Clar Sextet Theory for low-dimensional carbon nanostructures: an efficient approach based on chemical criteria

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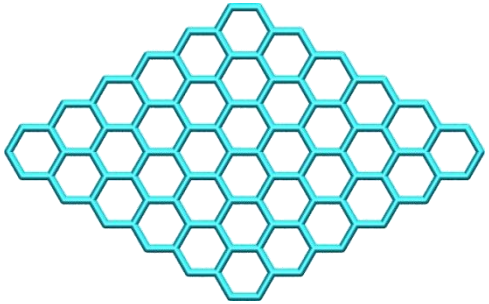
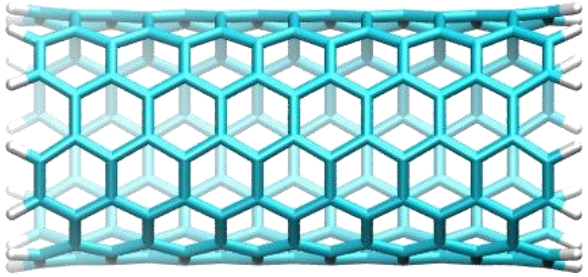
Carbon Nanostructures (CNSs)

0D

Graphene Quantum Dots (GQDs)

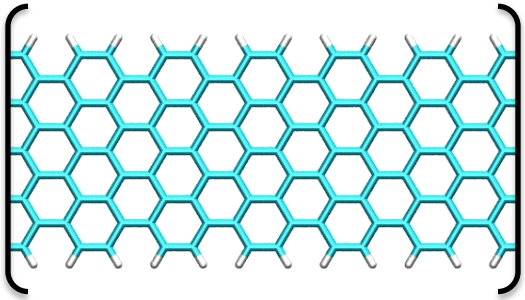


Finite length Carbon Nanotubes (FLCNTs)

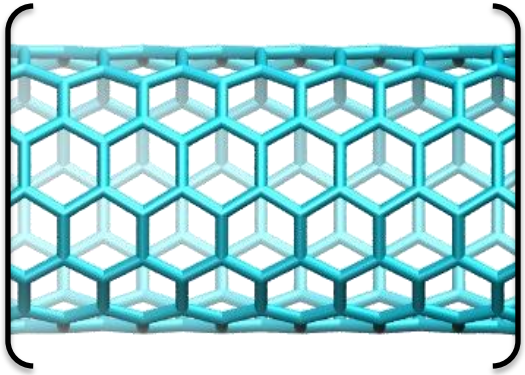


1D

Graphene Nanoribbons (GNRs)

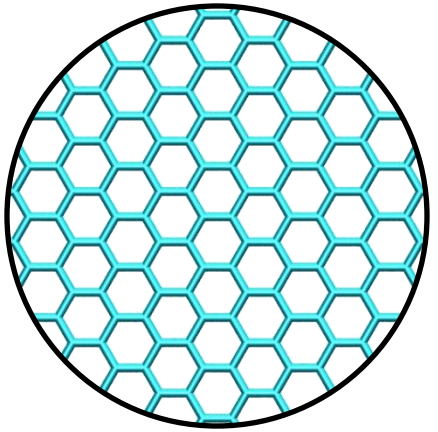


Carbon Nanotubes (CNTs)



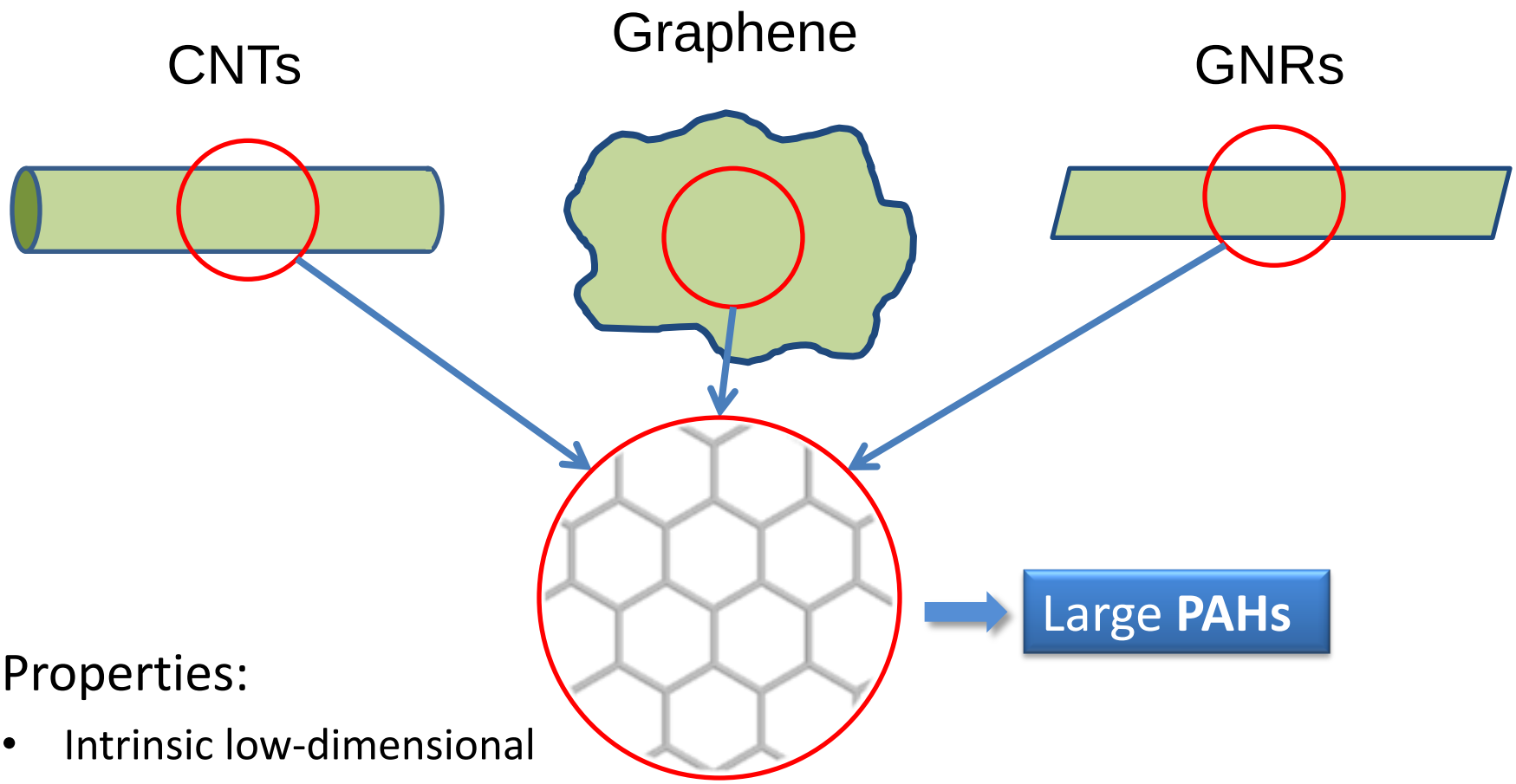
2D

Graphene



- Fullerenes
- Nano Onions
- Nano Cones
- Nano Horns
- etc…

Low-dimensional carbon nanostructures

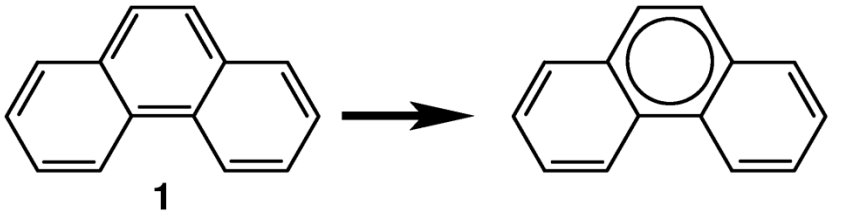


Properties:

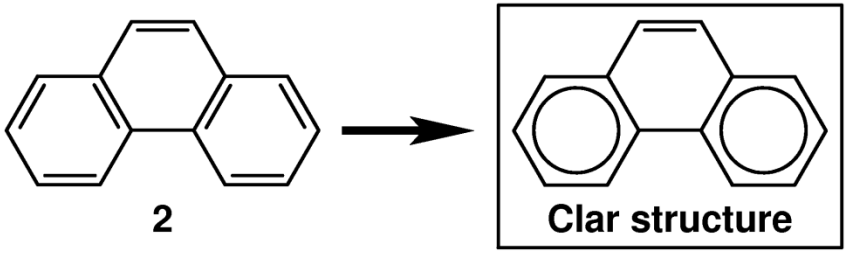
- Intrinsic low-dimensional
- Curvature/chirality

Real materials: ***terminations*** (non-infinite)

CLAR SEXTET THEORY



1



2

Clar VB model of the extra stability of 6n π-electron benzenoid species (PAH)

- Conventional two-electrons π-bonds (lines)
- Aromatic-sextets (six-electrons π-cycles) represented by circles

Clar's rule:

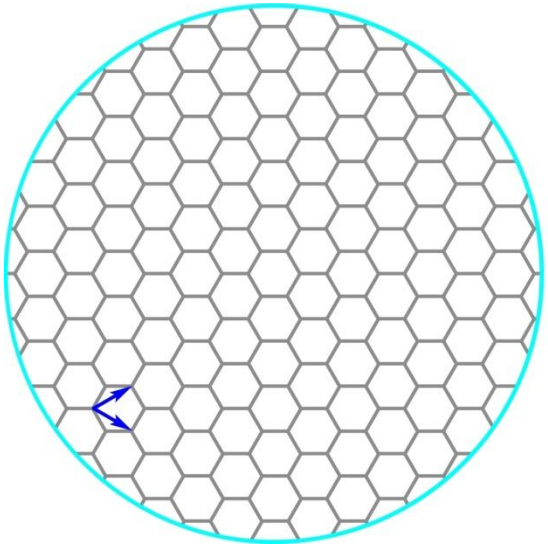
The most important Kekulè resonance structure is that with the largest number of disjoint aromatic-sextets

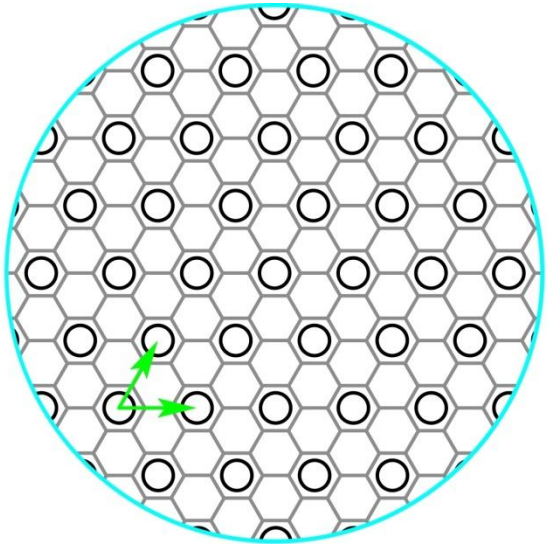
Clar structures with only aromatic-sextets is *fully-benzenoid*

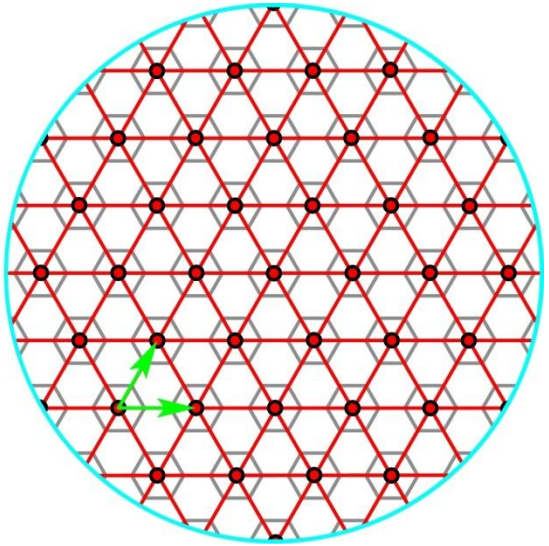
The number of Clar representations depends on the particular PAH considered

Confirmed by theory and experiments.

