

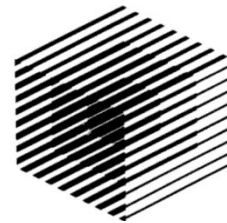
Electronic and optical properties of PAH families: a (time-dependent) DFT study

Giancarlo Cappellini¹

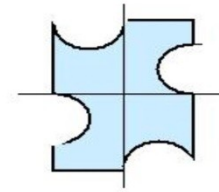
Giuliano Mallocci¹

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CNR-IOM



SLACS



UniCA Cagliari

Giacomo Mulas²

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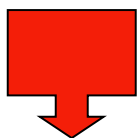
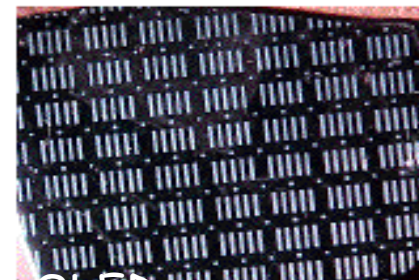
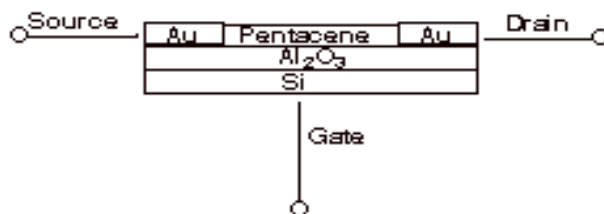


AstroC-Hemistry Group

Cagliari

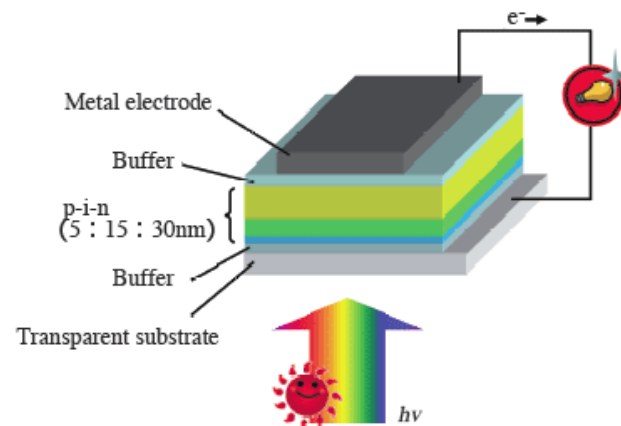
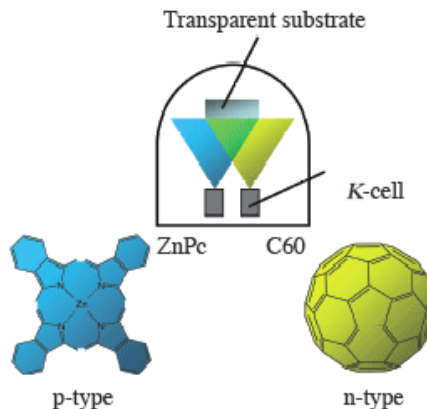
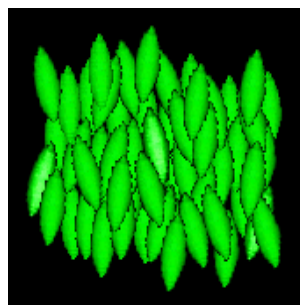
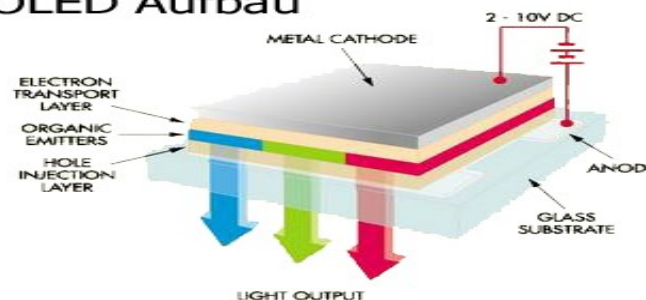
Polycyclic Aromatic Hydrocarbons (PAHs)

Large class of conjugated π -electrons systems of fundamental importance in chemistry, materials science and technology: e.g. Optoelectronics applications



PAHs can be found in devices such as organic Thin-Film FET, LED, Photovoltaic Cells and Liquid Crystals.

OLED Aufbau



The present study

Oligoacenes, N-Phenacenes, Circumacenes, Oligorylenes

A comprehensive comparative theoretical study of four homologous classes of PAHs in their neutral, cationic and anionic charge-states is proposed.

We calculate structural, electronic properties, absorption spectra, electronic transport properties of five members for each of the following families: oligoacenes, n-phenacenes, circumacenes and oligorylenes .

This choice of the families was motivated by the availability of reliable experimental data for the first members for each class.

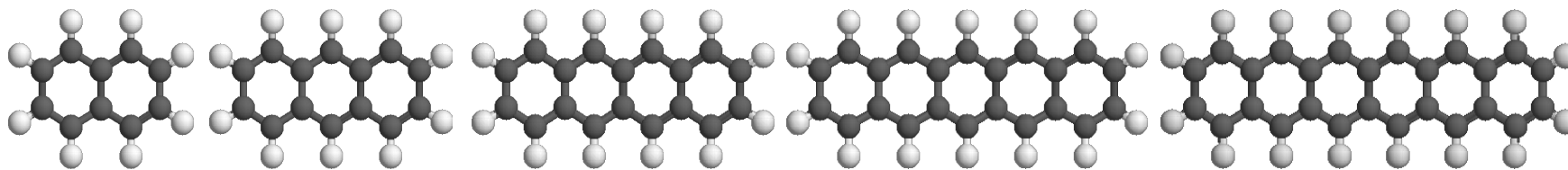
....moreover circumacenes and oligorylenes converge, at the infinite limit, to a zigzag and arm-chair edged graphene nanoribbon, respectively, and as such are promising candidates for organic and molecular electronics.

