Designing all-graphene nano-junctions by edge functionalization: Optics and Electronics

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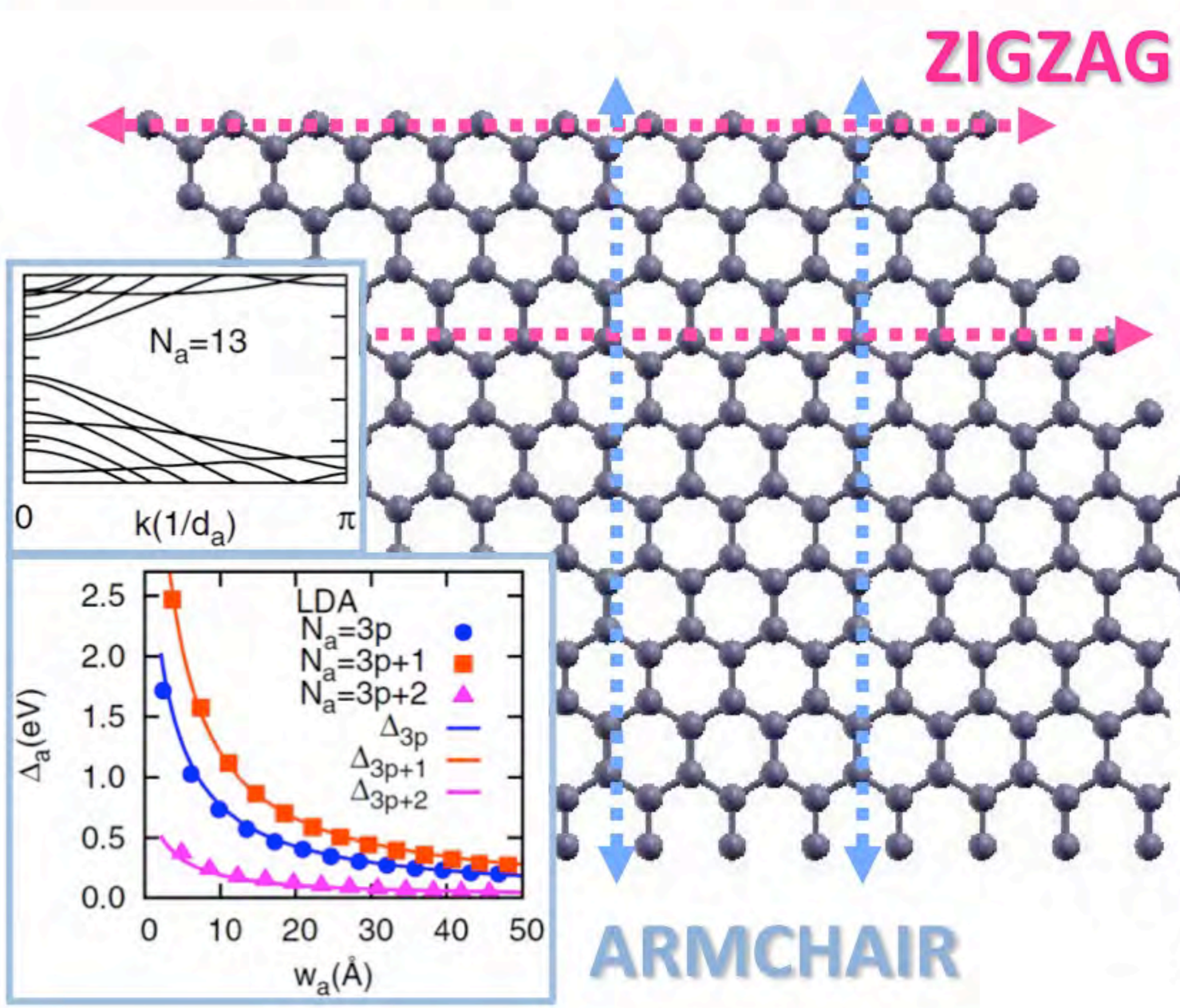
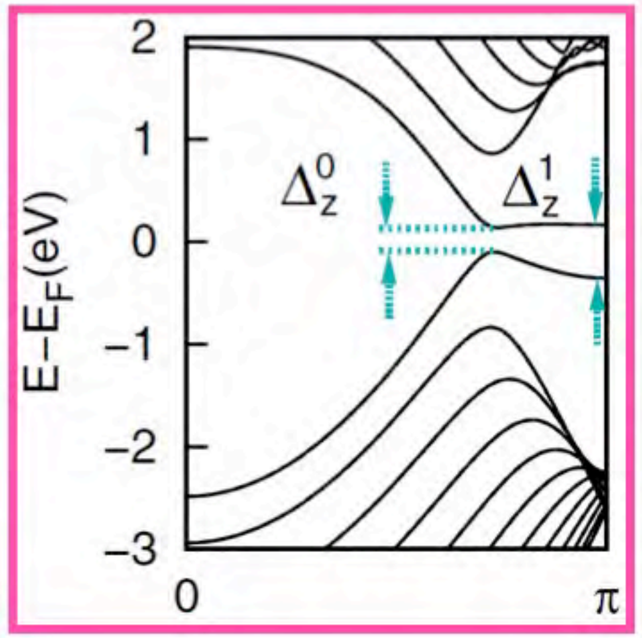
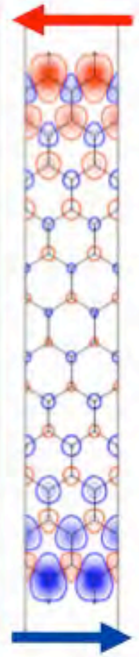
Graphene Nanostructures







Semiconductors

- ✓ Edge shape
- ✓ Edge termination
- ✓ Width modulation

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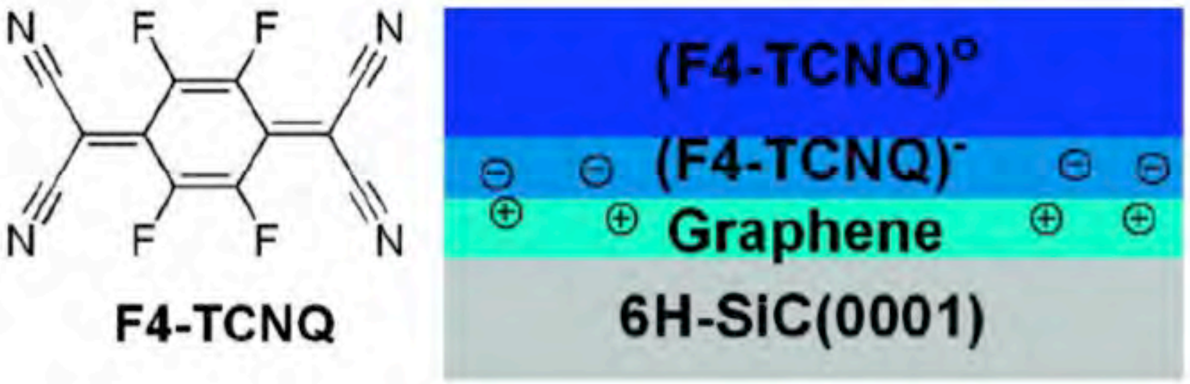
Molecular Functionalization

