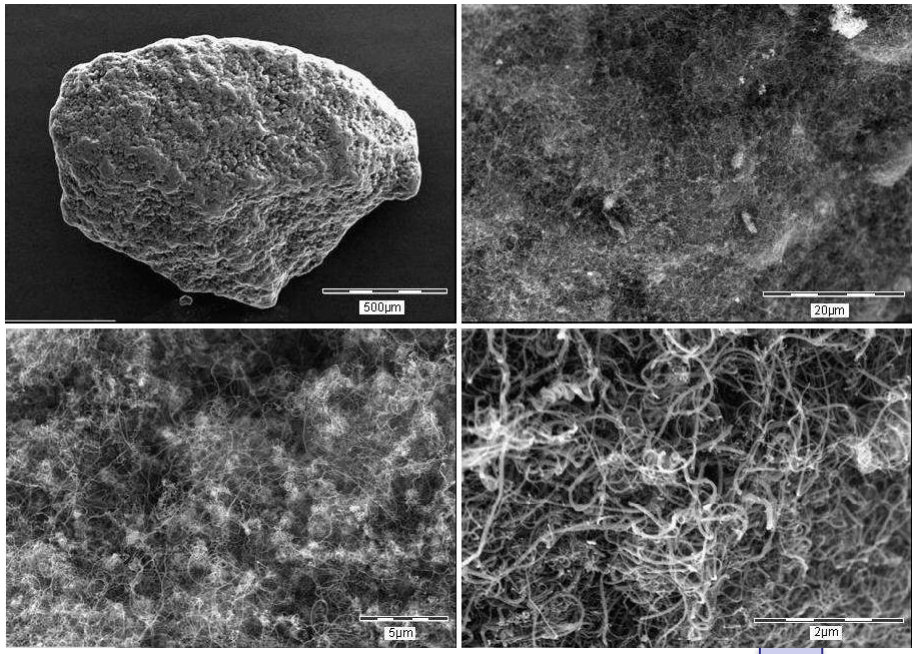
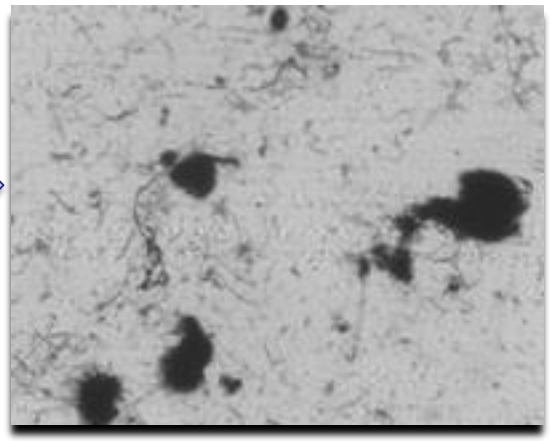
Introduction to CNT composites' problems: *Why conventional way fails*?



- I've made a composite with 2 w.% of nanotubes!

- Indeed… and looks like all of them are here.

* Micro photograph from *www.baytubes.com*



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Introduction to CNT composites' problems: *Why conventional way fails*?

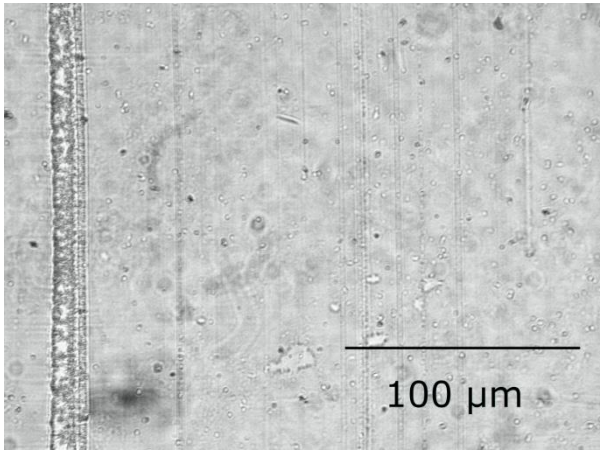


Jyri Tiusanen – sample preparation

Bernadeth Kiss-Pataki – microscopy

Anna Y. Matveeva – image analysis

Agglomerate size was determined from microscopy analysis of PC samples containing 3 vol. % of 1,5 um long CNTs.



Code	average agglomerate radius x_c, um	agglomerate radius dispersion w, um	Volume resistivity (ρv) average Ω.cm	stdev Ω.cm
F1	0.28	1.55	78,908	3,965
F2	0.40	1.47	6171,026	2205,548
F3	0.41	0.85	27,934	2,025
F4	0.10	0.66	46,451	6,973
F5	0.14	0.53	156,873	28,616
F6	0.10	0.76	23,274	4,244

Series of samples with close agglomerate parameters can exhibit **2 orders of magnitude difference** in resistivity.