APPLICATION OF CLAR SEXTET THEORY TO THE CASE OF CNSs







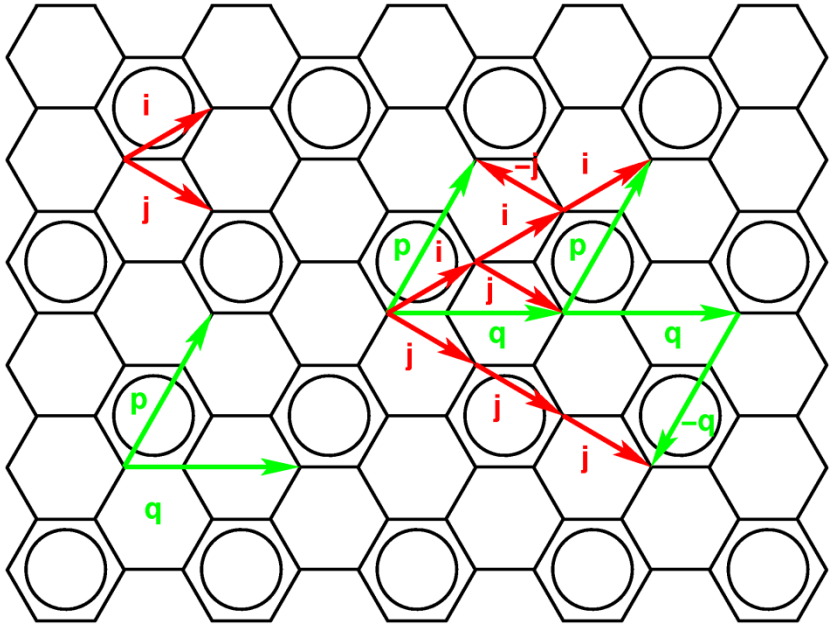
Conventional (*i,j*) basis vectors:

- 2 Carbon atoms
- Hexagonal pattern

Clar basis vectors:

- Aromatic sextet (6 carbon atoms)
- Triangular pattern
- Experimentally observed (STM)

APPLICATION OF CLAR SEXTET THEORY TO THE CASE OF CNSs



i,j unit vectors

$$n\boldsymbol{i} + m\boldsymbol{j}$$

Clar unit vectors

$$r\boldsymbol{p} + s\boldsymbol{q}$$

$$\boldsymbol{p} = 2\boldsymbol{i} - \boldsymbol{j} \qquad \boldsymbol{q} = \boldsymbol{i} + \boldsymbol{j}$$

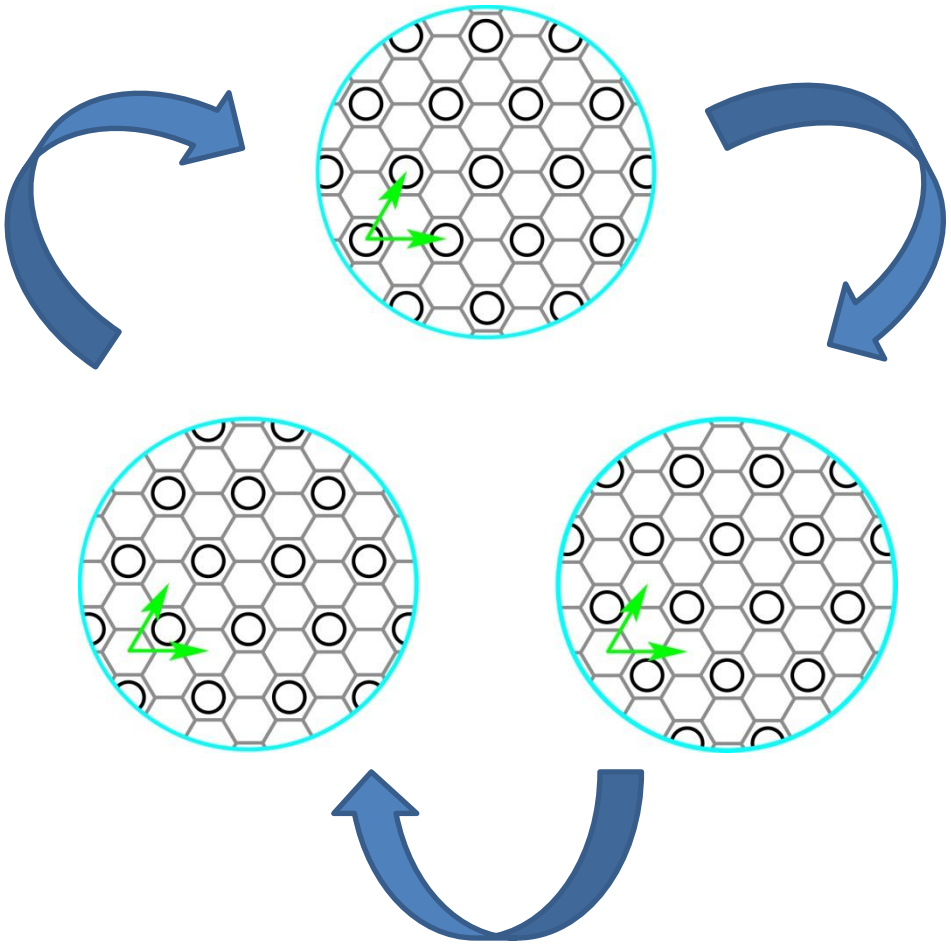
$$\boldsymbol{i} = \frac{\boldsymbol{p} + \boldsymbol{q}}{3} \qquad \boldsymbol{j} = \frac{2\boldsymbol{q} - \boldsymbol{p}}{3}$$

Relationship between ***i,j*** and Clar vector indexes

$$r = \frac{n - m}{3} \qquad s = \frac{n + 2m}{3} \qquad r, s \text{ integers}$$

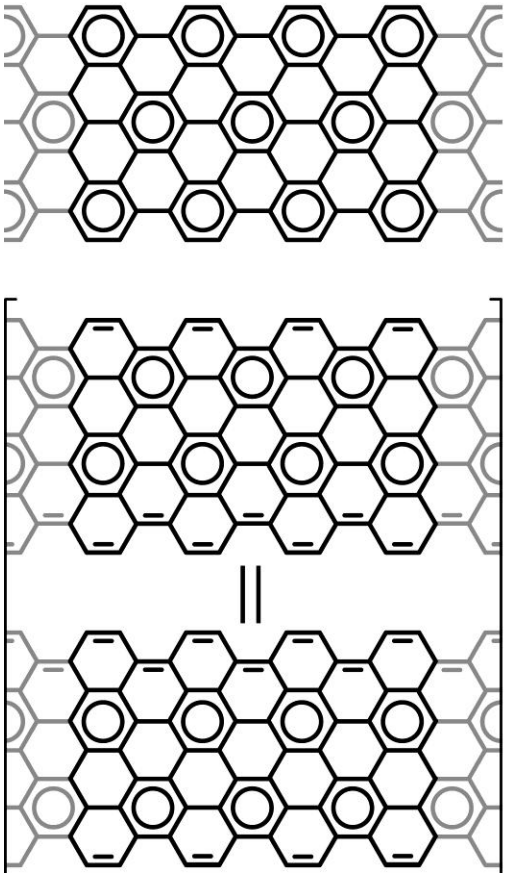
CNSs (n,m) fully benzenoid ⟺ mod(n-m,3)=0

Clar resonance hybrids for infinite length graphene (2D)

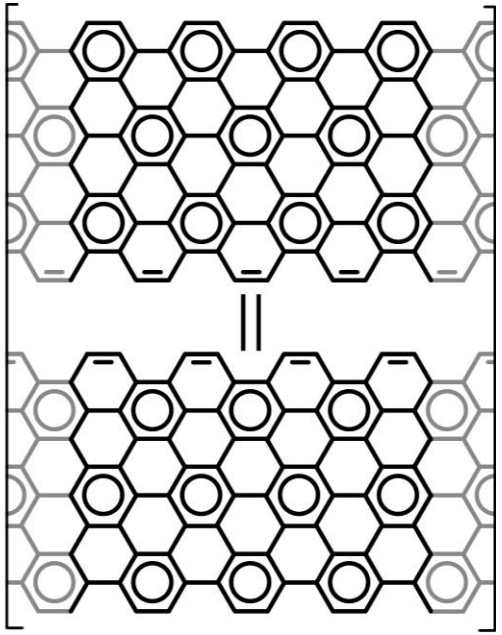


- Three equivalent Clar representation
- Each resonance hybrid has the same number of Clar aromatic sextet
- All C-C bond lengths are equivalent

Clar resonance hybrids for graphene nanoribbons (1D)



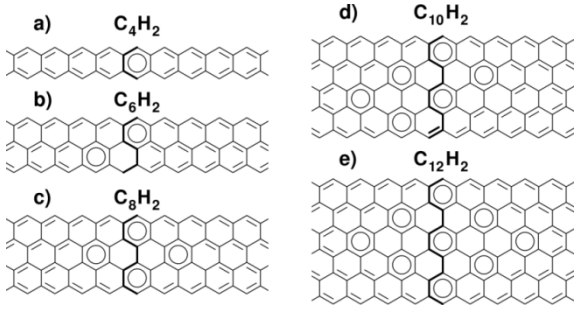
- **1D confinement**
- Unique best Clar representation (fully benzenoid)
- Less aromatic sextets in the other two Clar resonance hybrids



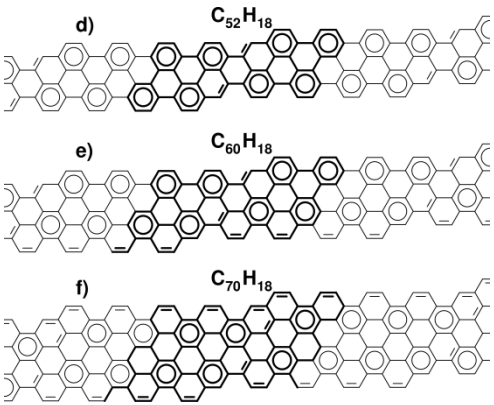
- Kekulé
- Best Clar representation is not unique