Oligoacenes

X in plane short direction

$C_{14}H_{10}$ anthracene

$C_{22}H_{14}$ pentacene



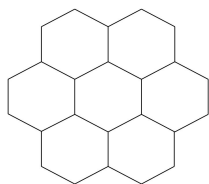
Y in plane long direction

$C_{10}H_8$ naphthalene

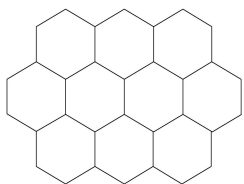
$C_{18}H_{12}$ tetracene

$C_{26}H_{16}$ hexacene

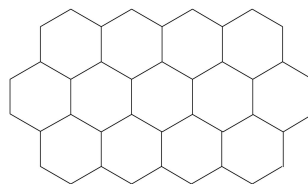
Circumacenes (first 4)



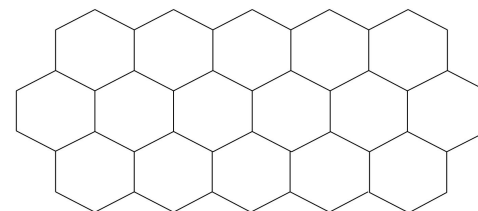
Coronene



Ovalene



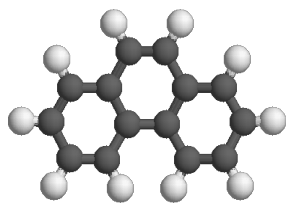
circumanthracene



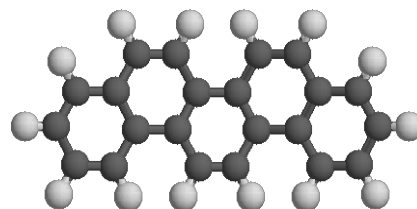
circumtetracene

N-phenacenes and Oligorylenes(first 4)

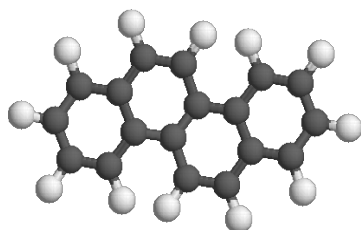
$C_{14}H_{10}$ phenanthrene



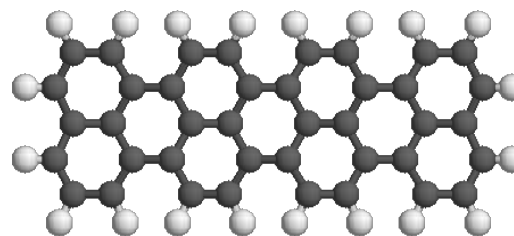
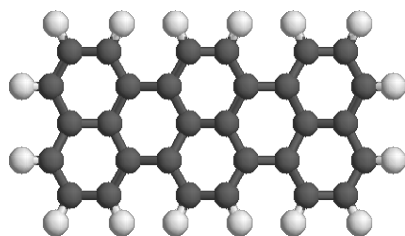
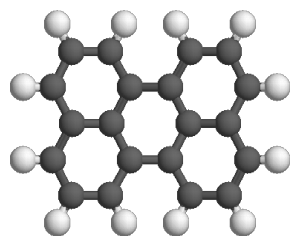
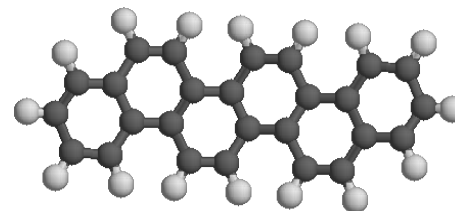
$C_{22}H_{14}$ picene



$C_{18}H_{12}$ chrysene

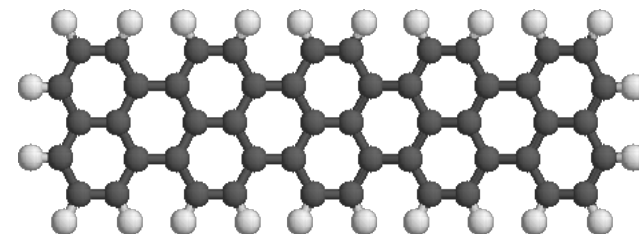


$C_{26}H_{16}$ fulminene



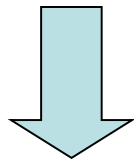
perylene($C_{20}H_{12}$), terrylene($C_{30}H_{16}$)

quaterrylene($C_{40}H_{20}$), pentarylene($C_{50}H_{24}$)

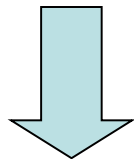


Computational Procedure

NWCHEM

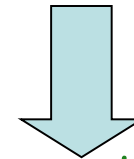
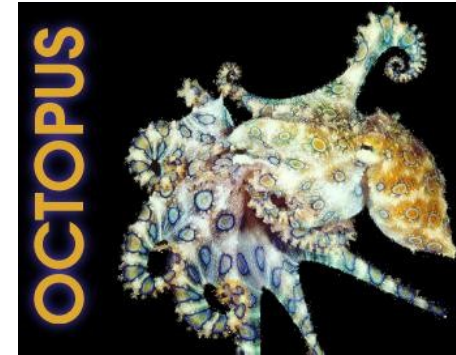