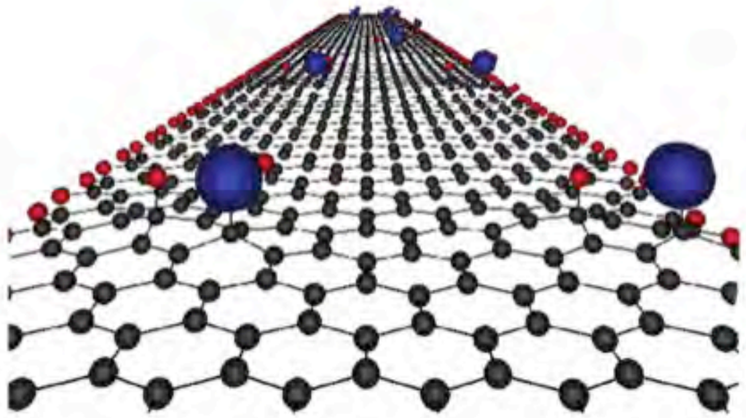
Non Covalent



Chen *et al.* JACS **2007,** 129, 10418-10422

- **doping** effects
- **unstable** structures

Covalent



Lopez-Bezanilla *et al.* Nano Lett. **2009,** 9, 2537-2541.

- **defects** in sp^2 C network
- **transport damaged**

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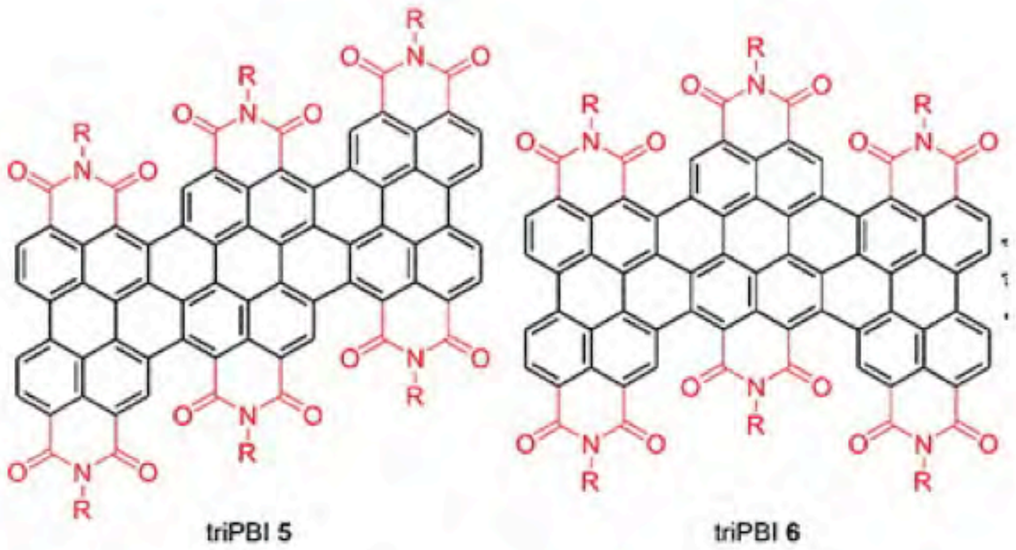
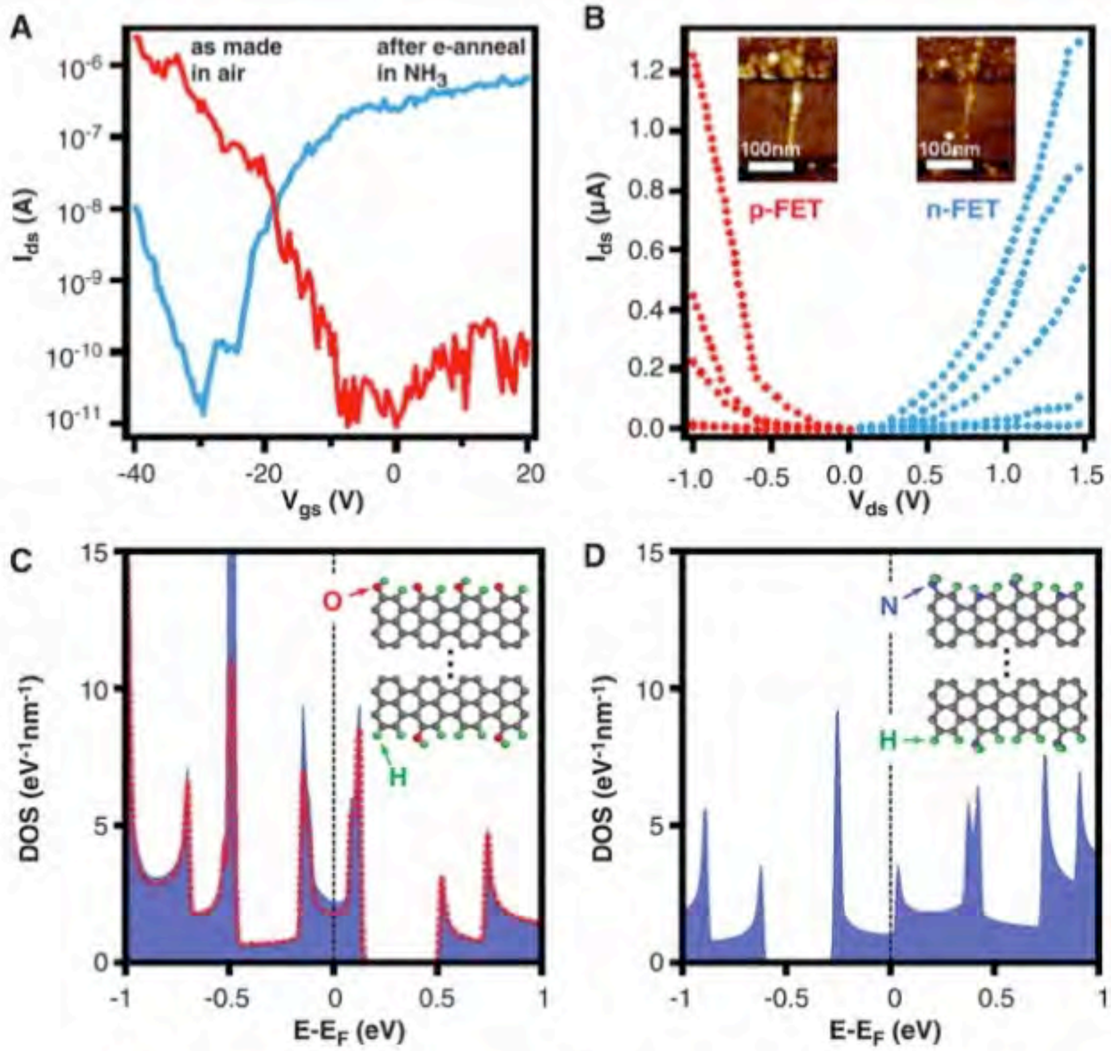
Edge Covalent Functionalization