Electronic properties of GNRs: edge effects and Clar's sextet theory

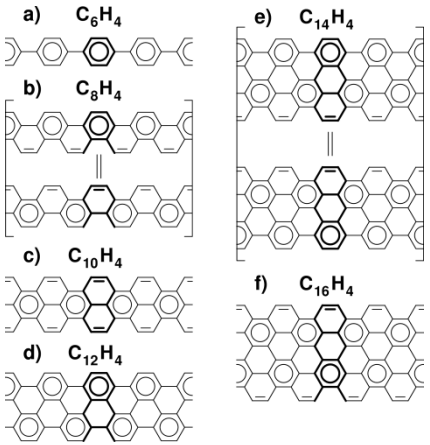
ZIG-ZAG

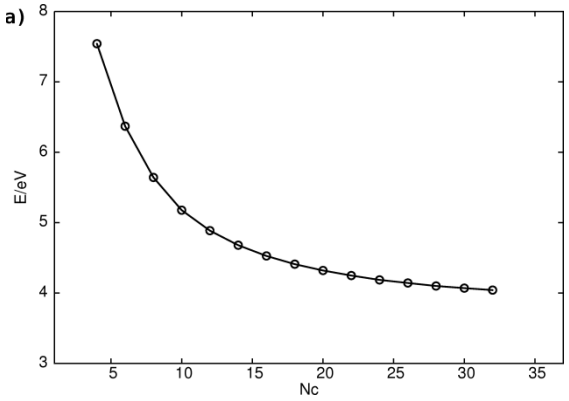


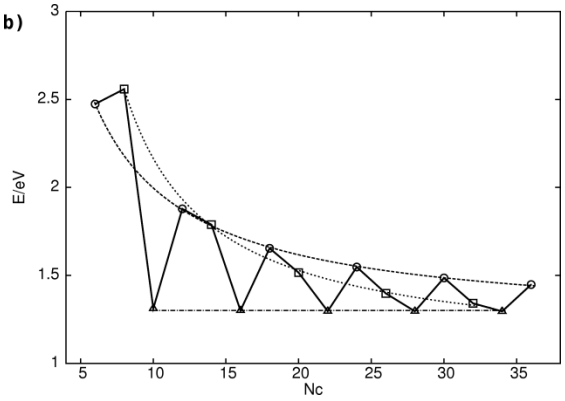
CHIRAL

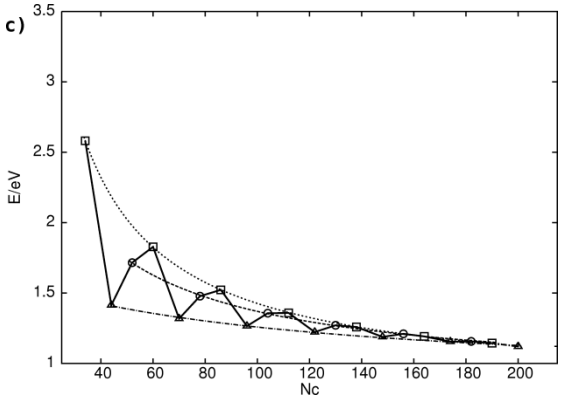


ARMCHAIR



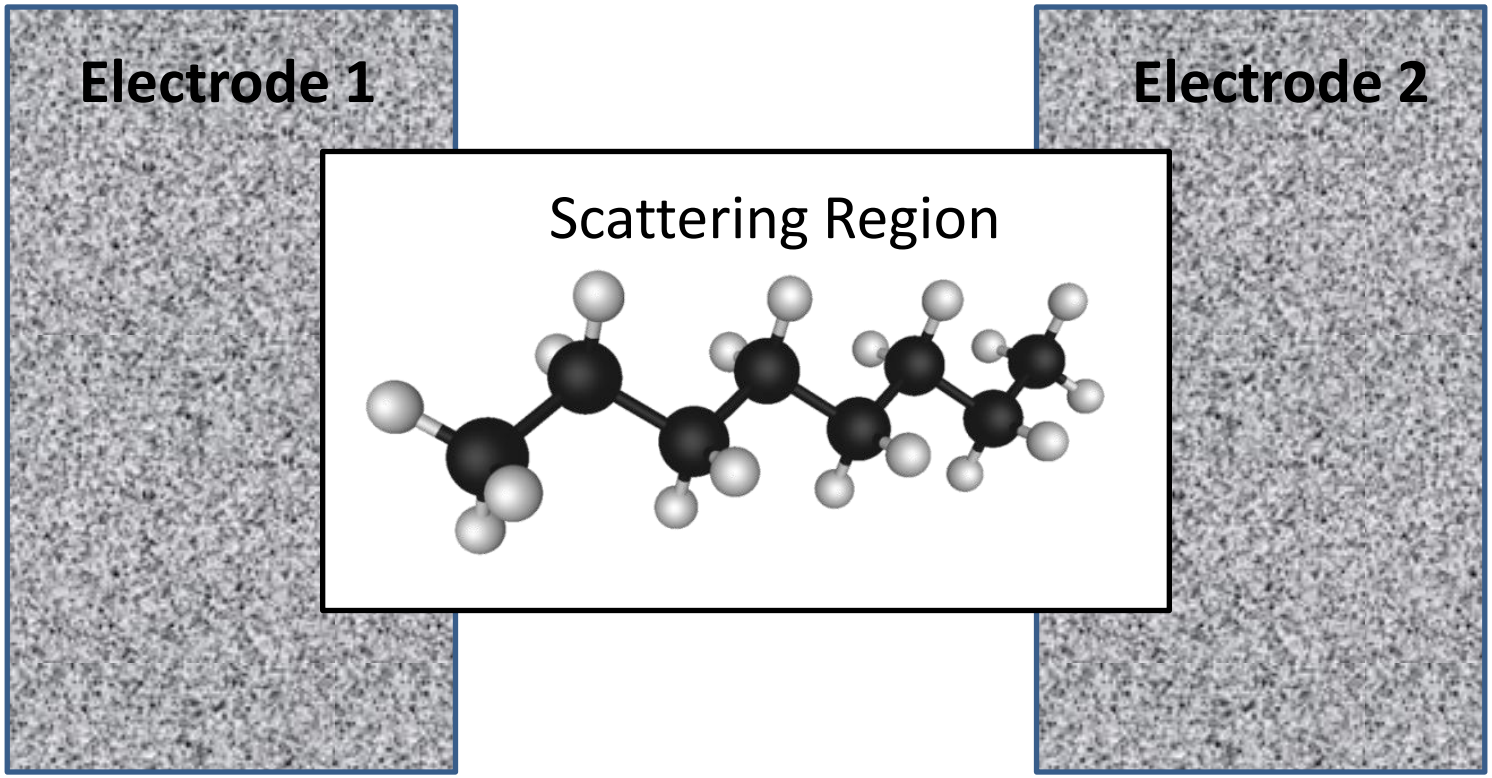






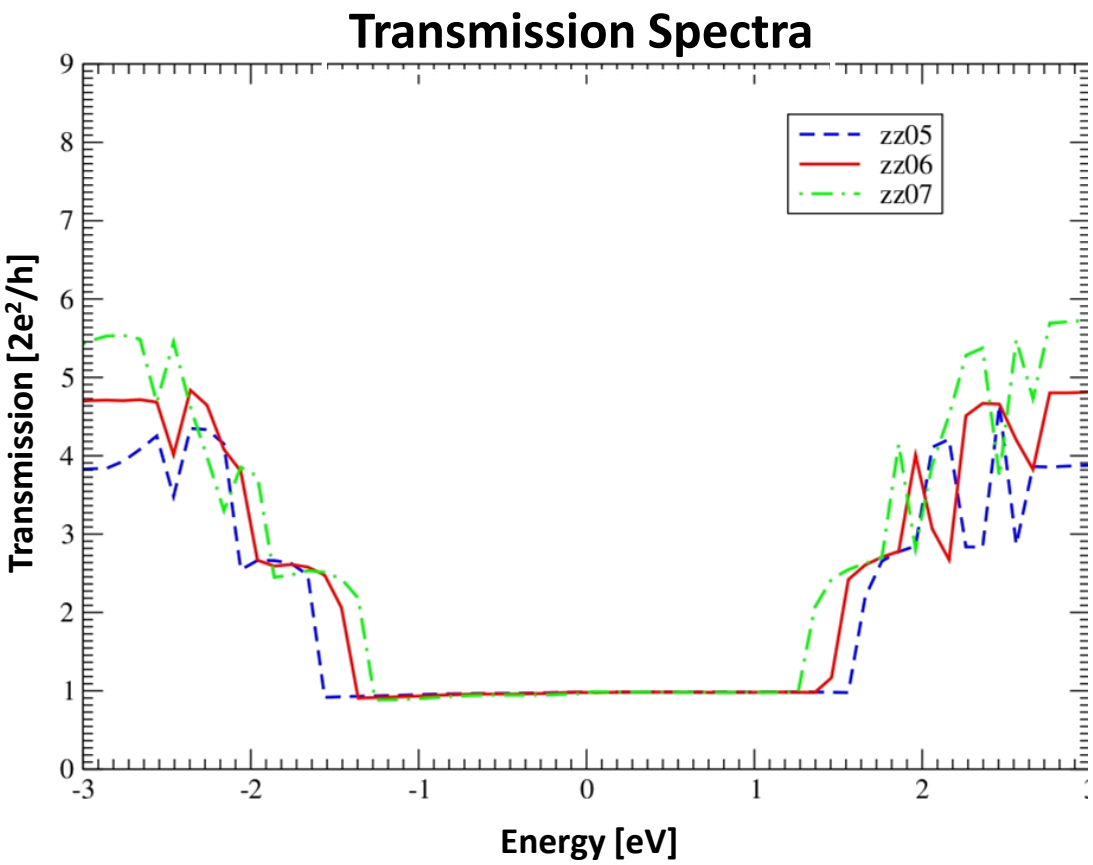
M. Baldoni, A. Sgamellotti and F. Mercuri, *Chem. Phys. Lett.*, **2008**, 464, 202

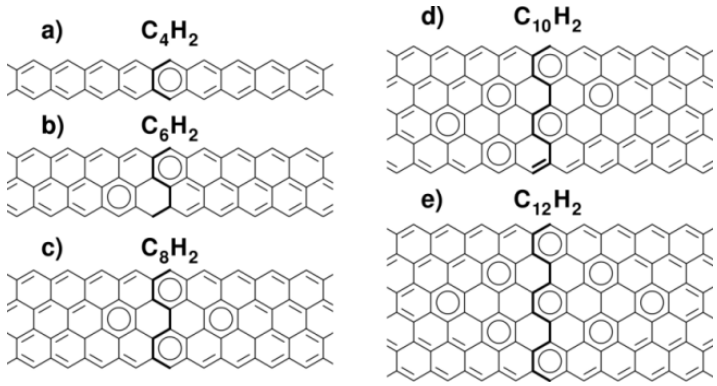
Transmission spectra



- Simulation of an electronic device at atomistic level (nm scale)
- Non-equilibrium Green Functions (NEGFs) formalism
- SIESTA 3.0 program package (TRANSIESTA)