Density
Functional
Theory

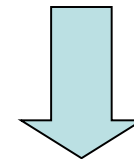


Ground-state
properties

OCTOPUS

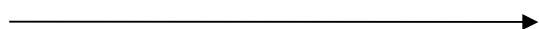
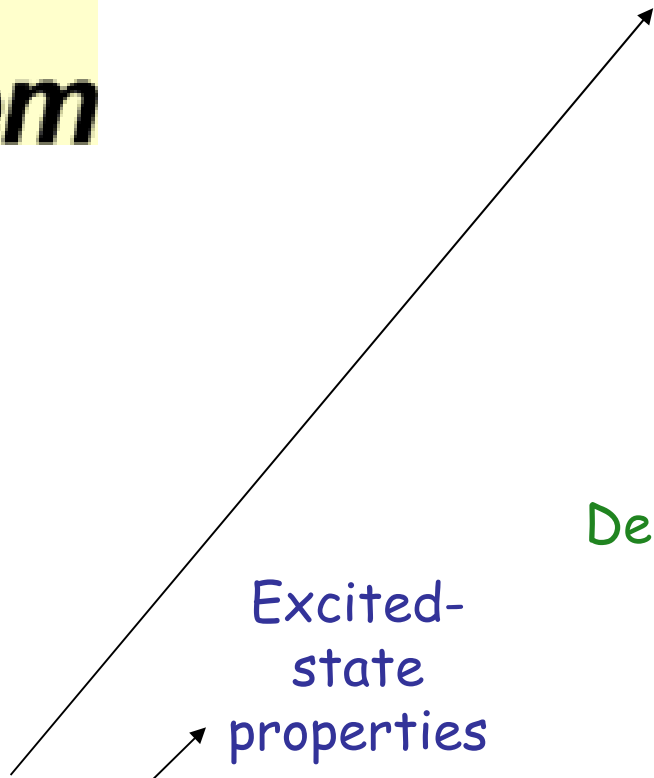


Time-Dependent
Density Functional Theory



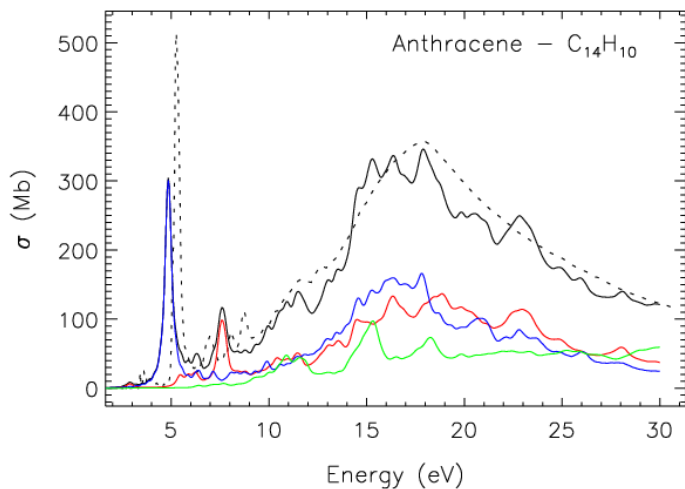
Excited-
state
properties
(Δ SCF)

PhotoAbsorption Spectra

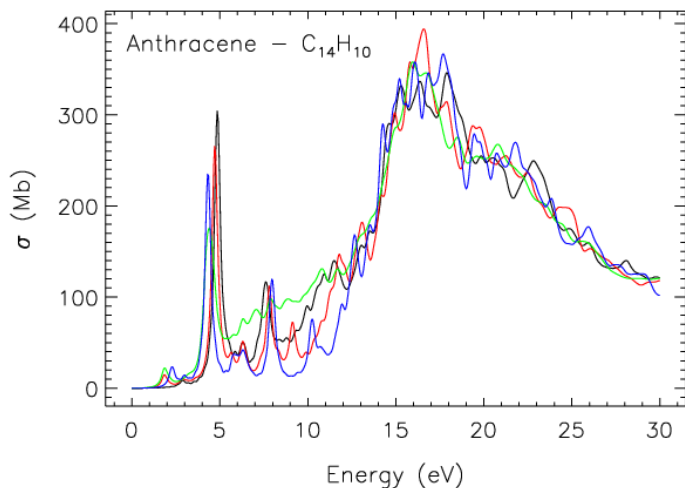


Electronic Excitations (Acenes-I)

neutral anthracenecomparison with experiment



Computed photo-absorption cross-section σ of neutral anthracene (continuous line) and the gas-phase absorption spectrum (dotted line) after Joblin et al. *Astrophys.J.* (1992). Three components: **blue** (y-axis, in-plane long), **red** (x-axis, in-plane short) and **green** (z-axis, out-of-plane). The real-time real-space TD-DFT approach provides results in good agreement with the available experimental data for neutral species up to about 30 eV. **The broad absorption band peaking at about 17.5 eV, which is due mainly to $\sigma \rightarrow \sigma^*$ spectral transitions, is well reproduced both in position and width.**