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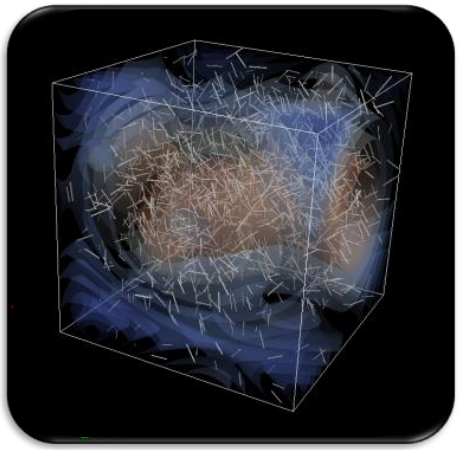
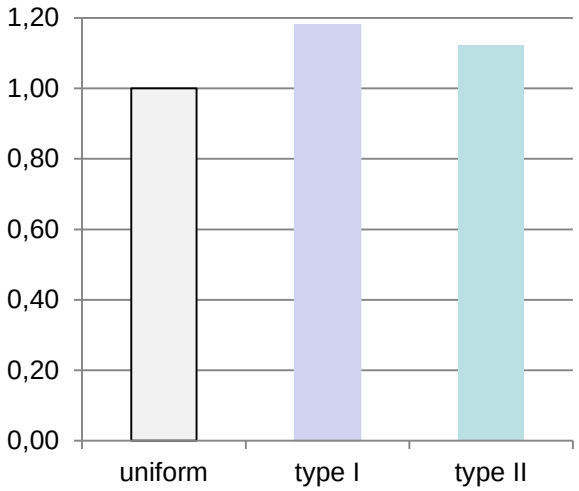
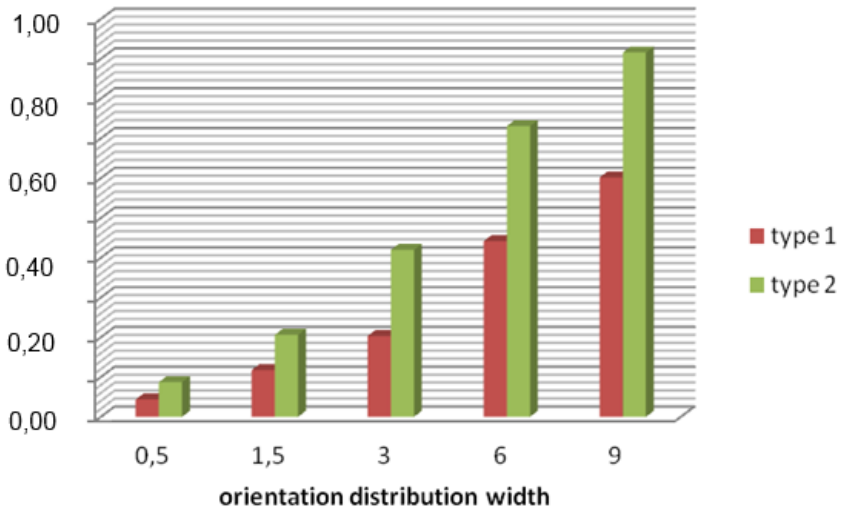
Introduction to CNT composites' problems: *Why conventional way fails*?



Resistor network model:

$$\begin{cases} \sum_i I_{ij} = 0 \\ I_{ij} = \dfrac{V_i - V_j}{R_{ij}} \end{cases} \rightarrow V_i \sum_{j=2}^{n+2} a_{ij} = \sum_{j=2}^{n+2} a_{ij} V_j + a_{i1} V_1 + a_{i0} V_0 \xrightarrow{V_0=0, V_1=1} (I - A)V = B$$





Conclusion: the 2 order of magnitude difference **cannot** be attributed solely to agglomerate size - should be attributed to different degree of CNT alignment

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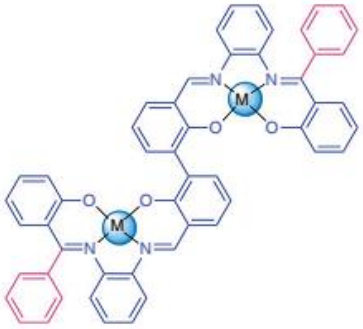
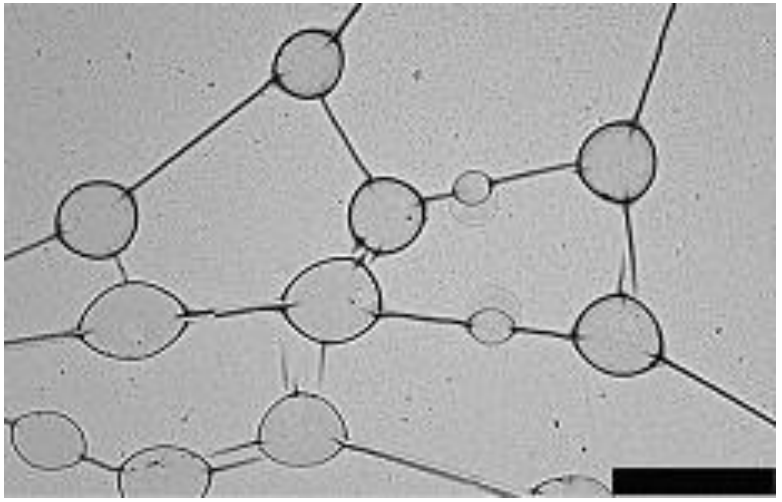
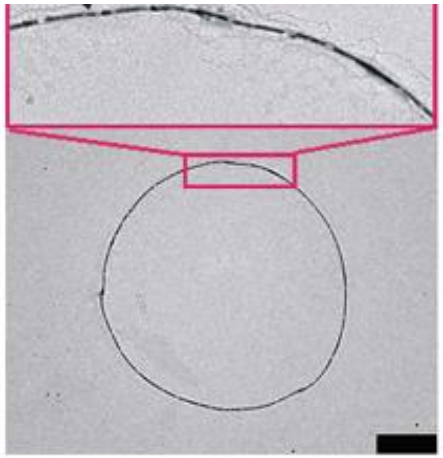
Introduction to CNT composites' problems: *Any other way*?

Self-assembling molecular networks:







Nature Commun. 2013;4:2648. doi: 10.1038/ncomms3648.

Nanorings and rods interconnected by self-assembly mimicking an artificial network of neurons.