Transmission spectra for zigzag terminated GNRs of different width

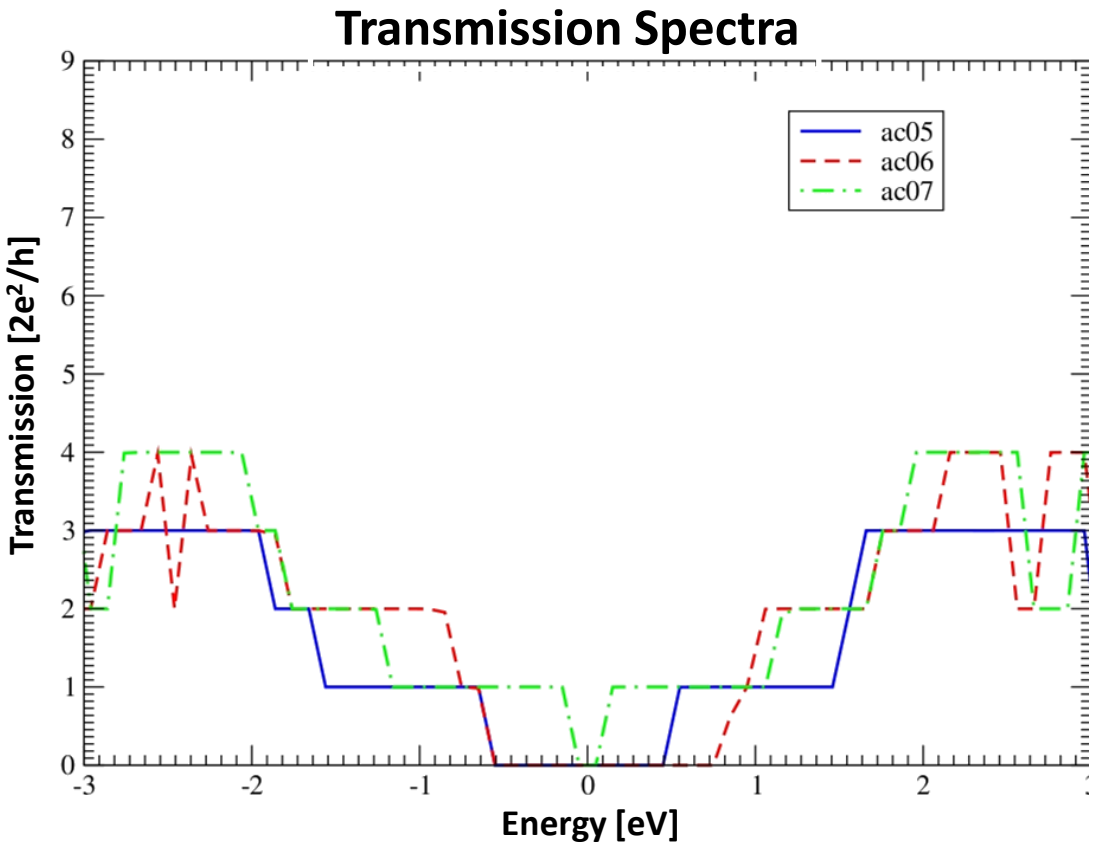


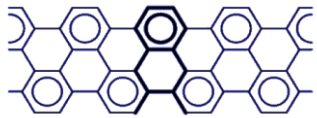


- Equivalent best Clar representation
- Similar conducting behavior

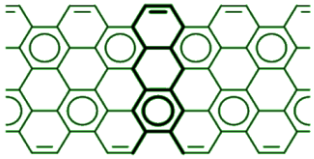
D. Selli, M. Baldoni, A. Sgamellotti and F. Mercuri, *in preparation*

Transmission spectra for armchair terminated GNRs of different width

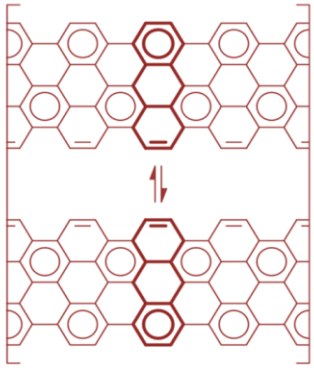




Fully benzenoid



Incomplete Clar

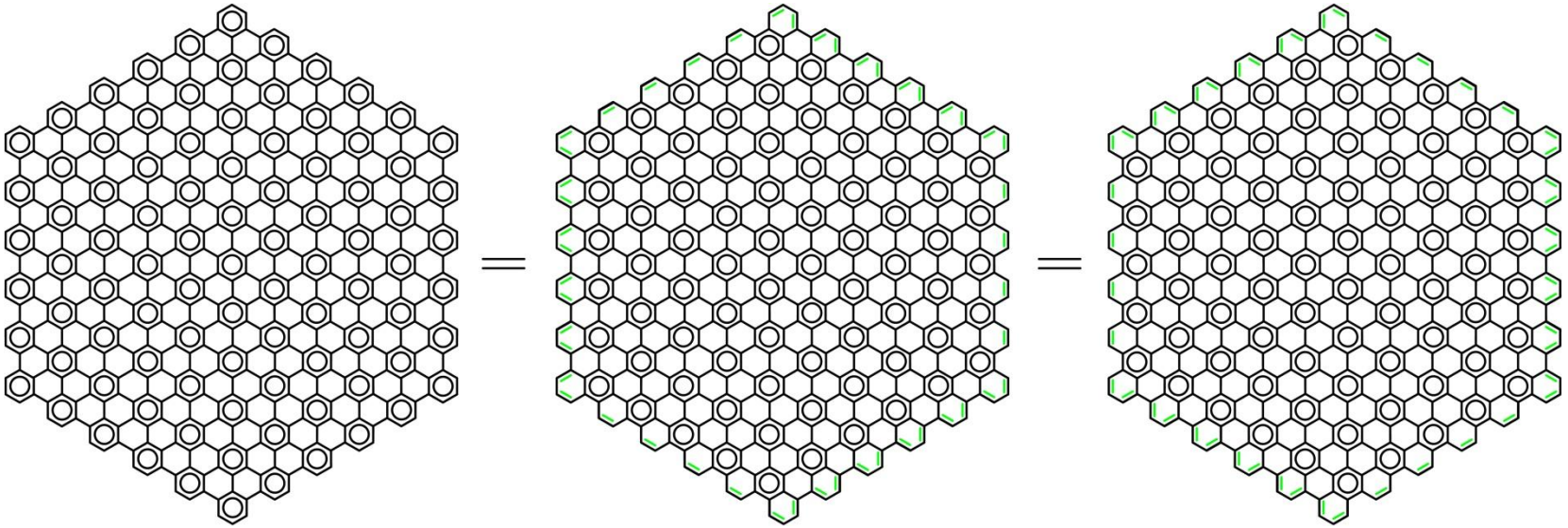


Kekulè

- Different best Clar representation vs. GNRs width
- Different conducting behavior
- Strongly quantized in unit of $2e^2/h$

Clar resonance hybrids for armchair graphene quantum dots (0D)

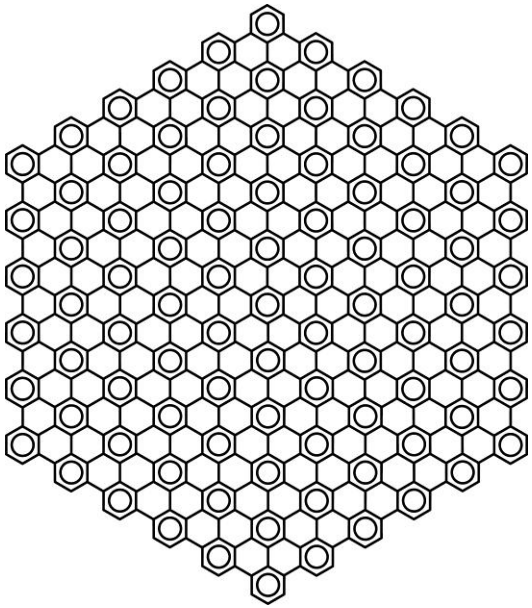
91 aromatic sextets | 75 aromatic sextets | 75 aromatic sextets

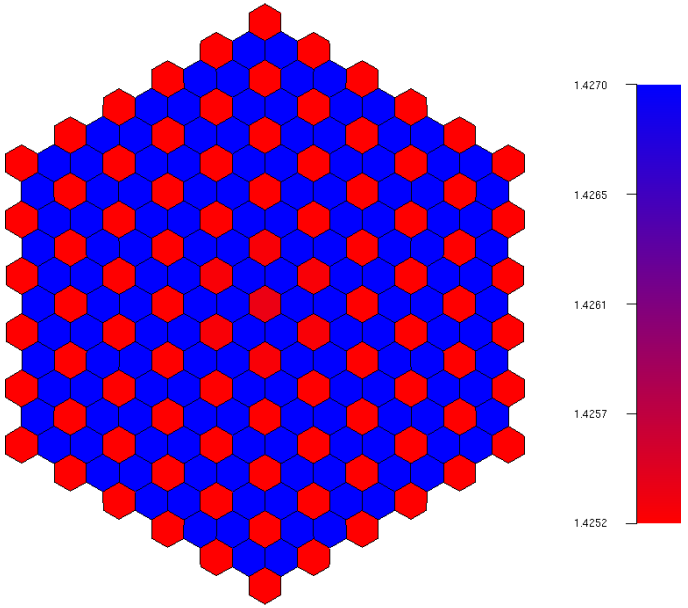


- No PBC
- Essentially large PAHs
- Best Clar representation (fully benzenoid) strongly stabilized

M. Baldoni, A. Sgamellotti and F. Mercuri, in preparation.

Bonds length analysis for armchair terminated GQD (0D)

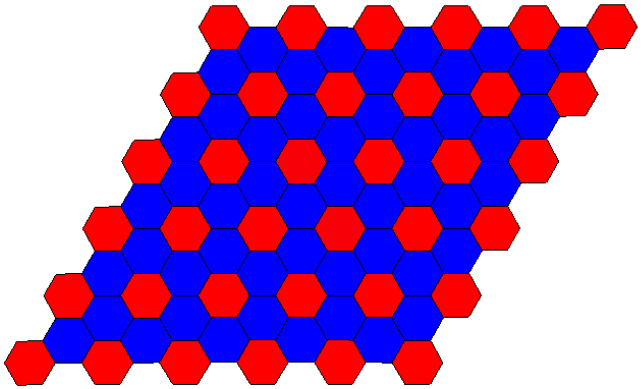


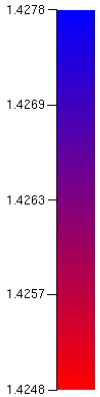


- DFT (B3LYP/3-21g) optimized structure
- Average C-C bond length analysis of each hexagon
- MO calculations strictly correlated with the VB pattern

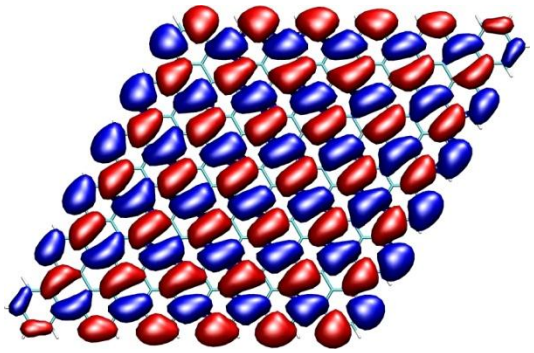
M. Baldoni, A. Sgamellotti and F. Mercuri, in preparation.

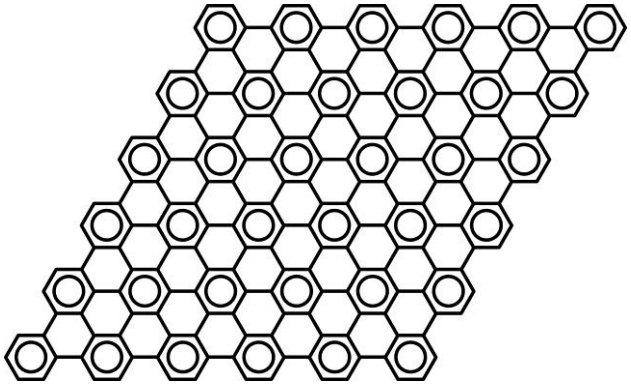
Electronic properties of armchair terminated graphene nanostructures through Clar's sextet theory