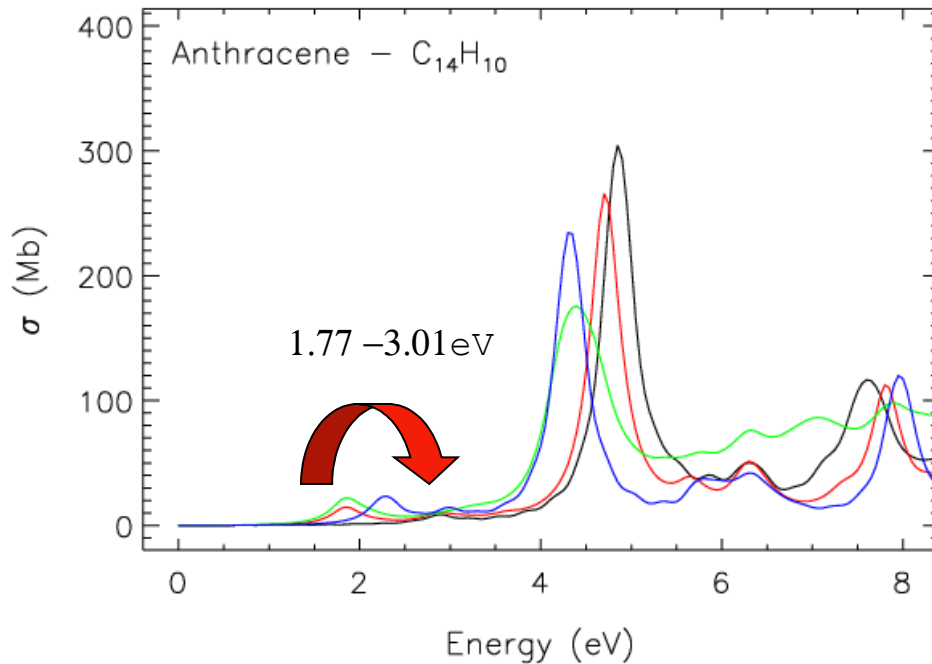


Computed averaged photoabsorption cross-section σ of neutral anthracene (black line), anionic (**green**), cationic (**red**), and dicationic (**blue**) charge-dicationic state considered for acenes only-.



Electronic Excitations(Acenes-II)

In the low energy range

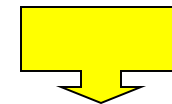


band	energy		Gas-phase
p(x)	3.21	[0.058]	3.43
α (y)	3.85	[<0.0 1]	3.84
β (Y)	5.14	[1.991]	5.24

Low-lying absorption bands/transitions (eV) p, α , β with corresponding oscillator strength [] and experimental data.

Neutral anthracene (black line), anionic(green), cationic(red), and dicationic (blue) charge.

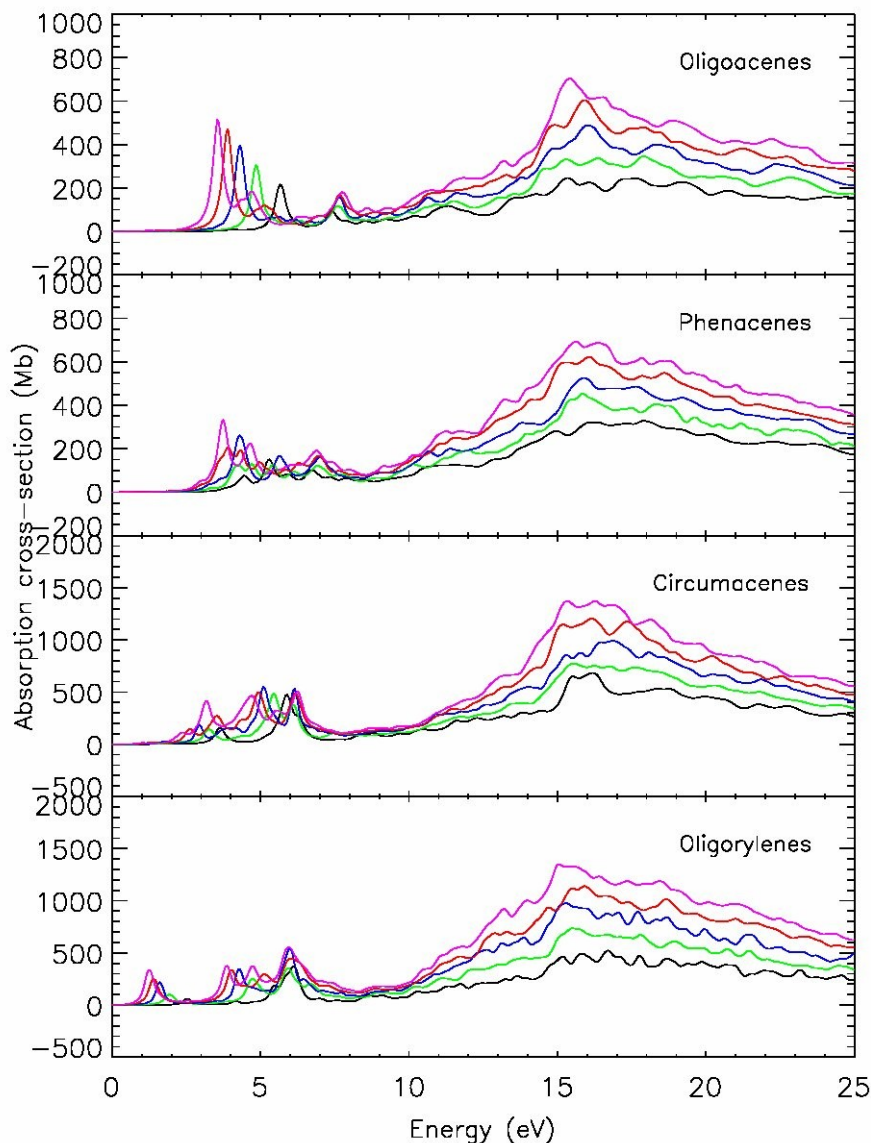
In opposition to neutral molecules anions, cations and **dications** (only acenes) show absorption in the visible