H. Qian *et al.* JACS **2008,** 130, 17970-17976

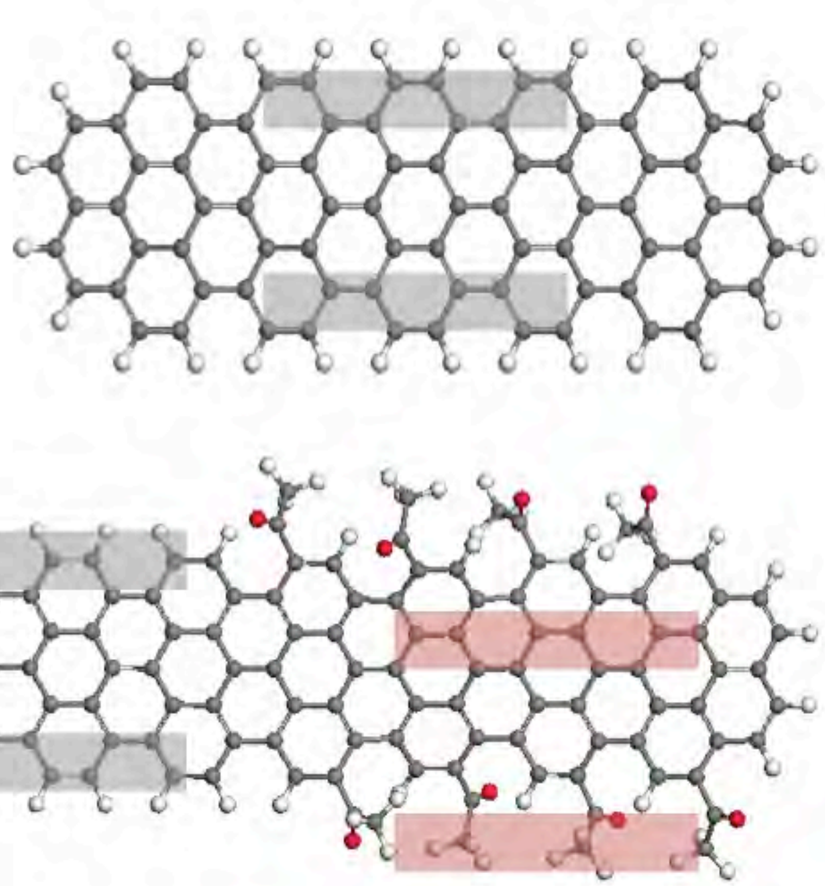


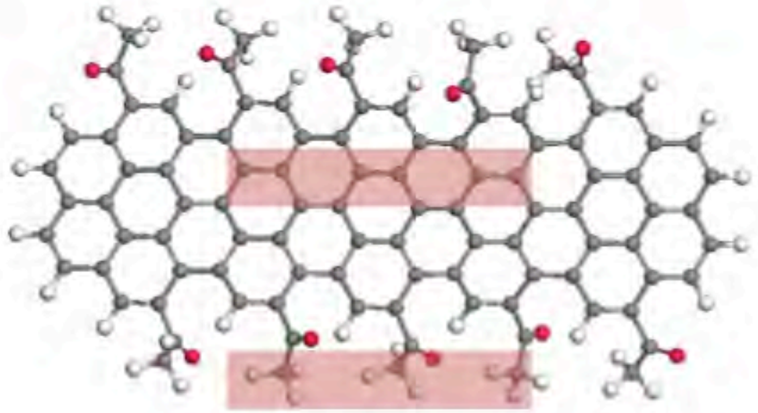
- ✓ **atomic control**
- ✓ **stable structures**

X Wang *et al.* Science **2009**,324,768-771

Our Scope

Edge covalent functionalization as an effective strategy towards **all-graphene *type II* nanojunctions**





- ✓ **charge separation**
- ✓ **optoelectronic applications**

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Method

Electronic Properties

- Hartree-Fock based semi-empirical method **AM1**[1];
- LCAO method: $\phi_i(\mathbf{r}) = \sum_j a_{ji}\chi_j(\mathbf{r})$
- Structural Optimization;
- *Vertical* Electron Affinity (EA) and Ionization Potential (IP) computed;
- *Electronic Gap* = IP – EA.

Optical Properties

- Hartree-Fock based semi-empirical method **ZINDO/S**[2];
- Configuration Interaction (CI) including Single excitations only (S).

Consistent with *ab-initio* calculations

[1] M. Dewar *et al.* JACS **107** 3902 (1985)
[2] Ridley, J., Zerner, M. Theor. Chem. Acta **32**, 111 (1973)