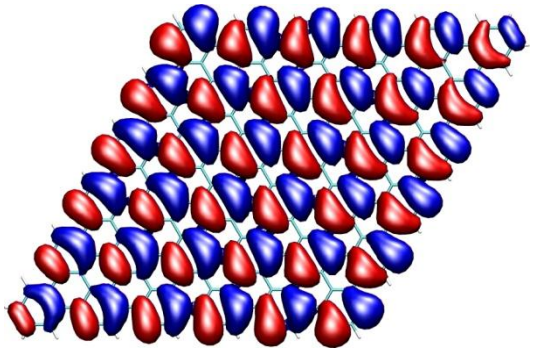
LUMO





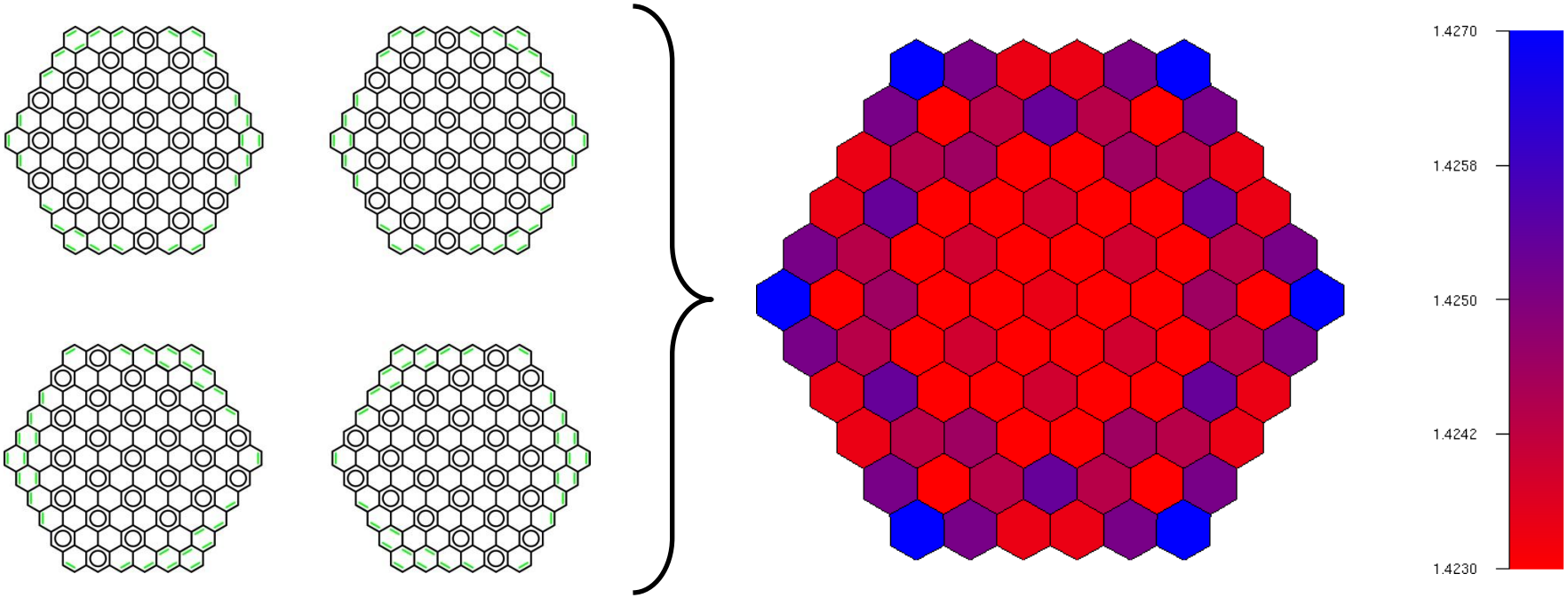
Frontier orbitals morphology as superimposition of benzenoid units

HOMO



M. Baldoni, A. Sgamellotti and F. Mercuri, in preparation.

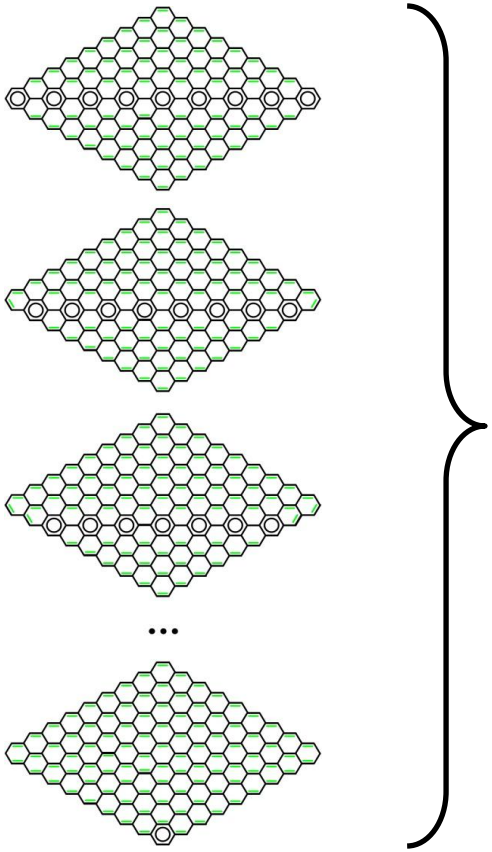
Clar resonance hybrids for zigzag terminated GQD (0D)

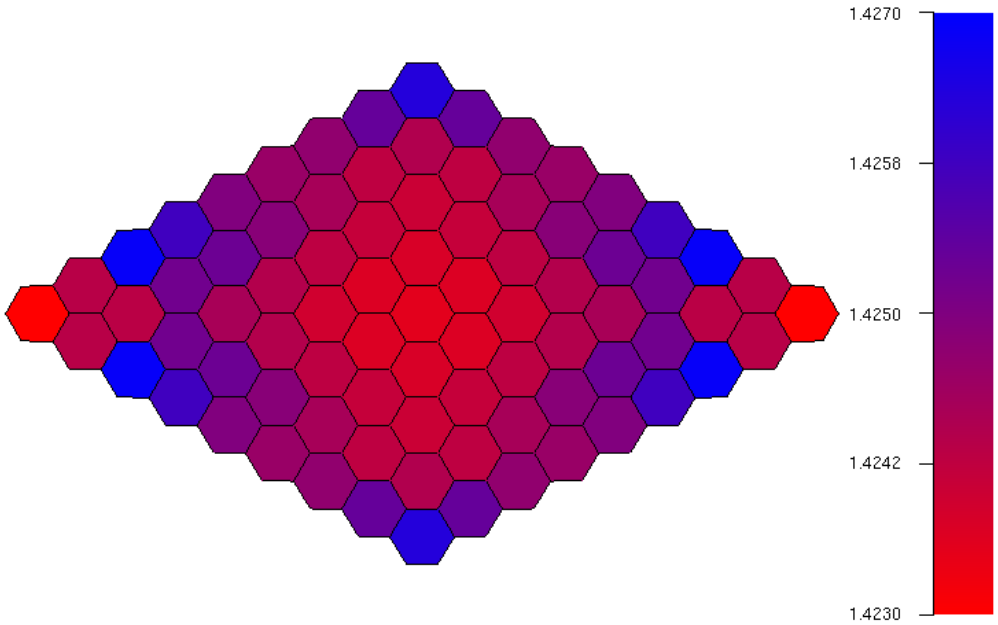


• MO calculations correlated with the VB resonance hybrid of the most important Clar representations

M. Baldoni, A. Sgamellotti and F. Mercuri, in preparation.

Clar resonance hybrids for zigzag terminated GQD (0D)





- All the VB resonance hybrids must be taken into account

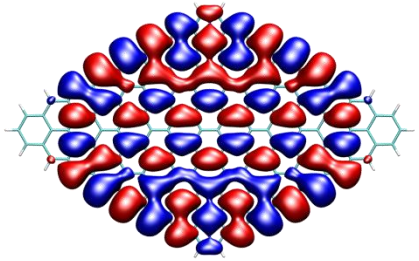
M. Baldoni, A. Sgamellotti and F. Mercuri, in preparation.

Electronic properties of graphene nanostructures through Clar's sextet theory

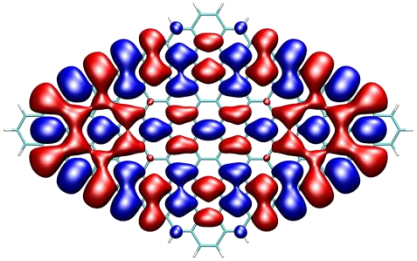
Zigzag-terminated NGs

Non-trivial best-Clar representation $\Rightarrow$ The topology of the MOs differs from a simple superposition of benzenoid rings

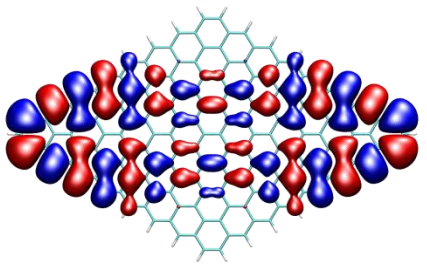
HOMO-2



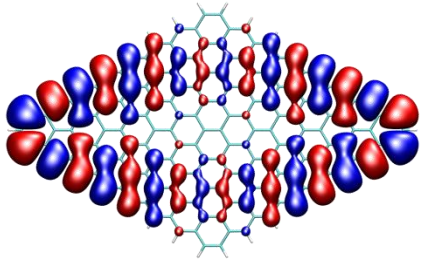
HOMO-1



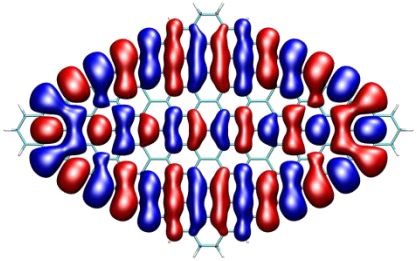
HOMO



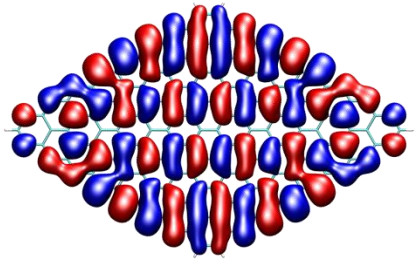
LUMO



LUMO+1



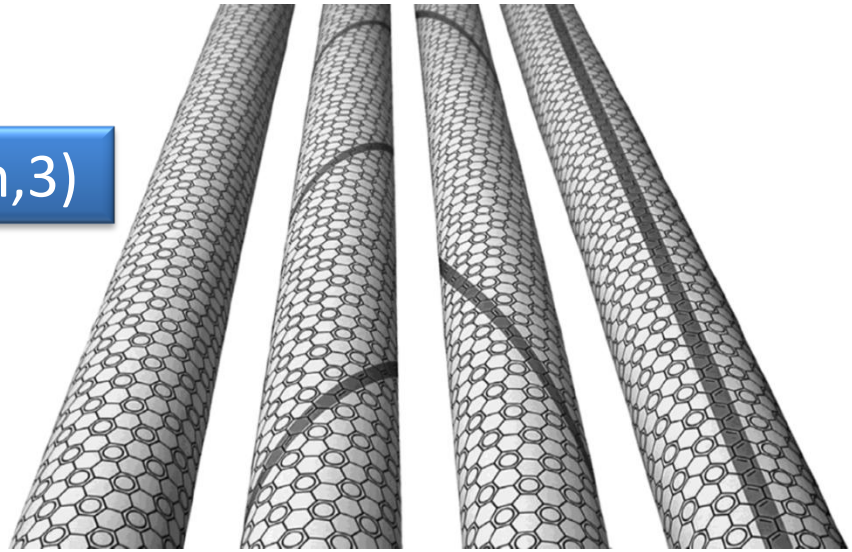
LUMO+2



M. Baldoni, A. Sgamellotti and F. Mercuri, in preparation.

APPLICATION OF CLAR SEXTET THEORY TO THE CASE OF CNTs

R(n,m) = mod(n-m,3)



R=0 (12,9) | R=1 (12,8) | R=2 (12,7) | R=1 (12,7)

R	Electronic structure	Conductivity
0	Fully benzenoid	Metallic
1	Row of double bond || *p*	Semiconducting
2	Row of double bond || *p* - *q*	Semiconducting

Ormsby, J.; King, B. *The Journal of Organic Chemistry* 2004, 69,4287–4291.