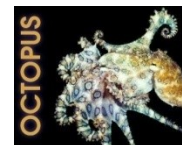
astrophysical consequences
(DIBs)



Absorption spectra for the neutral molecules



Computed photo-absorption cross-section σ of neutral molecules after TD-DFT real-time real-space method. All the spectra display a similar broad excitation peaking at 17-18 eV which involves mainly $\sigma \rightarrow \sigma^*$ transitions and which is relatively insensitive to the charge state of the molecule. The main differences among the families arise in the low-energy part of the spectrum from the near-UV up to about 8eV, which involves $\pi \rightarrow \pi^*$ transitions. **In particular each family displays a continuous redshift of the spectrum at increasing sizes.**



Formation Energies for the Ions (Acenes)

$$IE = E_{n-1} - E_n \text{ ionization energy}$$

$$EA = E_n - E_{n+1} \text{ electron affinity}$$

Adiabatic and vertical values (in parentheses), all data in eV, of electron affinities and single and double ionisation energies of the oligoacenes considered in this work ($C_{4n+2}H_{2n+4}$, $n=2, 3, 4, 5, 6$) as obtained through total energy differences at the B3LYP/6-31+G* level. For comparison we list also the experimental electron affinities and the single ionisation energies taken from the NIST Chemistry WebBook [44], as well as the second ionisation energies from the photon-impact measurements of Tobita et al. [31c].

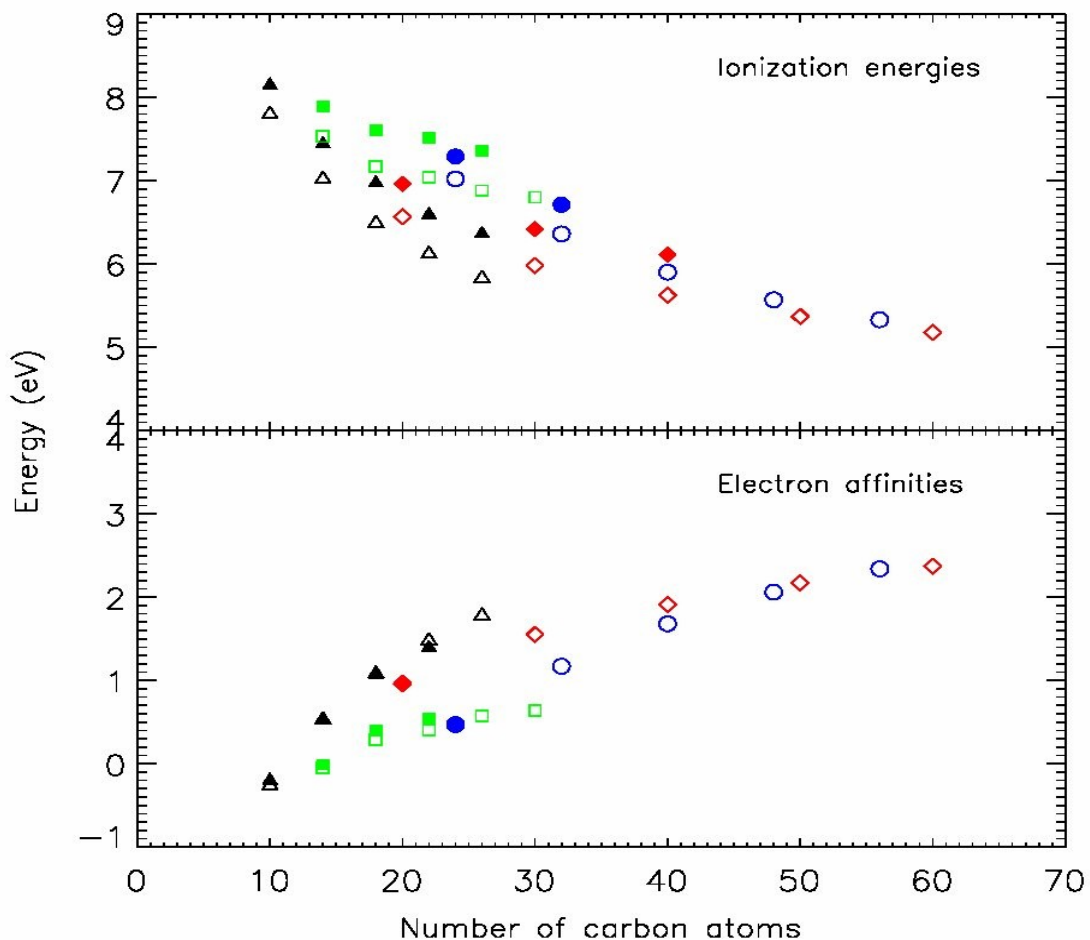
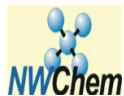
n	EA		First IE		Second IE	
	Ad.(Vert.)	Exp.	Ad.(Vert.)	Exp.	Ad.(Vert.)	Exp.
2	-0.26(-0.38)	-0.200±0.050	7.80(7.89)	8.144±0.001	20.99(21.35)	21.5±0.2
3	0.53(0.43)	0.530±0.005	7.02(7.09)	7.439± 0.006	18.70(18.95)	—
4	1.08(1.00)	1.067±0.043	6.49(6.55)	6.97±0.05	17.15(17.34)	18.6± 0.2
5	1.48(1.41)	1.392±0.043	6.12(6.16)	6.63±0.05	16.03(16.18)	17.4±0.2
6	1.78(1.72)	—	5.83(5.87)	6.36±0.02	15.18(15.30)	—