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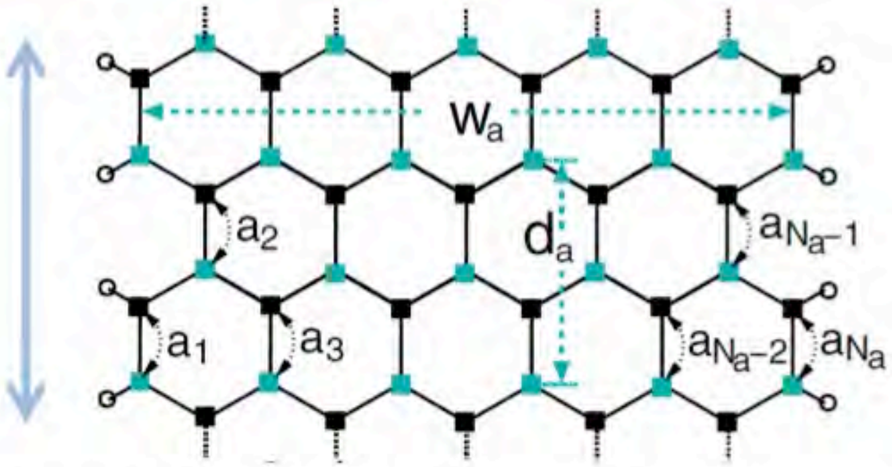
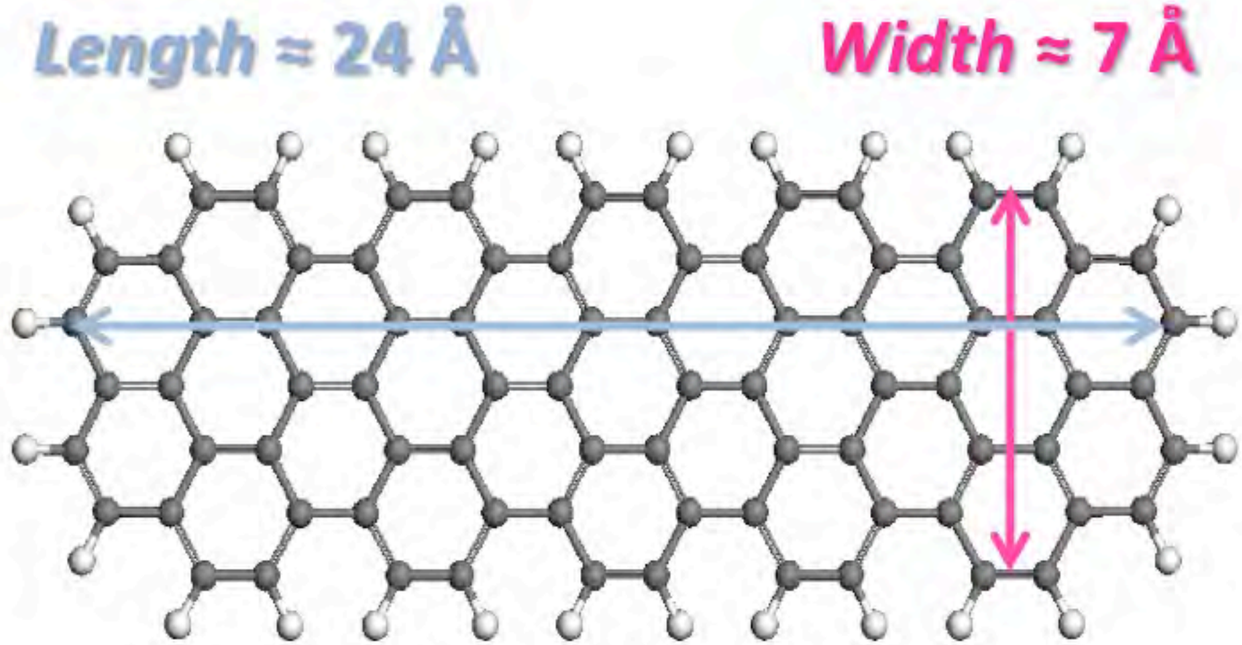
MATERIALS STUDIO

