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

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# Polycyclic Aromatic Hydrocarbons (PAHs)

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



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



# The present study

# Oligoacenes, N-Phenacenes, Circumacenes, Oligorylenes

A conprehensive comparative theoretical study of four homologous classes of PAHs in their neutral, cataionic 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 promosing candidates for organic and molecular electronics.



Circumacenes (first 4)



Coronene

Ovalene

circumanthracene

circumtetracene

## N-phenacenes and Oligorylenes(first 4)



### **Computational Procedure**



# Electronic Excitations (Acenes-I)

neutral anthracene ....comparison with experiment



Computed photo-absorption cross-section  $\sigma$  of neutral anthracene (continuous line) and the gasphase absorption spectrum (dotted line) after Joblin et al. Astrophys.J. (1992). Three components: blue (y-axis, in-plane long), red(xaxis,in-plane short) and green(z-axis, out-ofplane). 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 crosssection  $\sigma$  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	y Ga	s-phase
p(x)	3.21	[0.058]	3.43
α(γ)	3.85	[<0.0 1]	3.84
β <b>(</b> Ϋ)	5.14	[1.991]	5.24

Low-lying absorption bands/transitions (eV)  $p, \alpha, \beta$  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 crosssection  $\sigma$  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 incresing sizes.



# Formation Energies for the Ions (Acenes)

# IE = $E_{n-1}-E_n$ ionization energy EA = $E_n - E_{n+1}$ 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<sup>\*</sup> 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	${ m EA}$		First IE		Second IE	
	Ad.(Vert.)	Exp.	Ad.(Vert.)	Exp.	Ad.(Vert.)	Exp.
2	-0.26(-0.38)	$-0.200 \pm 0.050$	7.80(7.89)	$8.144 \pm 0.001$	20.99(21.35)	$21.5 \pm 0.2$
3	0.53(0.43)	$0.530 {\pm} 0.005$	7.02(7.09)	$7.439 \pm 0.006$	18.70(18.95)	
4	1.08(1.00)	$1.067 \pm 0.043$	6.49(6.55)	$6.97{\pm}0.05$	17.15(17.34)	$18.6{\pm}~0.2$
5	1.48(1.41)	$1.392 {\pm} 0.043$	6.12(6.16)	$6.63 {\pm} 0.05$	16.03(16.18)	$17.4 \pm 0.2$
6	1.78(1.72)		5.83(5.87)	$6.36 {\pm} 0.02$	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 $\triangle$ 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  $\triangle$ 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<sub>e</sub> c/p he<sup>2</sup>) $\sigma(\omega)$ 



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 funcion 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 lowenergy 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 selfexchange electron-transfer (ET) reaction scheme

$$M + M^{+} \longrightarrow M^{+} + M$$

with CT rate (mobility of the carriers)  $K^{ET} \sim \exp(-\lambda/4K_{B}T)$ where  $\lambda$  is the intramolecular reorganization energy in our case (isolated molecule)  $\lambda = \lambda_{1} + \lambda_{2}$ 

where  $\lambda_1$  (radical ion formation energy) = E(M<sup>+</sup>//M)-E(M<sup>+</sup>)

and  $\lambda_2$  (relaxation energy of the charged state) = E(M//M<sup>+</sup>)-E(M)

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

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

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

### Reorganisation energies for all the families



Molecular reoganization energies (RE) for acenes(black triangles), phenacenes( green squares), circumacenes(blue circles), and oligorylenes(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 oligorylenes 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 nanopyramids supported by silicon pedestals.