With respect to chemical accuracy (~0.1 eV) good accordance for EA , larger discrepancies for IE as expected.*

*Kadantsev, Stott, Rubio, J. Chem.Phys. 2006



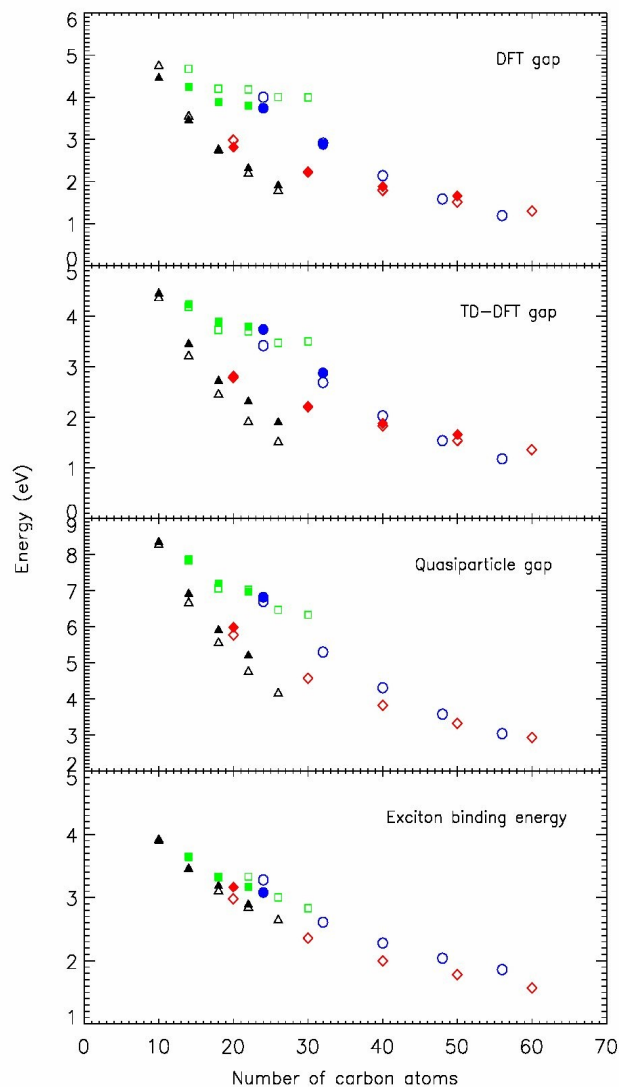
Ionisation energies and electron affinities.....trends for the families under study



Computed adiabatic ionization energies and electron affinities as a function of size for oligoacenes (black triangles), phenacenes (green squares), circumacenes (blue circles), and oligorylenes (red diamonds). If available the corresponding experimental values are represented by the filled symbols.

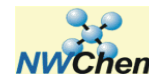
Oligoacenes display the largest variations for ionization energies and electron affinities as a function of molecular size. Phenacenes show the smallest ones. Circumacenes and oligorylenes behave in the same way at increasing sizes, with IE reaching the value of about 5.2 eV and EA of about 2.4 eV

Electronic excitation energies via Δ SCF calculations: trends for all the considered PAHs



Computed HOMO-LUMO, TD-DFT, quasiparticle corrected energy gaps, and exciton binding energy as a function of molecular size for oligoacenes (black triangles), phenacenes (green squares), circumacenes (blue circles), and oligorylenes (red diamonds) calculated within Δ SCF scheme. If available, the corresponding experimental values are represented with filled symbols.

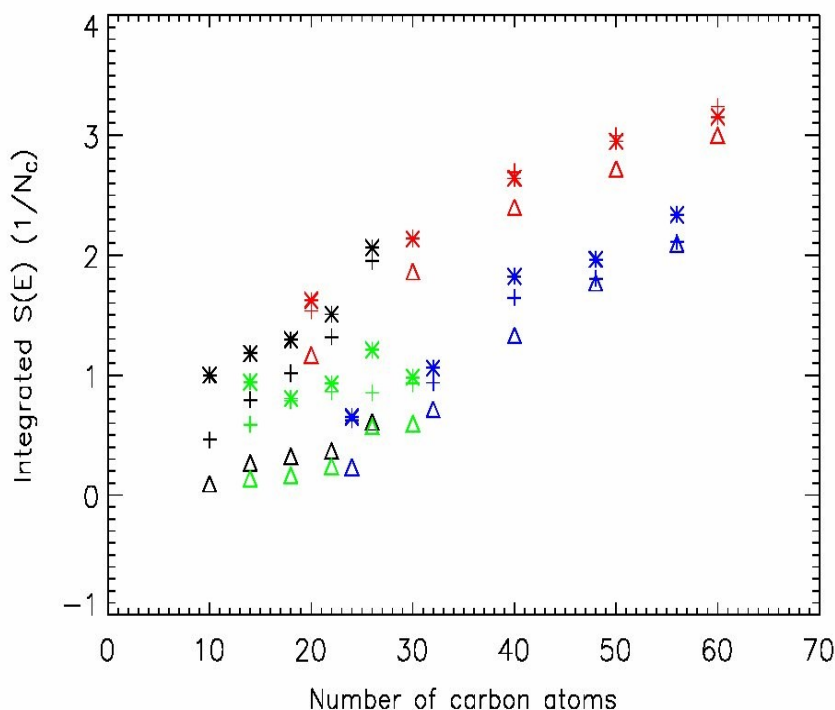
QP energies and excitonic binding energies decrease with increasing N . Strong excitonic effects ranging for acenes from 3.9 eV for naphthalene to 2.6 eV for hexacene take place. We found in all cases excitonic effects due both to quantum confinement and reduction of the screening; E_b decreases as the size of the molecule increases with similar slope for the different families and approaches the value of about 1.6-1.8 eV for the largest molecules considered.