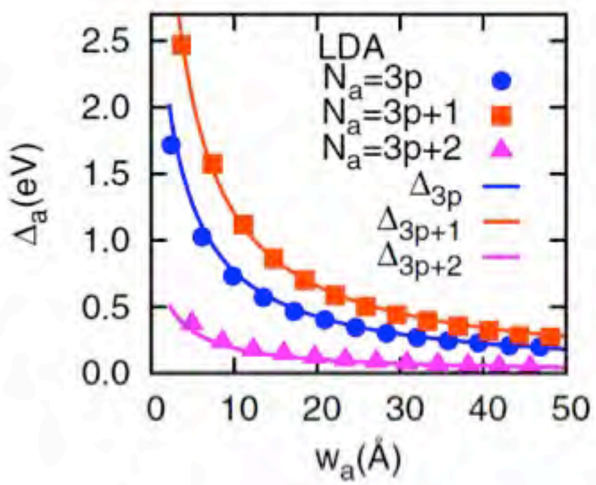
Our System



N=1 2 3 4 …



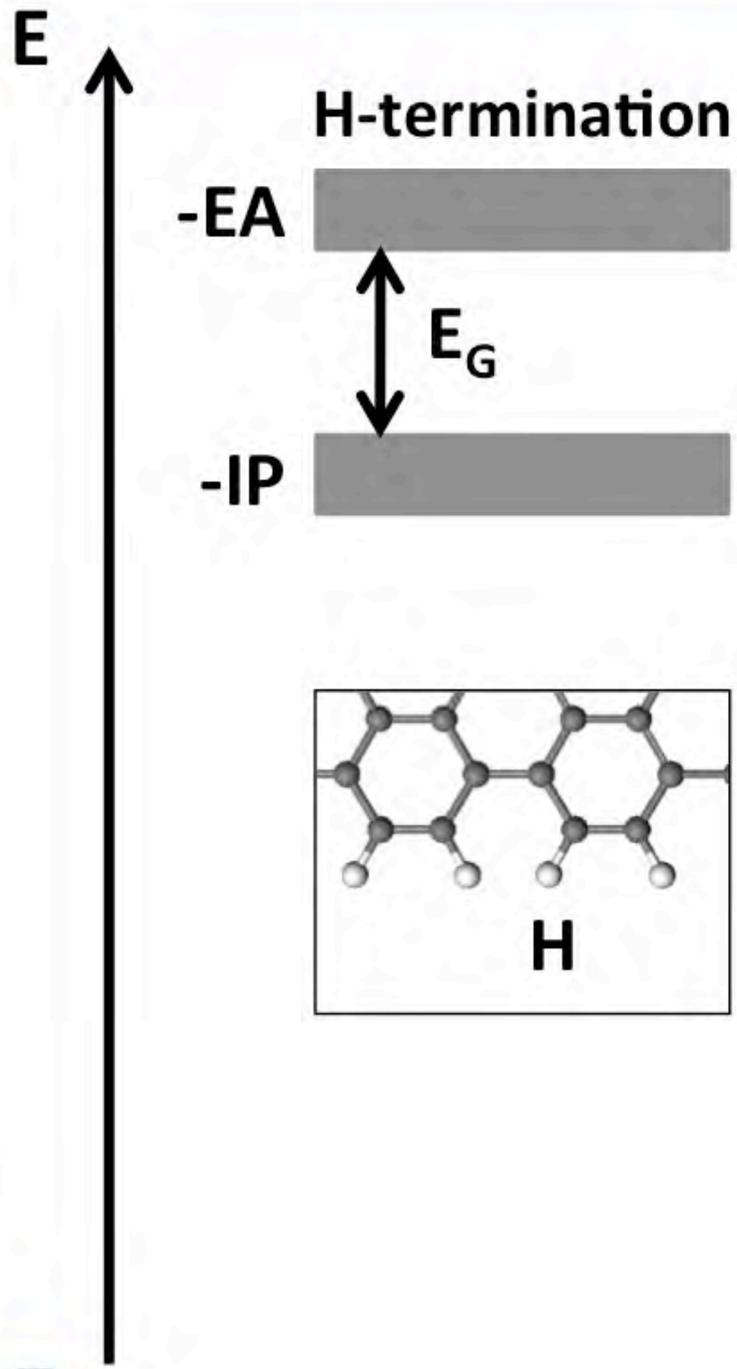
ARMCHAIR

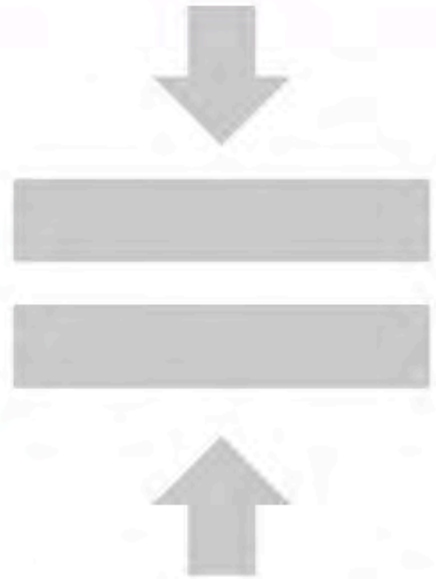


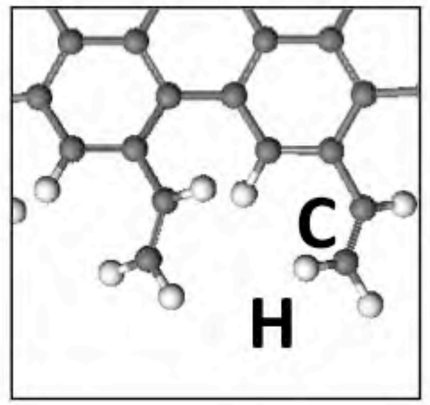
- ✓ **Finite graphene flakes**
- ✓ **Armchair-shaped edges**