Escárcega-Bobadilla MV[1], Zelada-Guillén GA, Pyrlin SV, *et al.*

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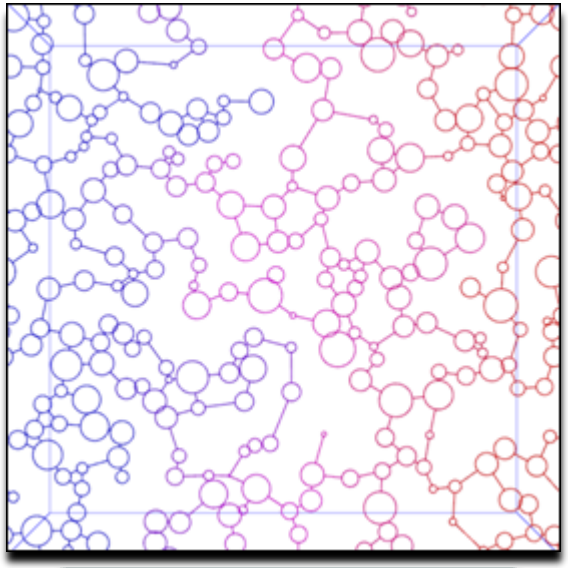
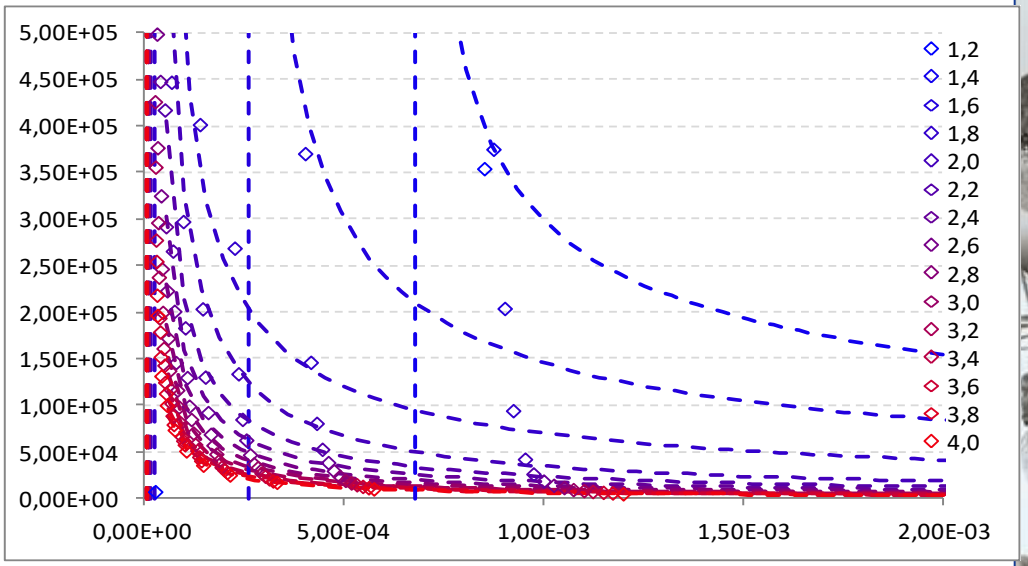
Introduction to CNT composites' problems: *Any other way*?

Self-assembling molecular networks: Monte Carlo study





Variation of volume resistivity (in *a.u.*) vs. average volume per ring (um^3/ring)

Parameters:

Diameter 5,5+/-2,0 µm;
Rim 0,11+/-0,01 µm;
Rods per ring 2,8+/-0.7
CNT aspect ratio 65

Percolation threshold:

- 2D down to ~0,06 surf. % (vs ~0,1 theory);
- 3D down to ~10^{-5} vol. % (vs ~1,0 theory);

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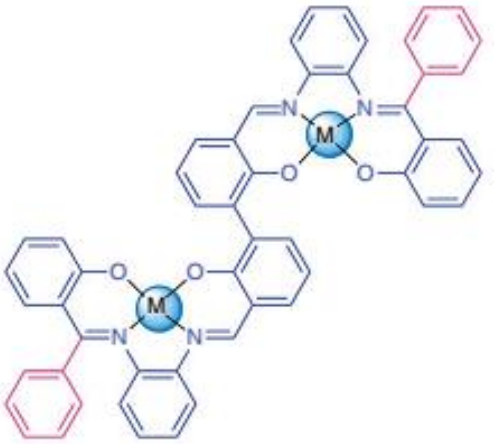
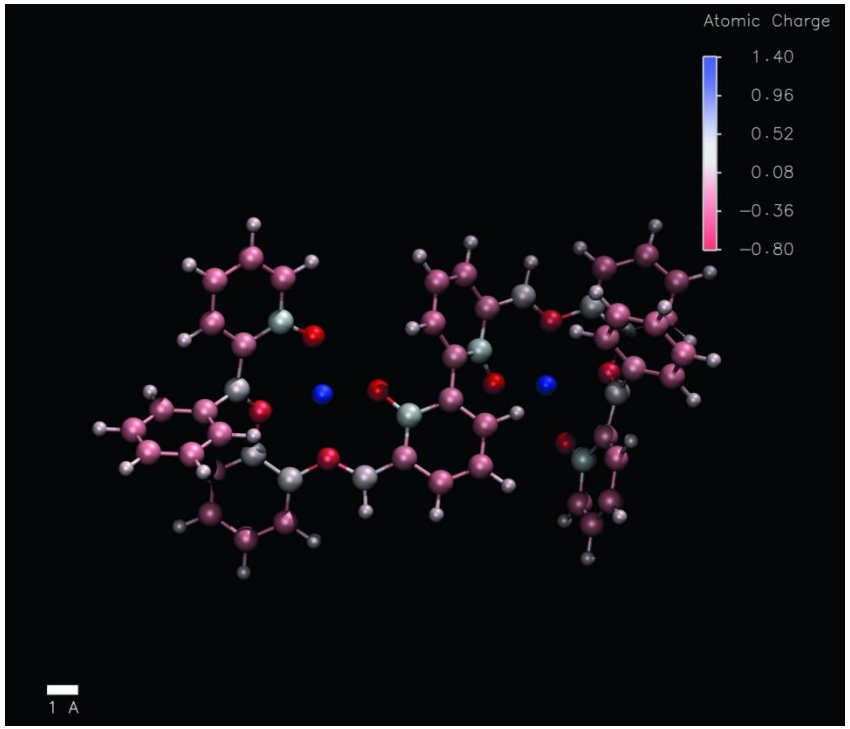
Computer study of self-assembly in double base compounds:

DFT study of single tetrakis-Schiff molecule





- *ONETEP:* http://www2.tcm.phy.cam.ac.uk/onetep/
- *SIESTA:* http://departments.icmab.es/leem/siesta/
- *NWCHEM:* http://www.nwchem-sw.org/
- *LAMMPS:* http://lammps.sandia.gov/

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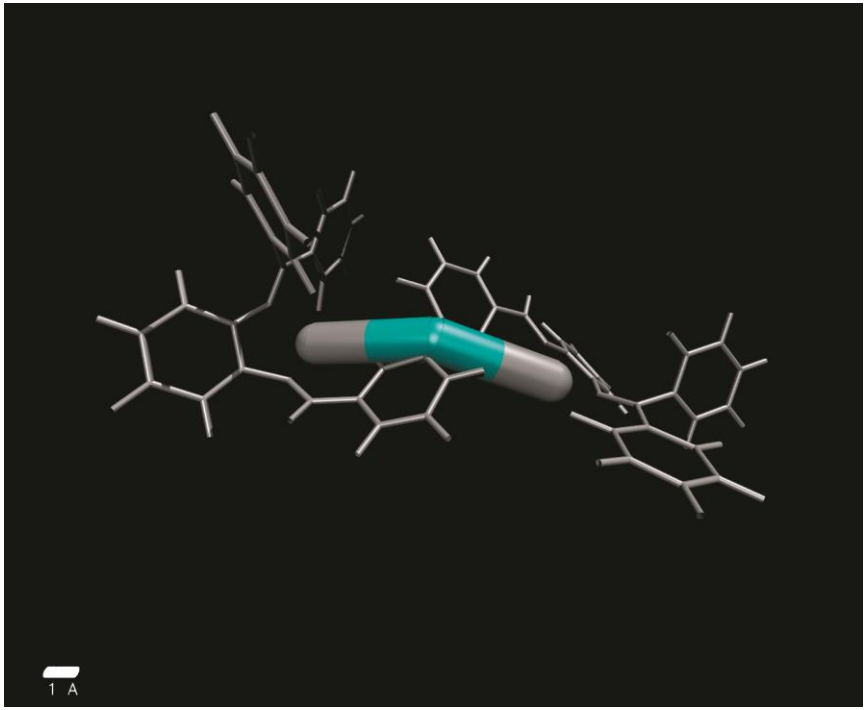
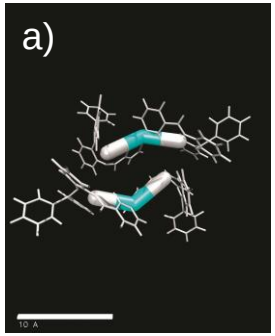
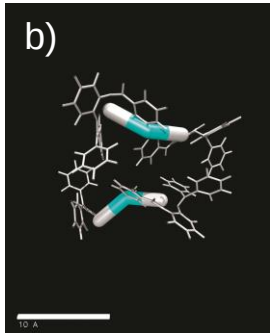
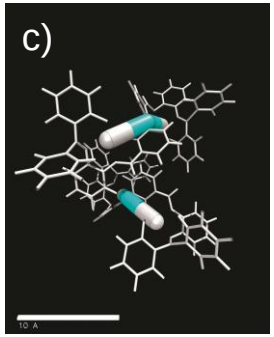
Computer study of self-assembly in double base compounds:

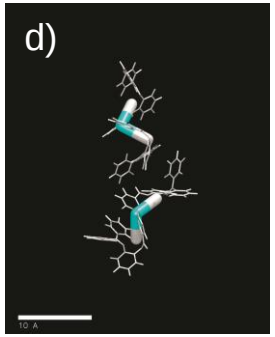
DFT & MD study of tetrakis-Schiff molecule dimer











	Bimolecular configuration	van der Waals binding energy (kcal/mol)	Coulomb binding energy (kcal/mol)	Total binding energy (absolute values, kcal/mol)
a)	Back-to-back	~-40	+6 to +7	> 30
b)	Face-to-face	~-20	-6 to -7	~ 30
c)	Stacked	~-30	-4 to 0	~ 30
d)	Side contact	~ 20	~ -7 to 0	~ 15 to 30