Intergrated S(E).....

Dipole-strength function;

$$S(\omega) = (m_e c / p h e^2) \sigma(\omega)$$



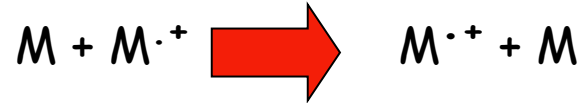
Comparison between the integrated values in the range 1.0-3.0 eV of the individual dipole strength-function $S(E)$ divided by the total number of the carbon atoms for the anions(asterisks), neutrals(triangles), cations(crosses) of acenes(black), phenacenes(green), circumacenes(blue), and oligorylenes(red) as a function of molecular size.

The integrated strength function does increase when going from the neutral to the cation and anion. The effect is more pronounced for acenes and phenacenes. The scatter between different charge states decreases with increasing molecular size. Oligorylenes appear to be more efficient in absorbing low-energy photons in comparison to other classes.(e.g. 80% more for quaterrylene than circumantracene).



Charge Transfer (CT) parameters

From chemical standpoint the CT process can be expressed as a self-exchange electron-transfer (ET) reaction scheme



with CT rate (mobility of the carriers) $K^{ET} \sim \exp(-\lambda/4K_B T)$

where λ is the **intramolecular reorganization energy**

in our case (isolated molecule) $\lambda = \lambda_1 + \lambda_2$

where λ_1 (radical ion formation energy) = $E(M^{\cdot+}/M) - E(M^{\cdot+})$

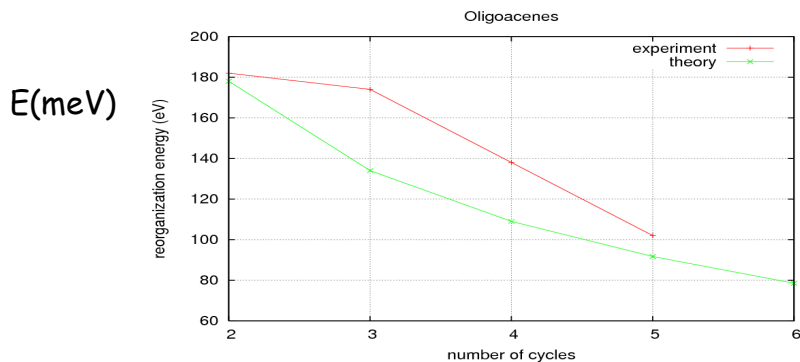
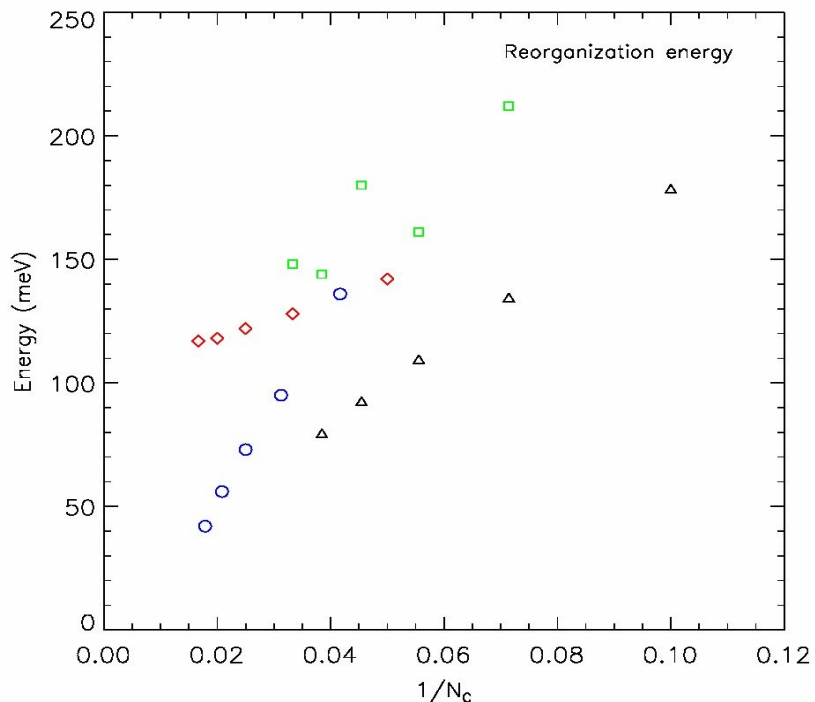
and λ_2 (relaxation energy of the charged state) = $E(M/M^{\cdot+}) - E(M)$

$E(M)$ and $E(M^{\cdot+})$ are the energies of the neutral and ionized molecules at their equilibrium structures respectively