Y. Son *et al.*, PRL **97**, 216803 (2006)

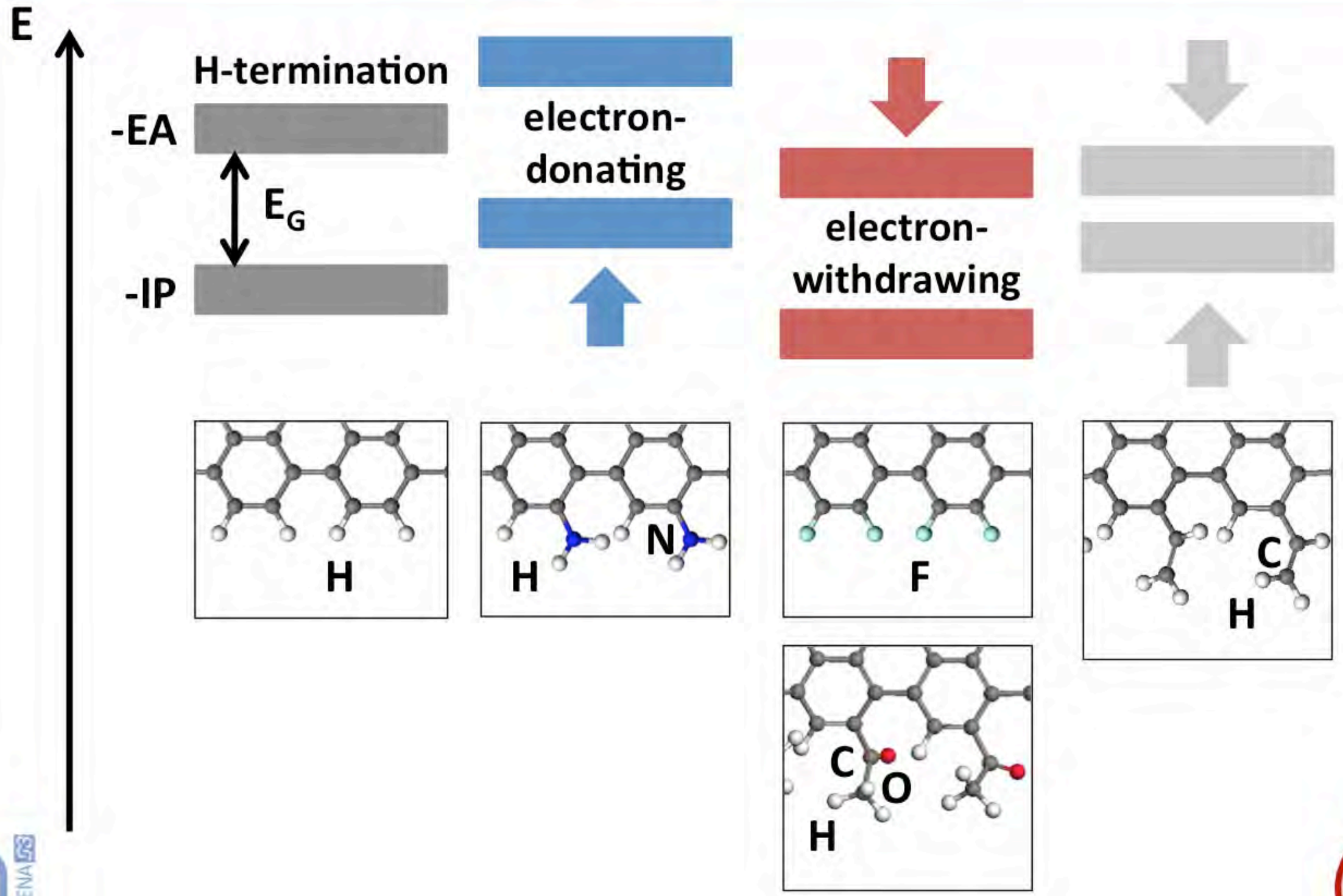
Tuning Gap Offsets





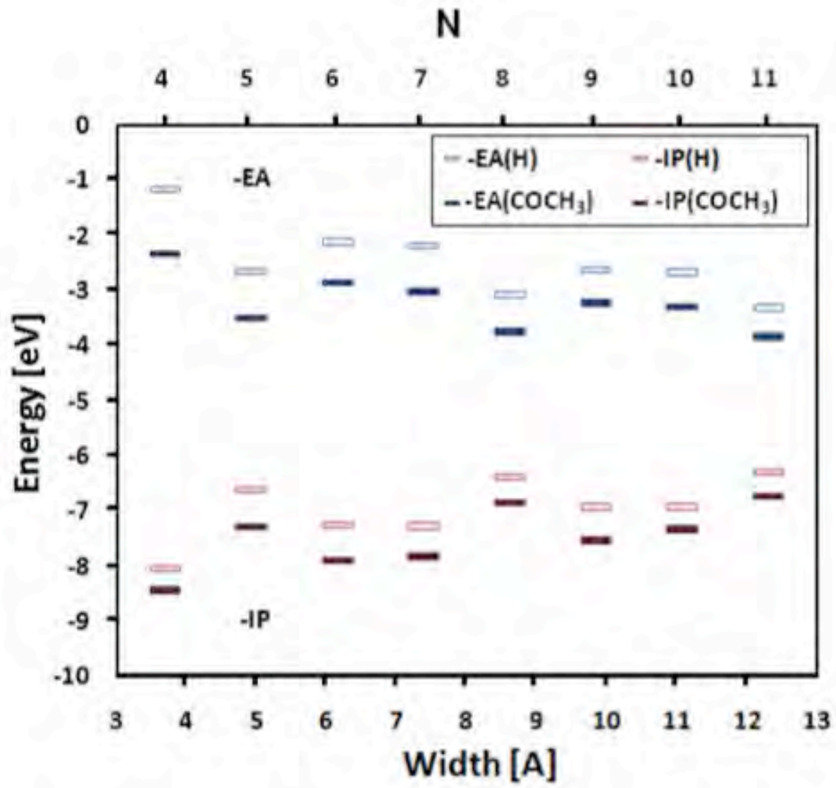


Tuning Gap Offsets

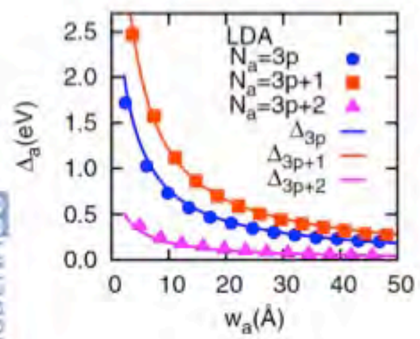


C. Cocchi *et al.* J. Phys. Chem. C **115**, 2969-2973 (2011)

Stability and Modulation



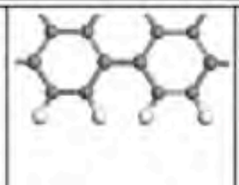
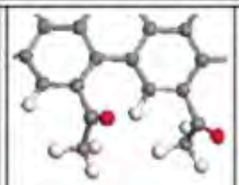
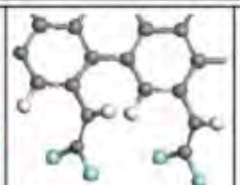
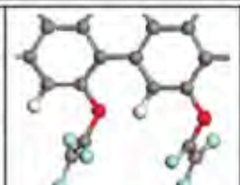
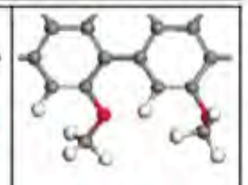
Width of graphene flake: "family" behavior



Y. Son *et al.*, PRL **97**, 216803 (2006)

	H	2	4	6	8	10
E_G [eV]	5.13	5.01	5.01	4.99	4.96	4.86
ΔEA [eV]	0.00	0.21	0.29	0.37	0.47	0.69
ΔIP [eV]	0.00	0.09	0.17	0.23	0.30	0.42

Number of covalently bonded groups ($-COCH_3$)

					
	H	$-COCH_3$	$-CH{=}CF_2$	$-OCF{=}CF_2$	$-OCH_3$
E_G [eV]	5.13	4.86	4.65	4.74	4.75
ΔEA [eV]	0.00	0.69	0.67	0.70	-0.12
ΔIP [eV]	0.00	0.42	0.19	0.31	-0.50