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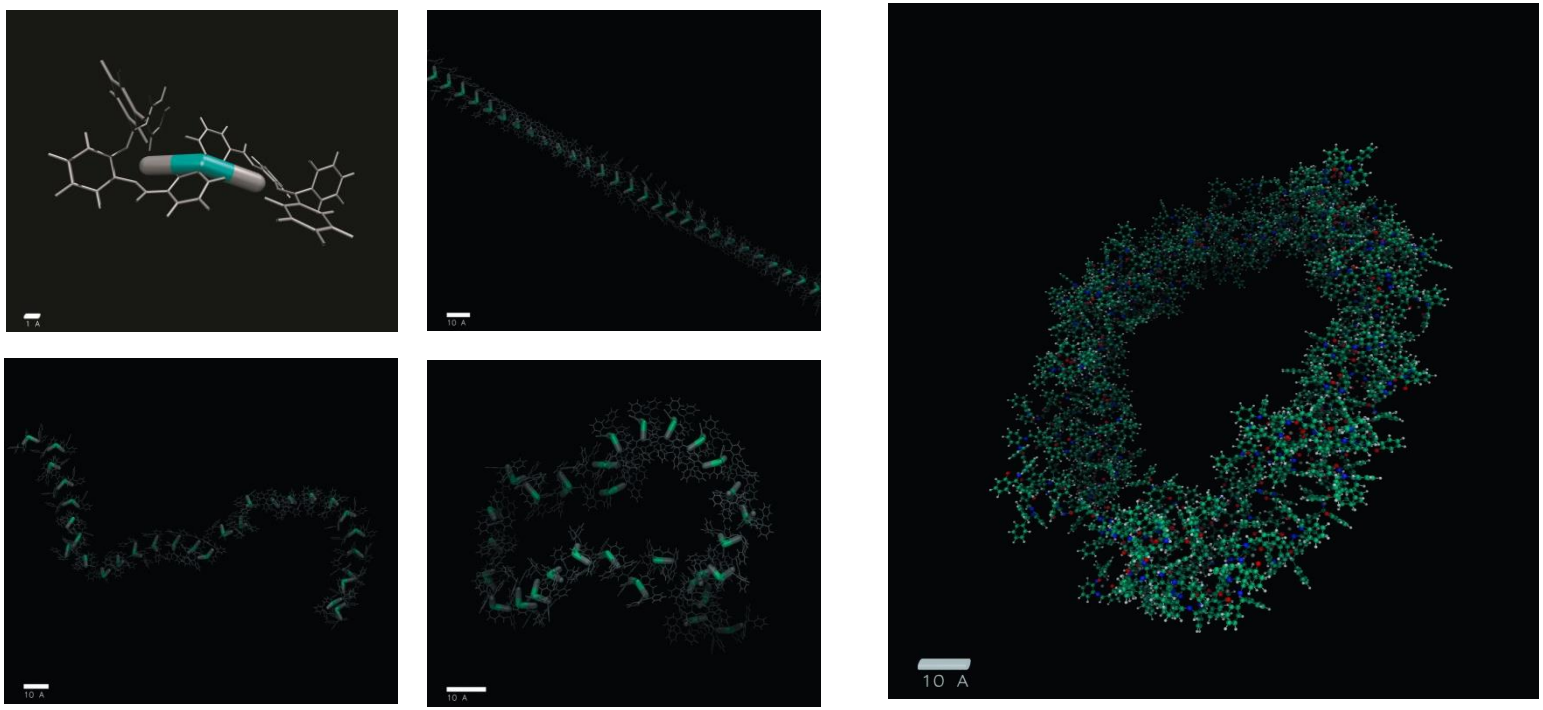
MD study of tetrakis-Schiff molecular rings:



DREIDING force-field + DFT derived charges

Single and multi-molecular thick strings collapse into ring-like structures show no structural changes over microsecond simulation times

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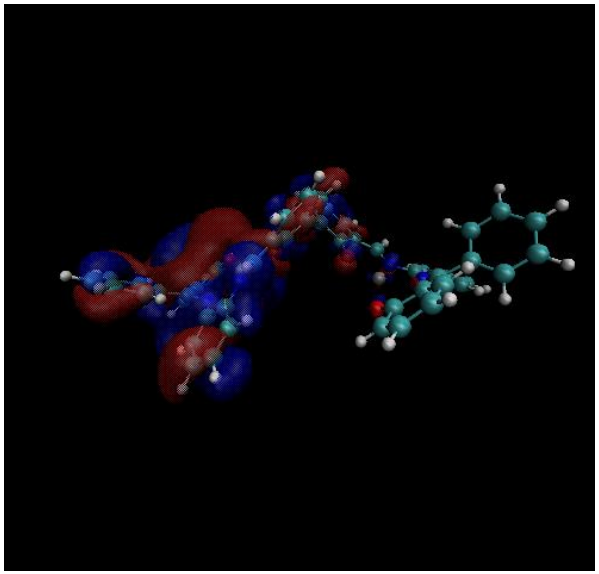
Electron transfer in single tetkaris-Schiff base molecular system

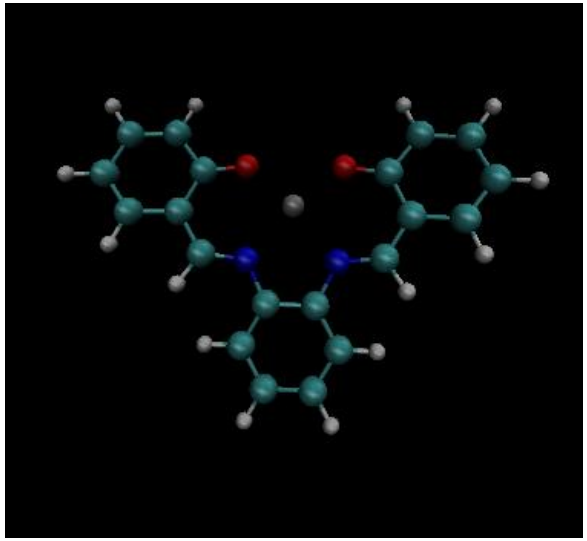


Flexible wedge-like structure:

- consists of 2 symmetric bases;

- provides stability in multi-molecular systems ;

- Is a hell to optimize!