$E(M/M^{\cdot+})$ is the energy of the neutral molecule when adopting the radical-cation geometry

$E(M^{\cdot+}/M)$ is the energy of the radical-cation when adopting the optimal neutral geometry

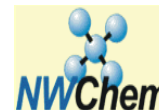
Reorganisation energies for all the families

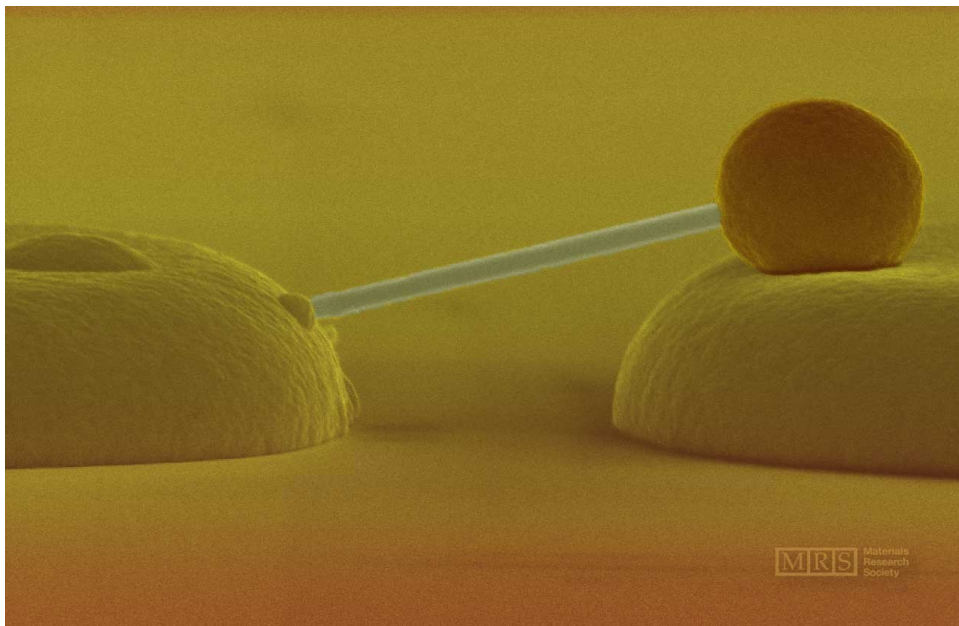


Molecular reorganization energies (RE) for acenes (black triangles), phenacenes (green squares), circumacenes (blue circles), and oligoarylenes (red diamonds), as a function of the inverse of Carbon atoms.

RE is expected to be inversely proportional to the total number of Carbon atoms. This general trend is here confirmed aside from phenacenes which display an oscillatory behaviour. While the RE of oligoarylenes decreases slowly as a function of molecular size, circumacenes display a more pronounced slope as compared to oligoacenes. These results are consistent with previous findings by other authors and confirm that circumacenes are good candidates for new emerging electronic transport technologies.

Reorganisation energies for oligoacenes: theory versus experiment



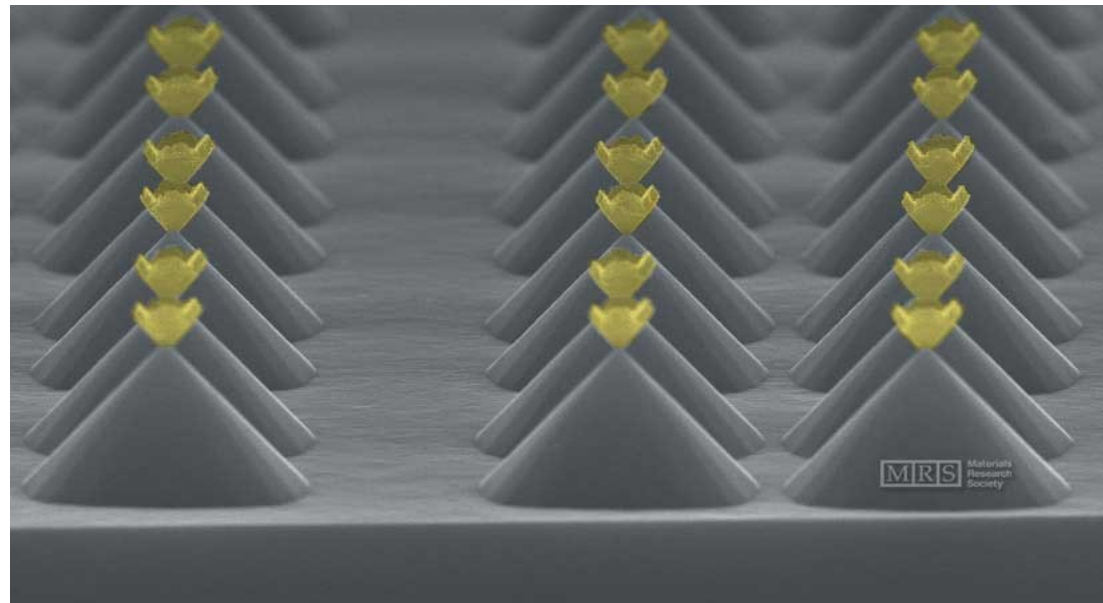


Seminar dedicated to the memory of Prof. Rodolfo Del Sole

Nano-pop

This picture is showing side-view of a silicon-nanowire held between and resting on two opposite nickel electrodes

Thank You for Your attention



Gold Nanopyramids

High resolution scanning electron micrograph (SEM) of gold nanopillars supported by silicon pedestals.