Functional groups

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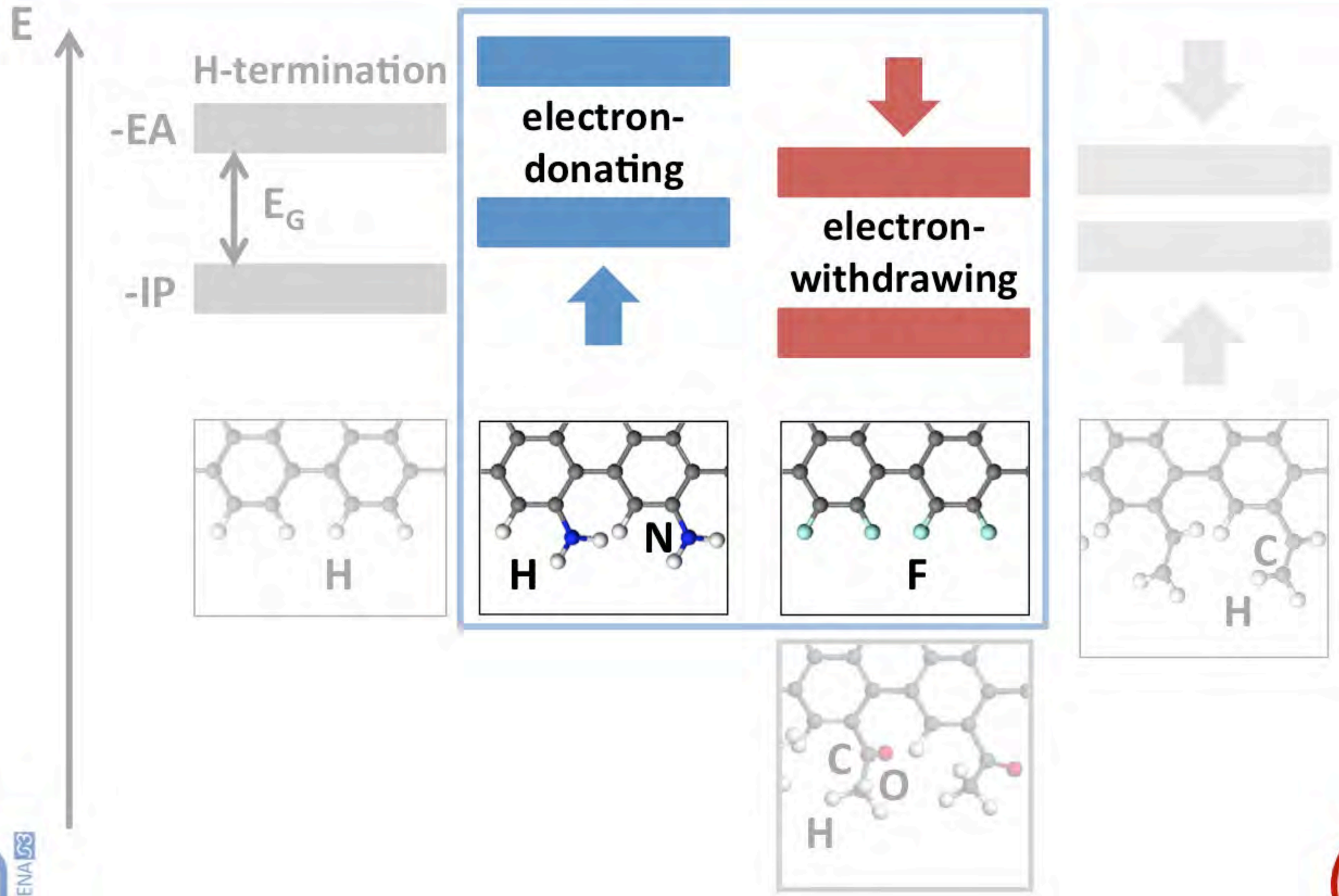
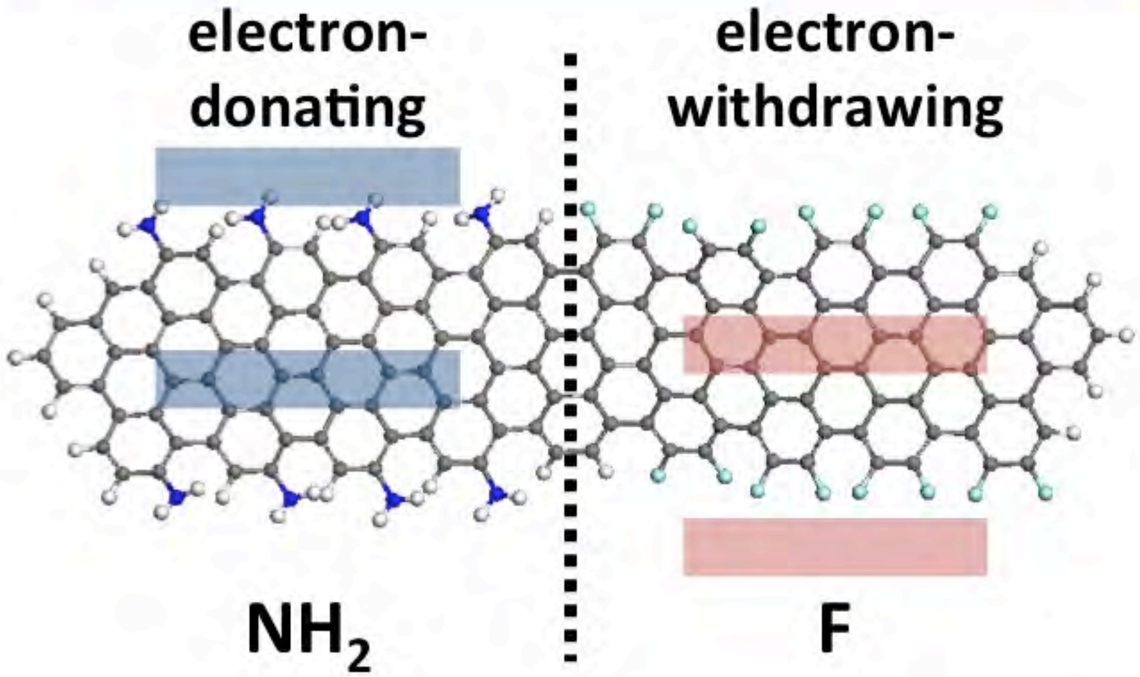
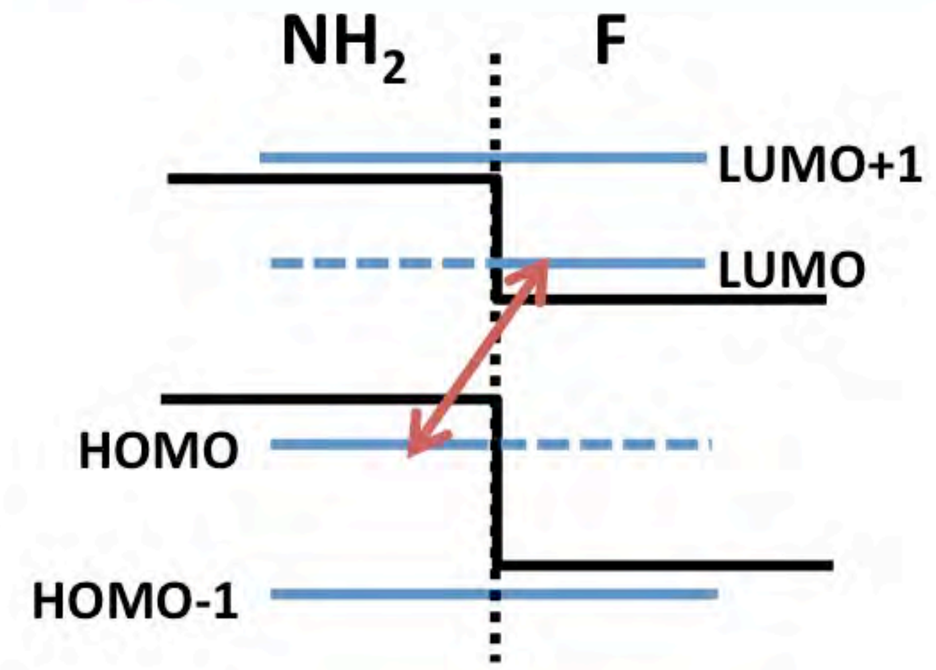
Tuning Gap Offsets



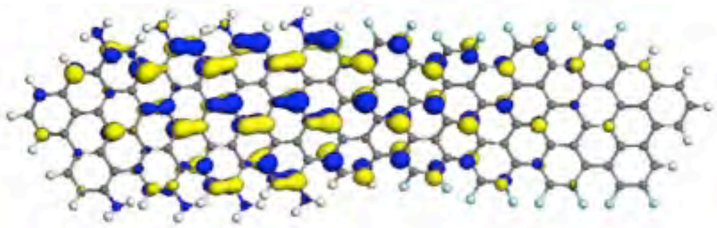
All-graphene *type II* nanojunction: NH_2//F