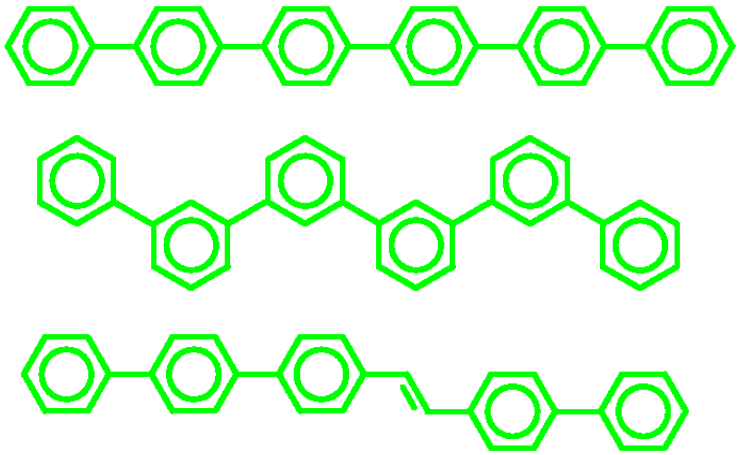
Clar unit cells

Clar sextet theory:

⇒ definition of *unit cells* based on Clar theory

⇒ *network of benzenoid units* (connected by single and/or double bonds)

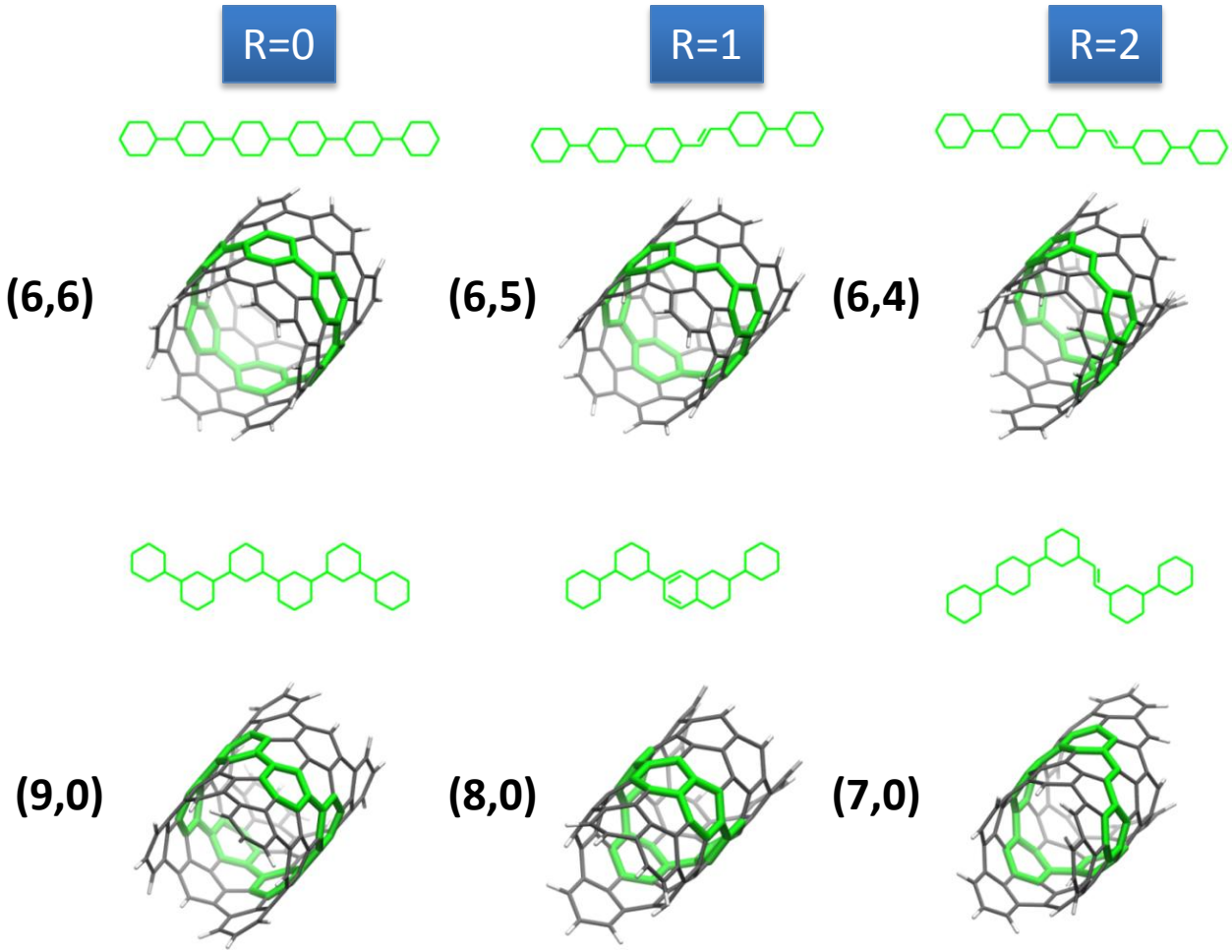
- Common representation of *all* CNSs (CNTs, graphenes, etc.)
- Chemically "simple" building blocks



Representation of a carbon nanostructure ⇒ replication of Clar unit cells

M. Baldoni, A. Sgamellotti and F. Mercuri, *Organic Letters*, **2007**, 9, 4267

FLCC approach: Models



Computational Details

- FLCCs (2-6 Clar cells)
- Geometry Optimization
- B3LYP
- 3-21G
- Gaussian 03

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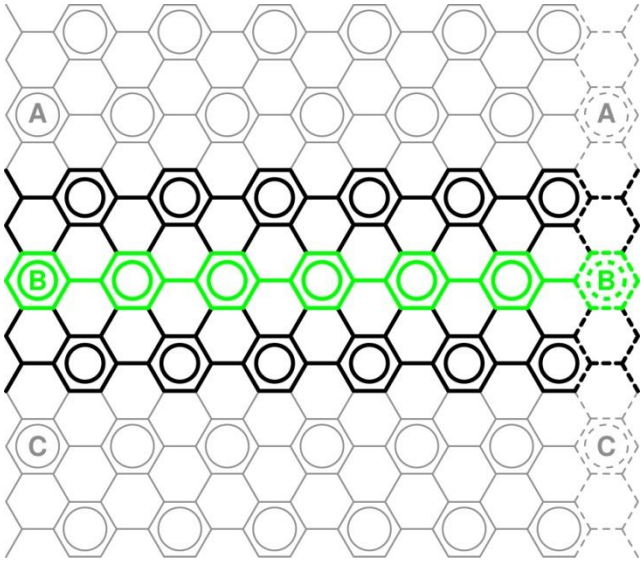
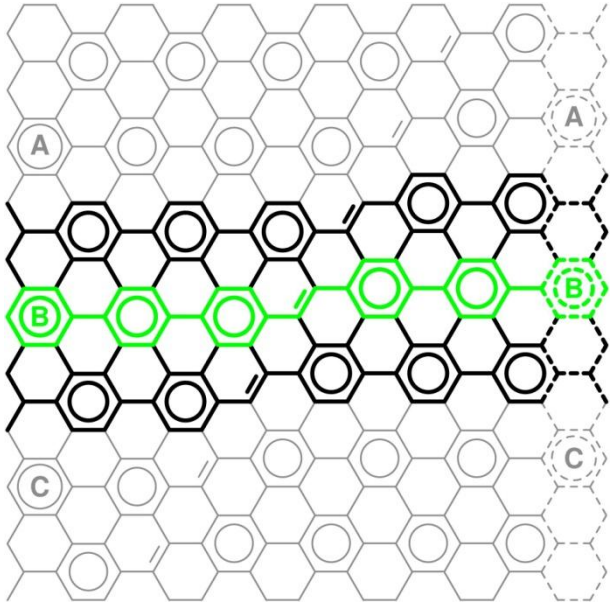
FLCC approach: Models

(6,6)



(6,5)



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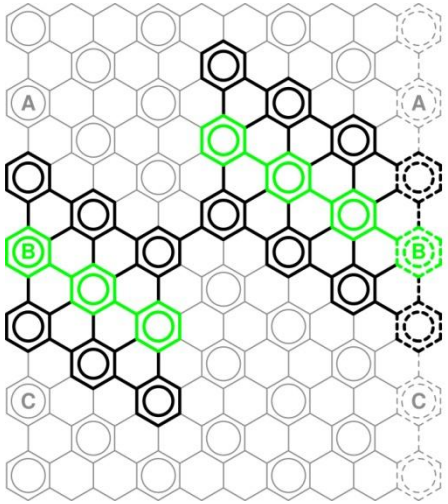
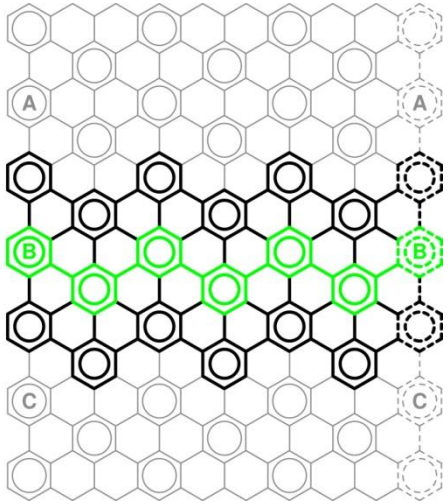
(9,0)

Canonical Clar

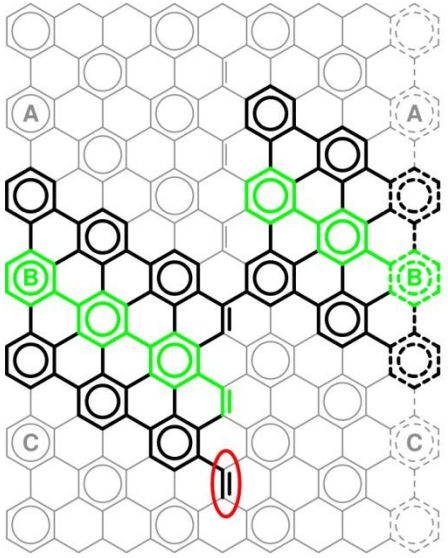


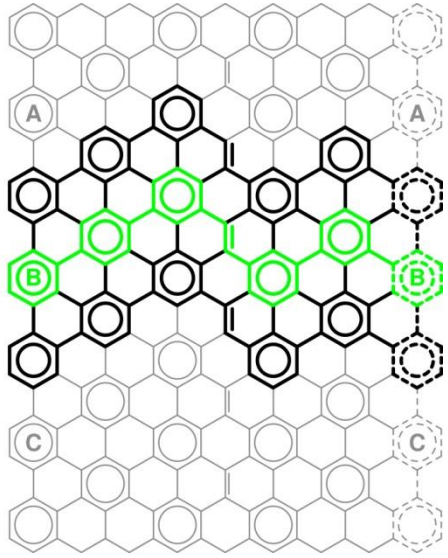


Used in calculations

(8,0)