Single base compound:

- easier to optimize;

- features the basic phenomenon: cation-pi interaction;

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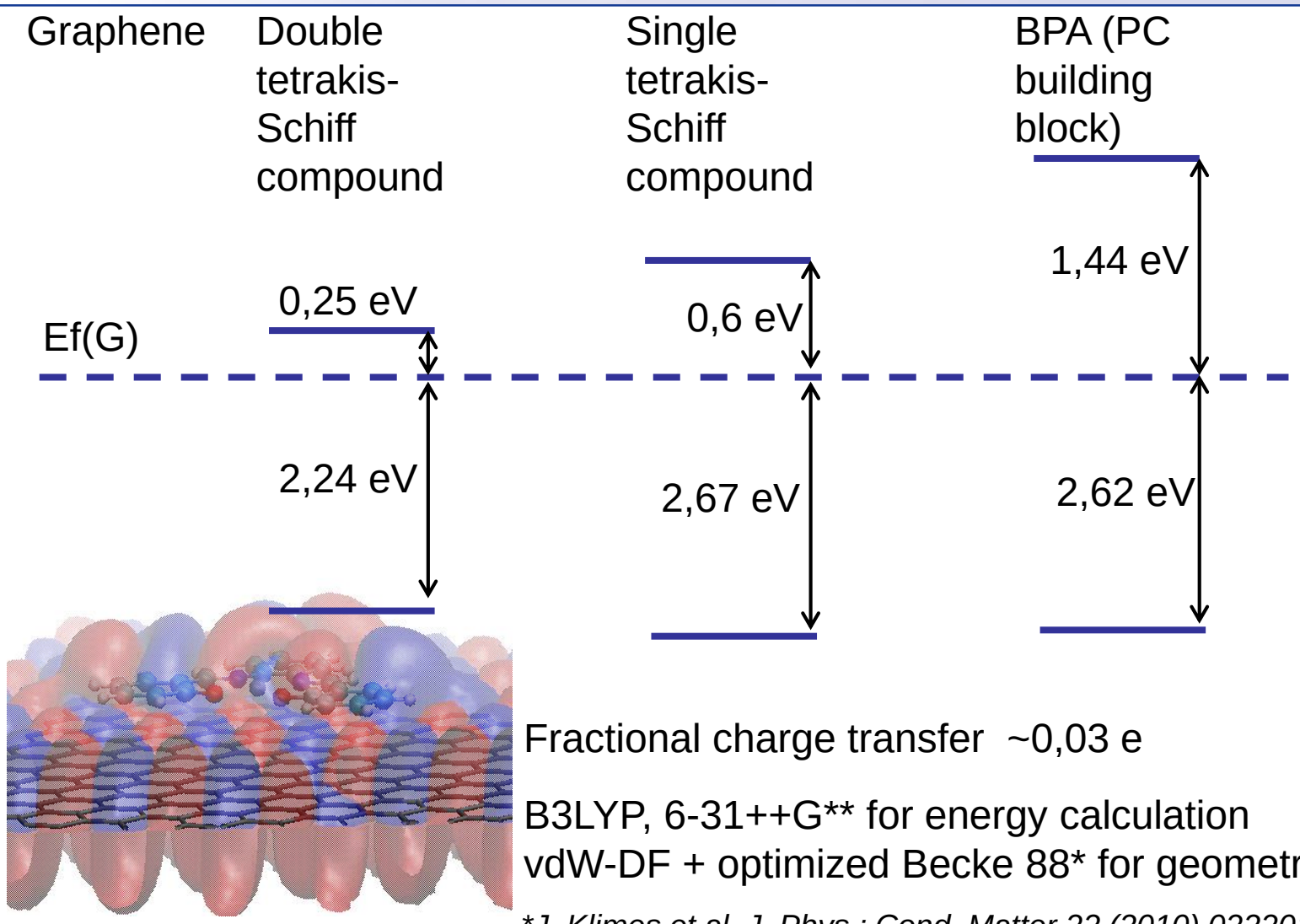
Single molecule electronic structure



Fractional charge transfer ~0,03 e

B3LYP, 6-31++G** for energy calculation
vdW-DF + optimized Becke 88* for geometry

**J. Klimes et al. J. Phys.: Cond. Matter 22 (2010) 022201*

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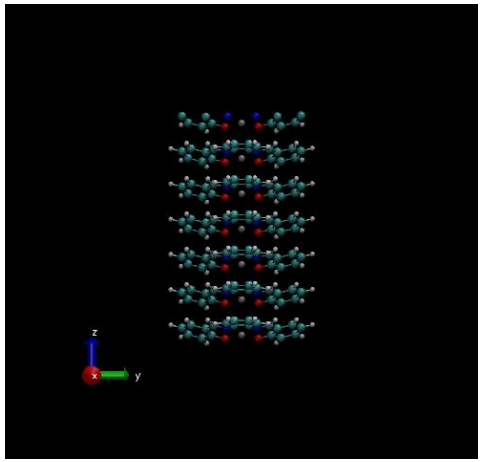
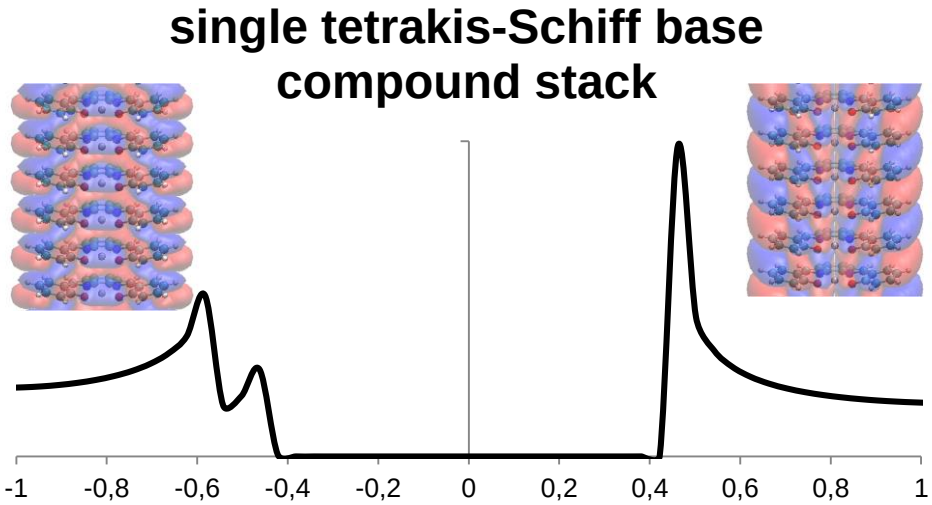
Electron transfer in single tetkaris-Schiff base molecular system





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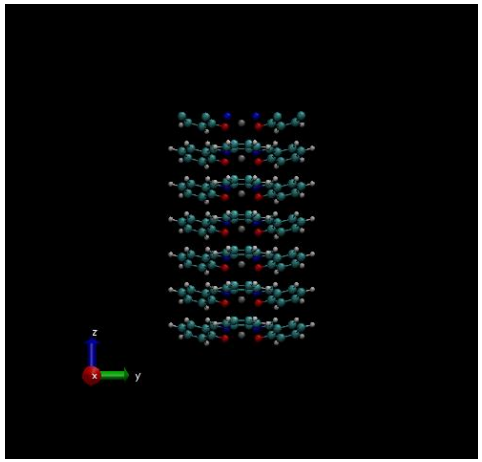

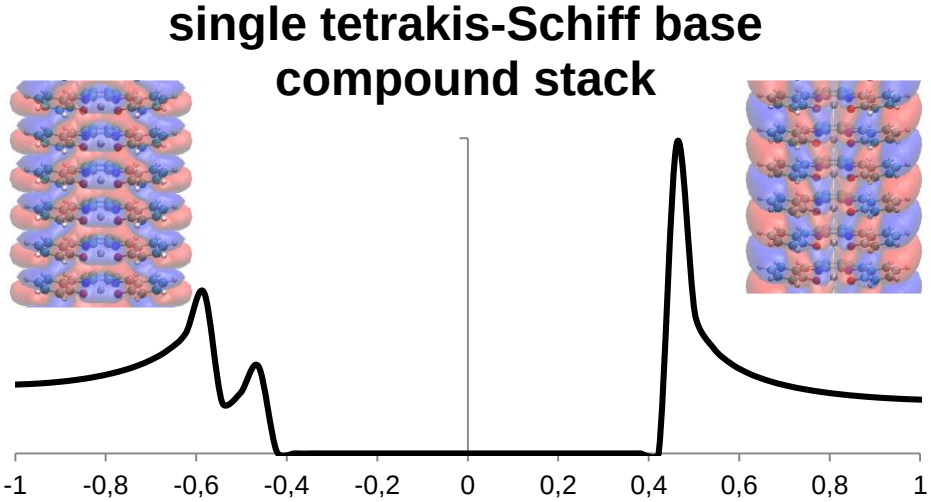

Expectation

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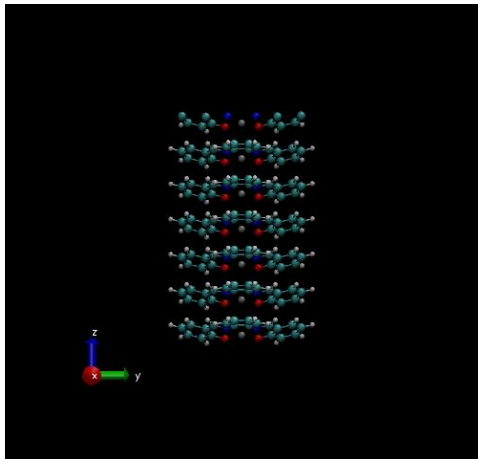

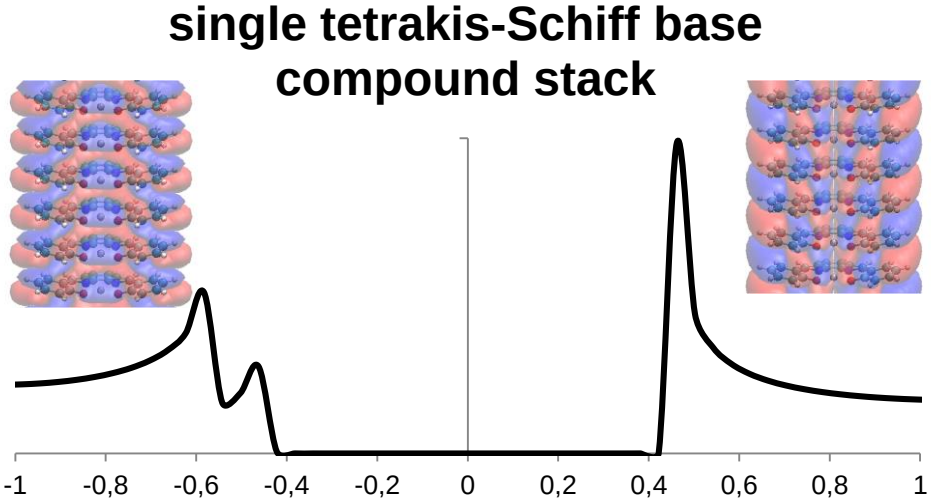

Expectation

Reality

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Electron transfer in single tetkaris-Schiff base molecular system

$$\lambda = \left(E_0^- - E_0\right) + \left(E_{-1}^0 - E_{-1}\right)$$ → 146,4 meV

$$V = \frac{J - S_{ij}\left(E_{ii} + E_{jj}\right)/2}{1 - S_{ij}^2}$$ → 152,3 meV

$$K = \frac{|V|^2}{\hbar}\left(\frac{\pi}{\lambda k_B T}\right)^{1/2} \exp\left(\frac{\lambda}{4 k_B T}\right)$$ → $2{,}5 \times 10^{14}\ s^{-1}$