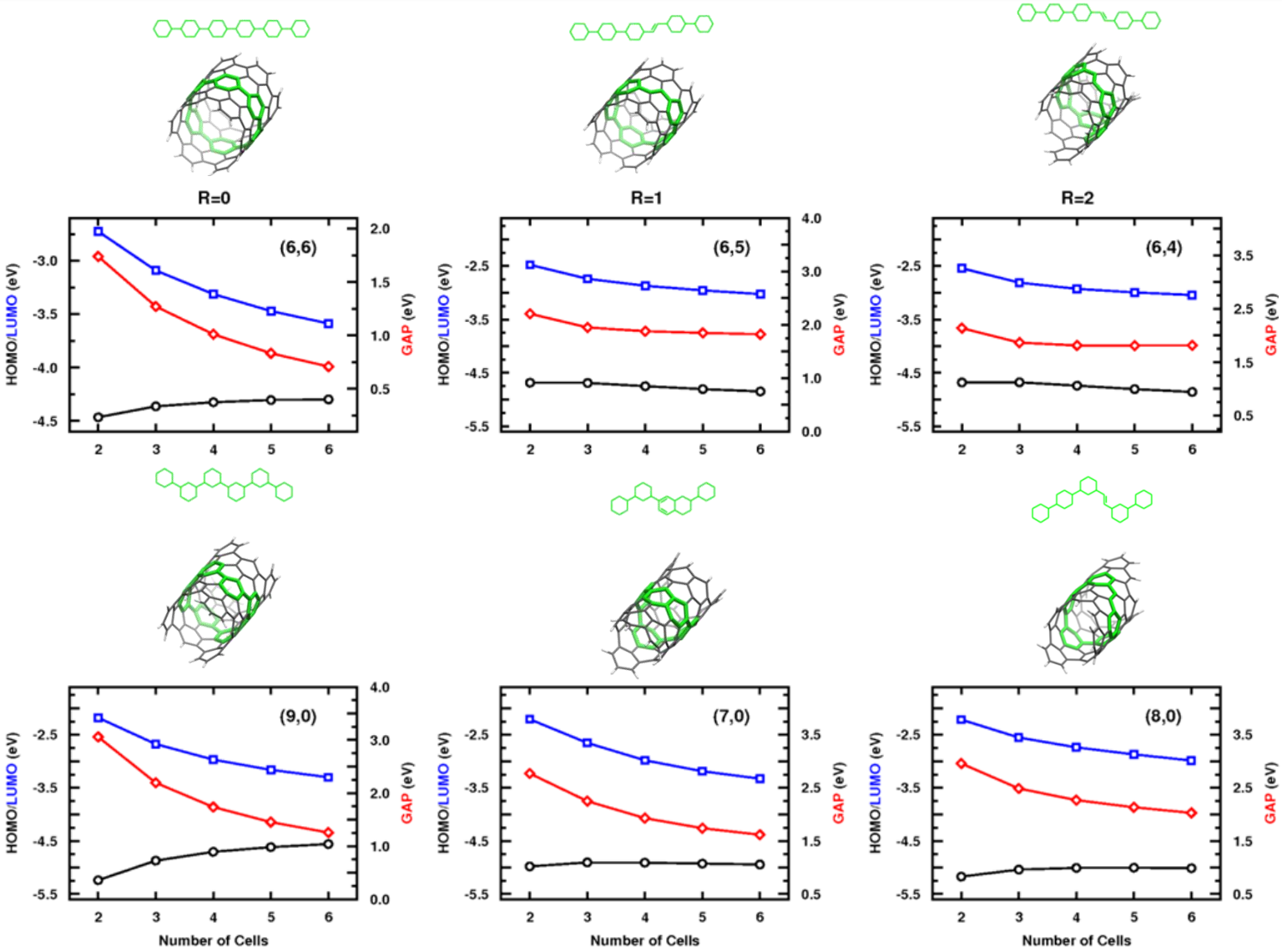
Canonical Clar





Used in calculations

Electronic properties of FLCC models of CNTs



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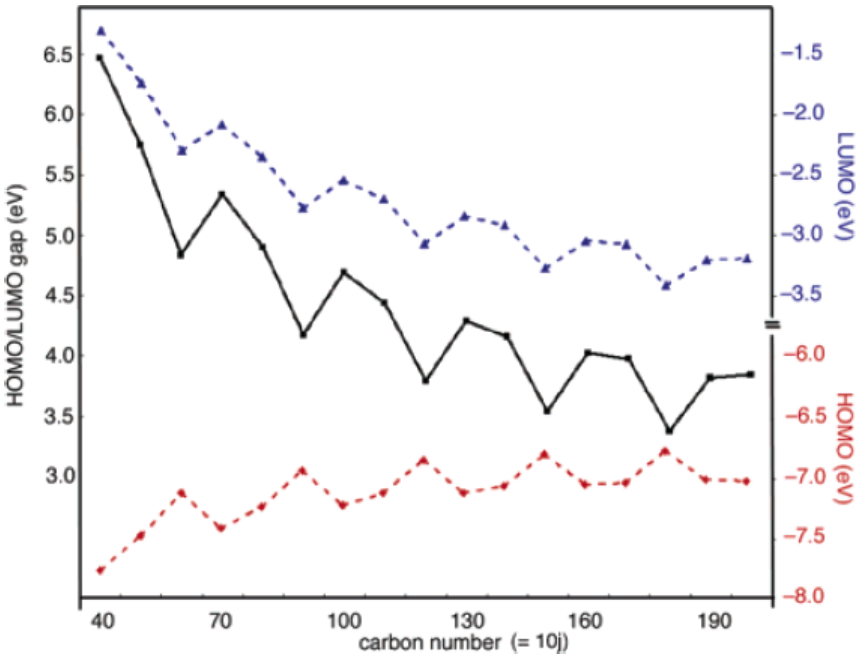
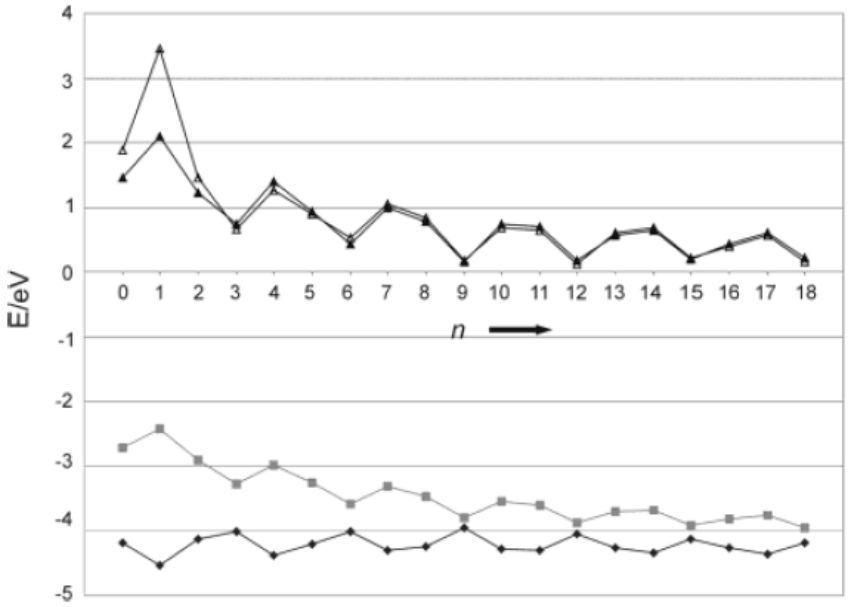
Results from literature



Y. Matsuo, et al. *Organic Letters*, **2003**, 5, 3181



H. F. Bettinger, *Organic Letters*, **2004**, 6, 731

The use of finite-length cluster models, when applied through purely size-based criteria, provide **contrasting results** and **slow convergence**.

Electronic properties of CNTs and Clar's sextet theory

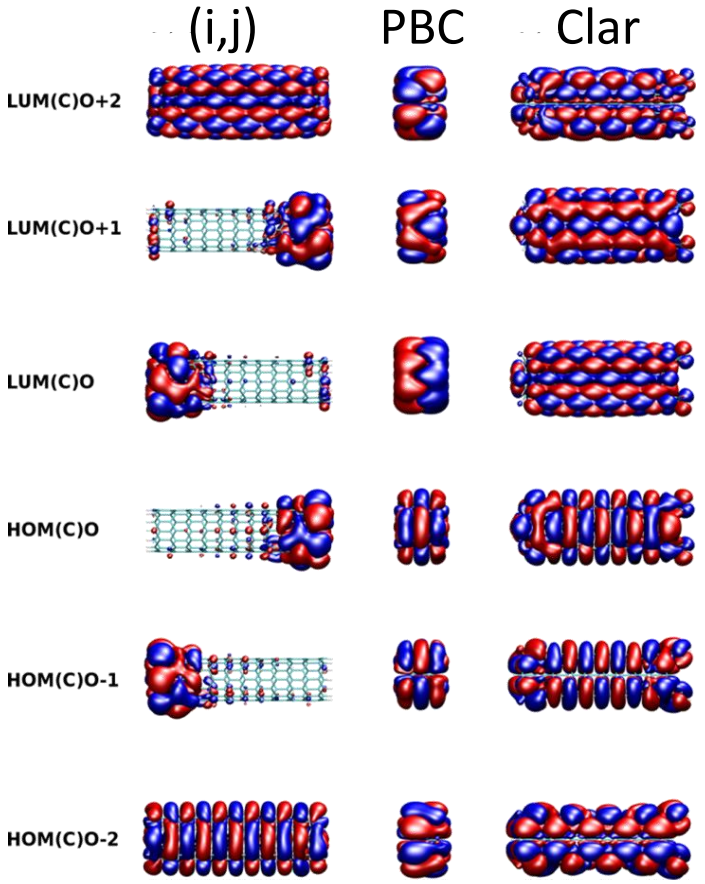
Electronic properties of finite-length models of (7,0) CNTs

Non-Clar cluster/edges ("crystallographic" (*i,j*) basis):

- Localized orbitals in the MO description
- High-spin ground states

FLCCs:

- Singlet ground state
- Delocalized frontier MO
- 1:1 correlation of MOs with the PBC description



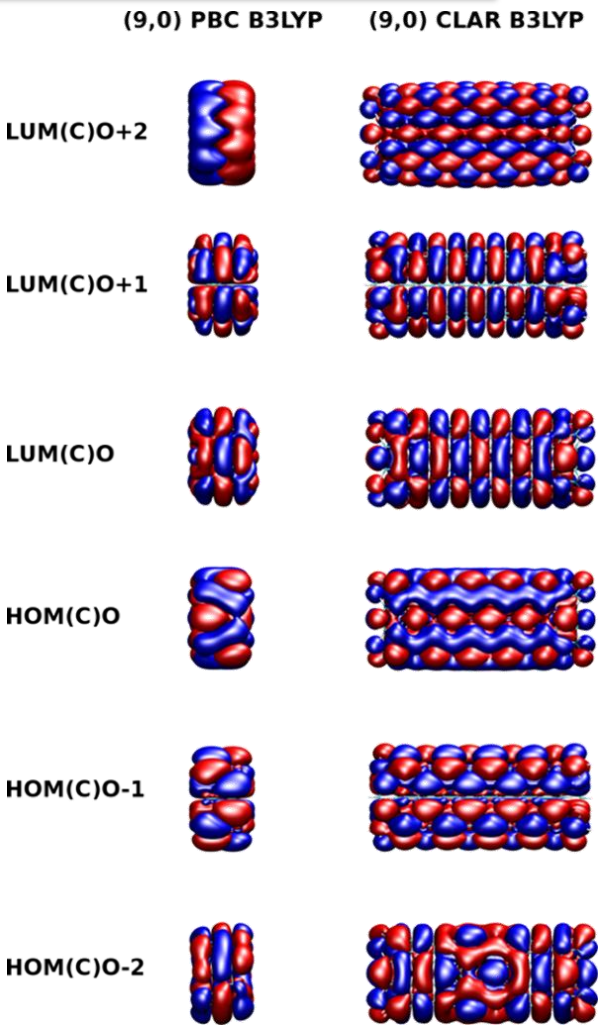
M. Baldoni, A. Sgamellotti and F. Mercuri, *in preparation*

Electronic properties of CNTs and Clar's sextet theory

Relationship with the PBC description:

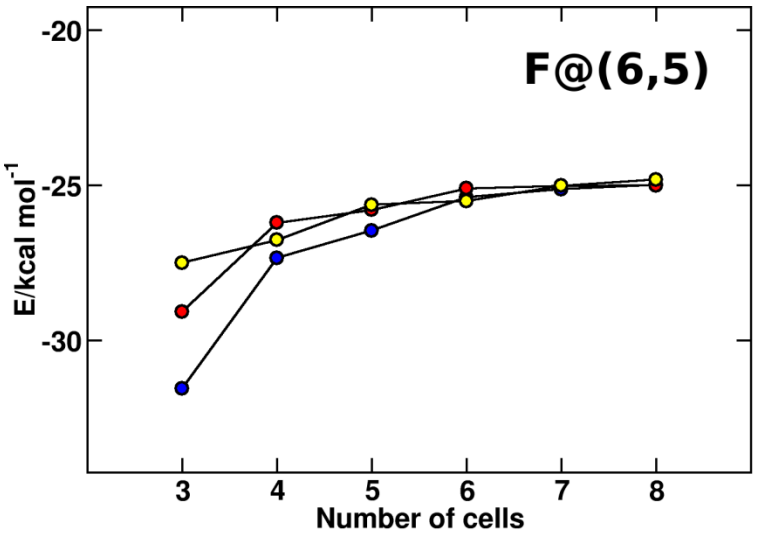
Electronic properties of FLCC models: Strong relationship with the bands of the corresponding periodic systems (crystal orbitals at Γ point)

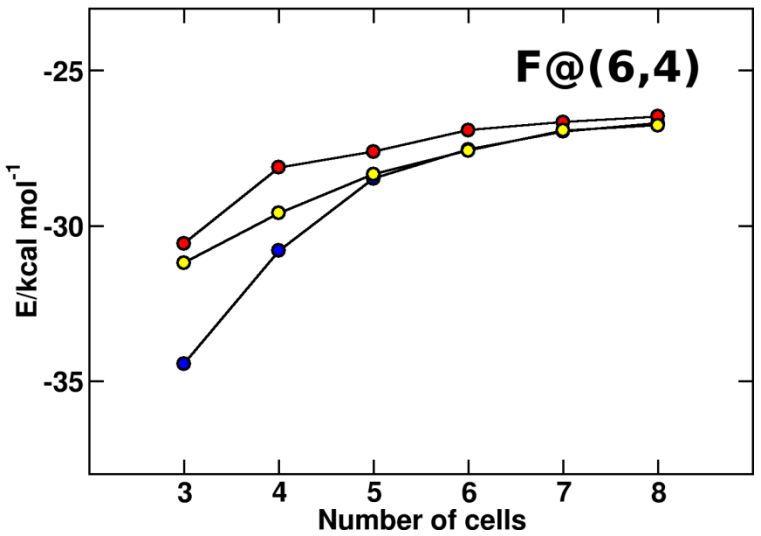
$\Rightarrow$ Consistent description of the electronic structure and related properties (reactivity, etc.)

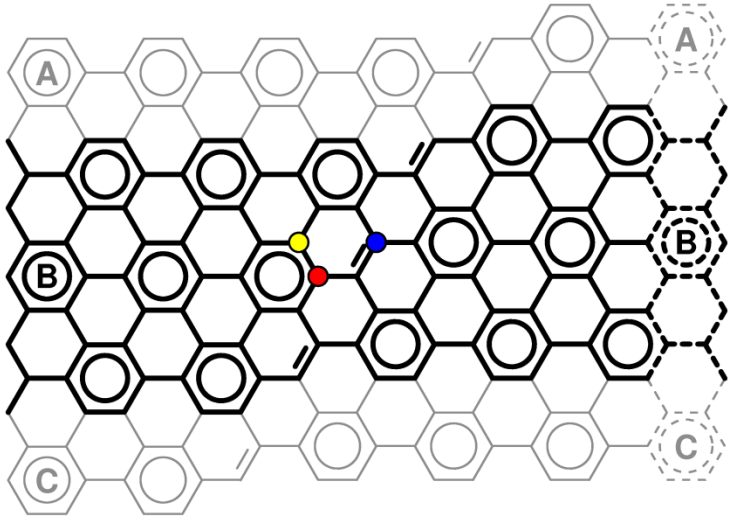


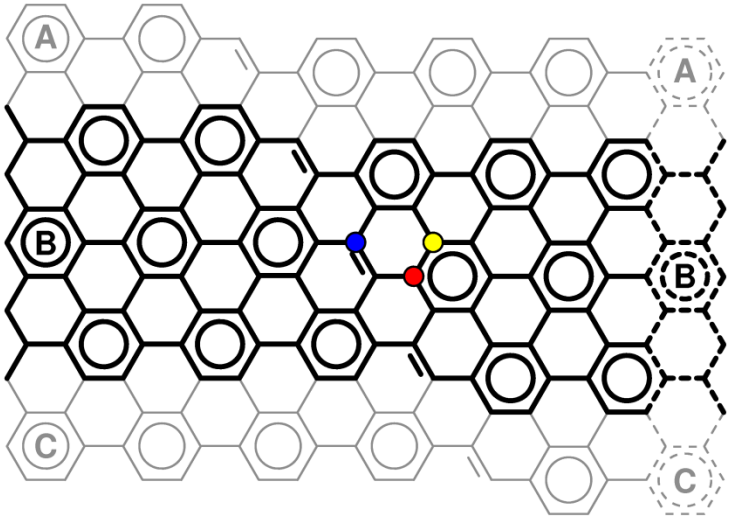
M. Baldoni, A. Sgamellotti and F. Mercuri, *in preparation*

The reactivity of semiconducting chiral CNTs : F chemisorption



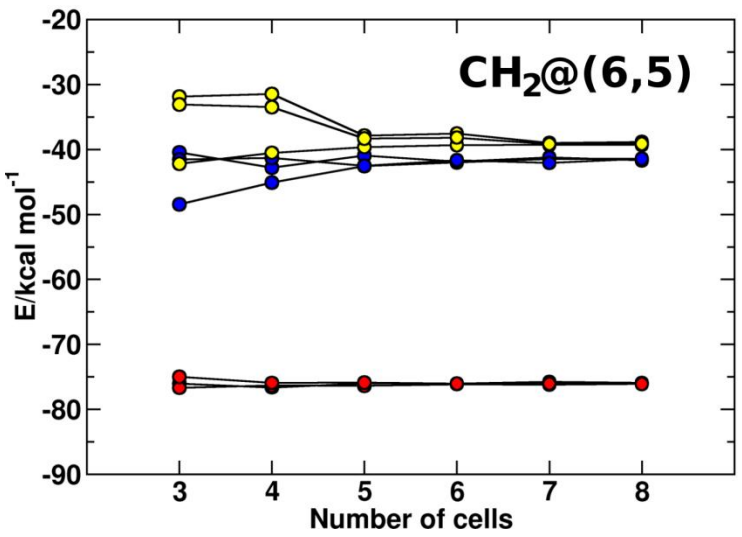


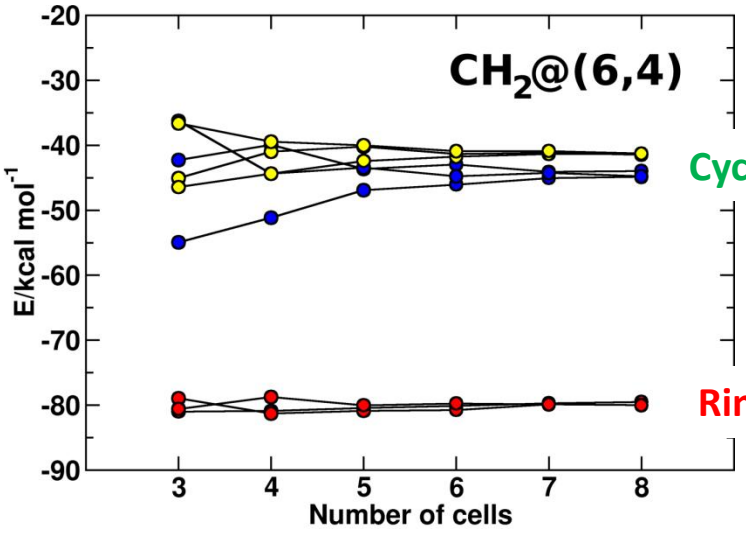




M. Baldoni, D. Selli, A. Sgamellotti and F. Mercuri, **2009**, 113, 862

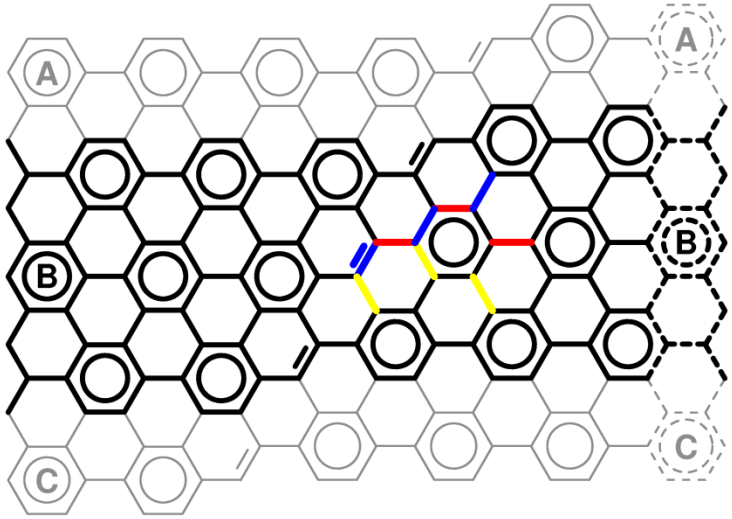
The reactivity of semiconducting chiral CNTs: CH_2 chemisorption

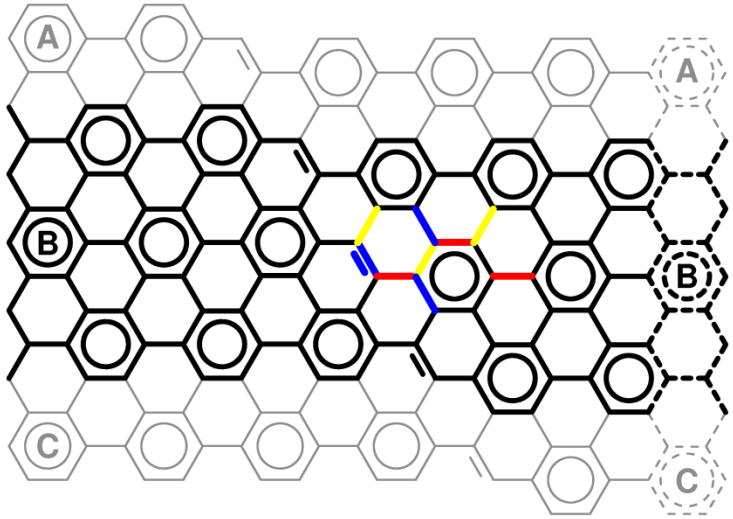




Cyclopropanation

Ring opening





M. Baldoni, D. Selli, A. Sgamellotti and F. Mercuri, *J. Phyc. Chem. C.* **2009**, 113, 862

Conclusions

- Unified description of the electronic properties of low-dimensional carbon nanostructures
- “Well-behaved” electronic properties (edge effects);
- Fast and monotonic convergence of electronic properties (frontier orbital energies, reaction energies, etc.);
- Bridge between the VB representation and the local electronic structure of the hexagonal network in terms of resonance hybrids and MO calculations $\Rightarrow$ better understanding of the electronic situation (“chemical” interpretation of results);
- Computationally cheap & good accuracy (higher accuracy with lower computational cost vs. periodic or other finite-length models).

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