$$D = \frac{1}{2n}\sum_i r_i^2 K_i P_i$$ → $2{,}33 \times 10^{-2}\ cm^2/s$

$$\mu = \frac{eD}{k_B T}$$ → $0{,}9\ cm^2/Vs$

R. Marcus Rev. Mod. Phys. 65, 599, 1993.

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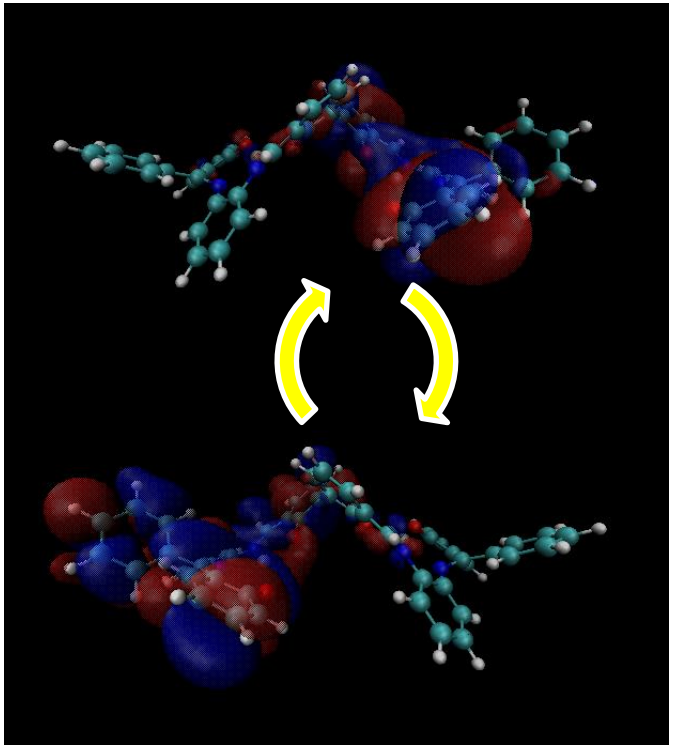
Work in progress:

- *Constrained DFT study of charge transfer in double-base compounds;*



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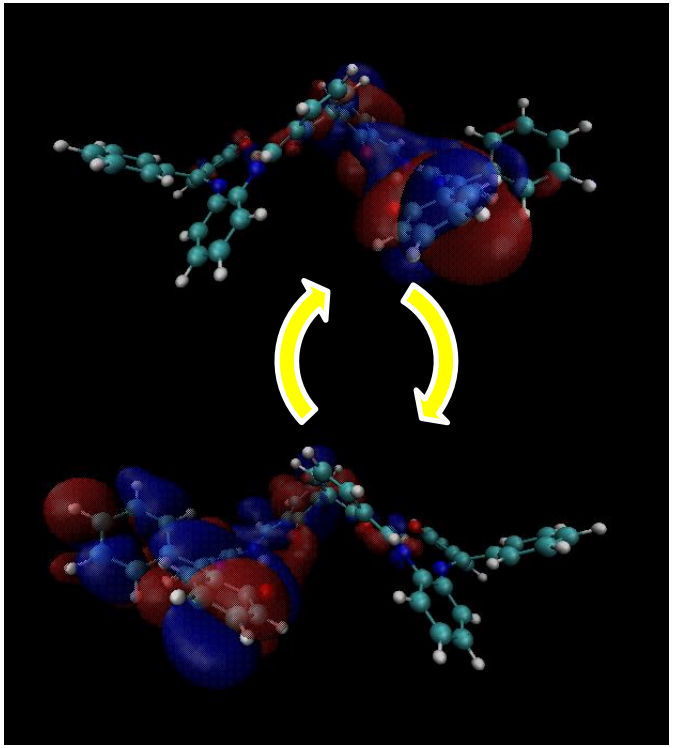
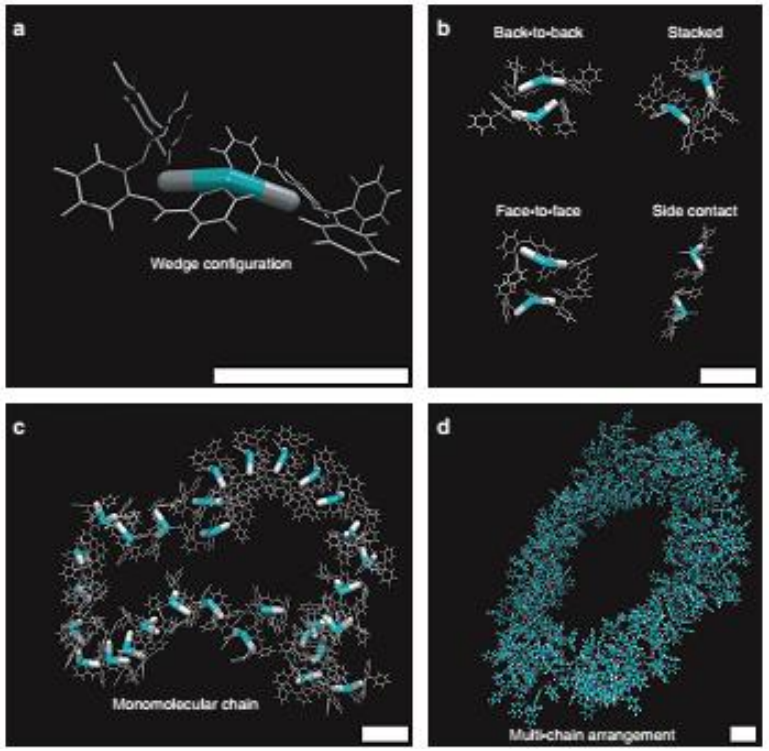


•*MC study of charge transport in CNT-tetrakis-Schiff base compounds;*



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CONTACT

THANK YOU!

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SEVENTH FRAMEWORK PROGRAMME

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