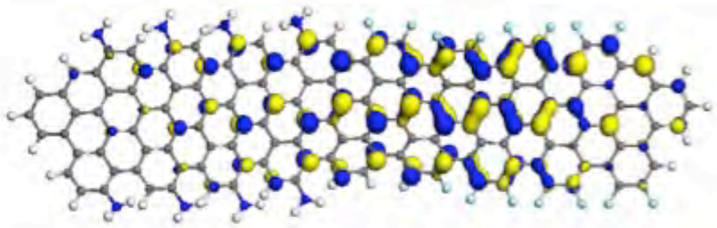




✓ Localized <u>frontier orbitals</u>

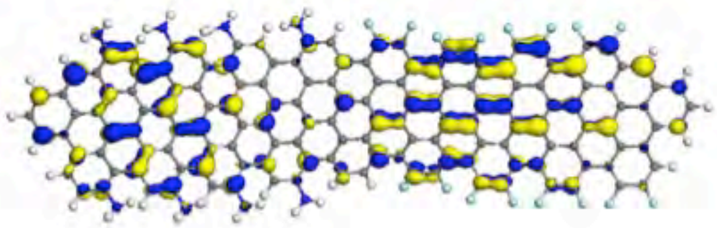
<u>HOMO</u>

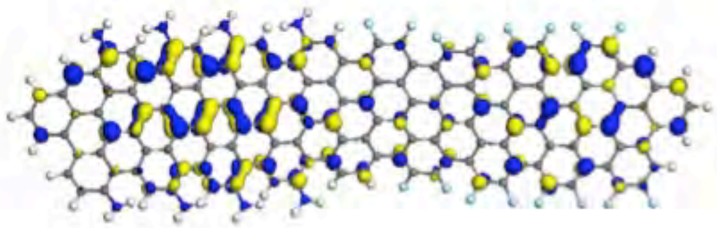




<u>LUMO</u>

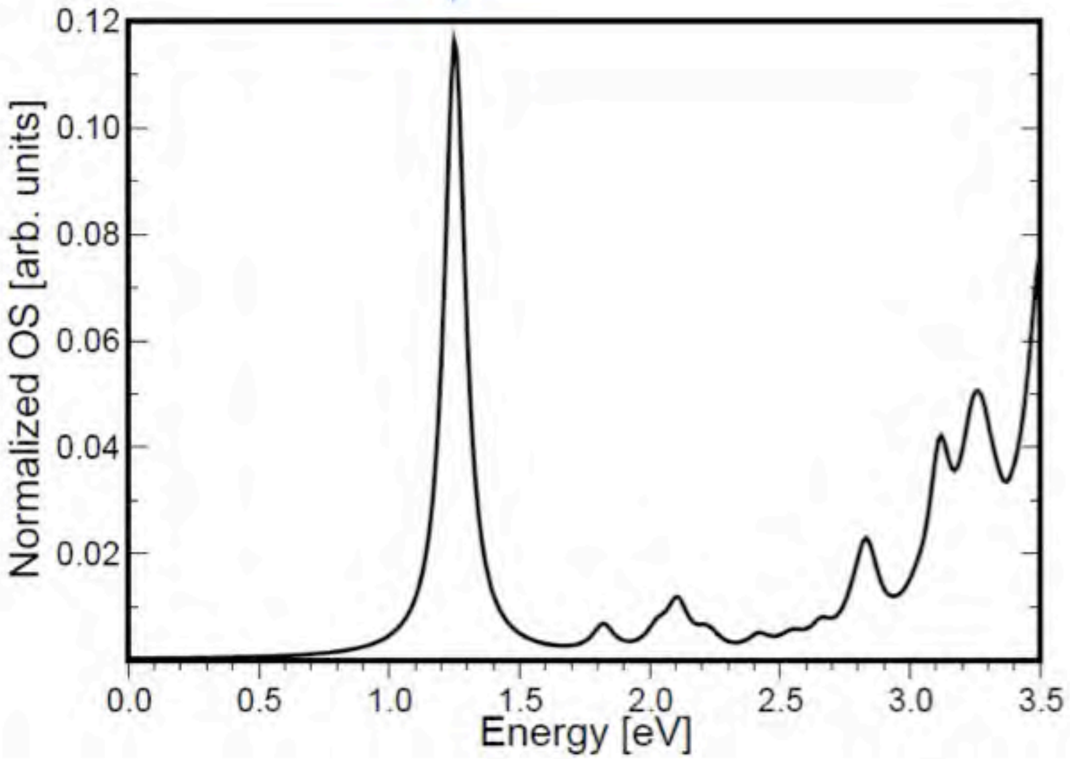
HOMO-1

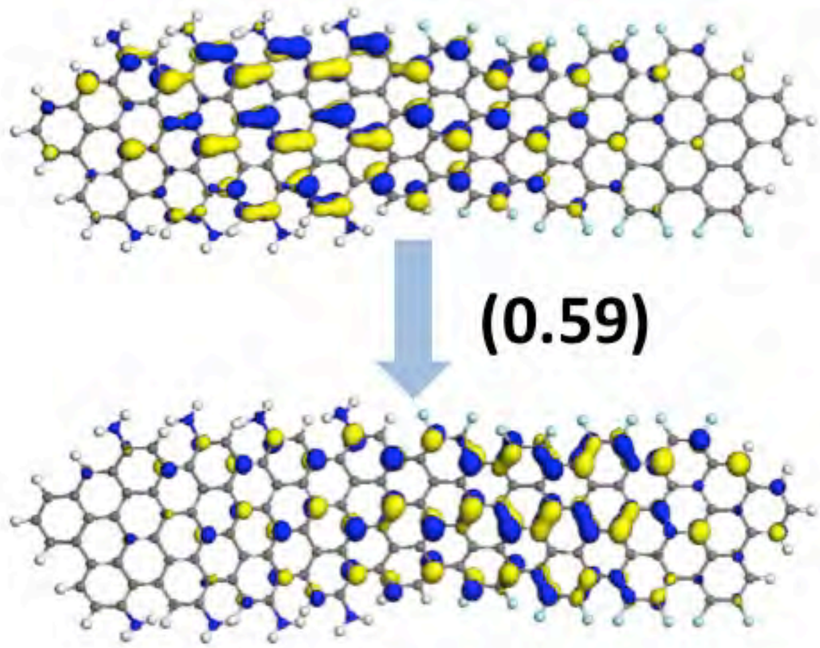




LUMO+1

Optical Properties of NH_2//F





- ✓ **Large oscillator strength**
- ✓ **Charge transfer character** expected

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Hole/Electron Density

HOLE density

$$\rho_h^I(\mathbf{r}) = \sum_{\alpha\beta} |c_{\alpha\beta}^I \cdot \phi_\alpha(\mathbf{r})|^2$$

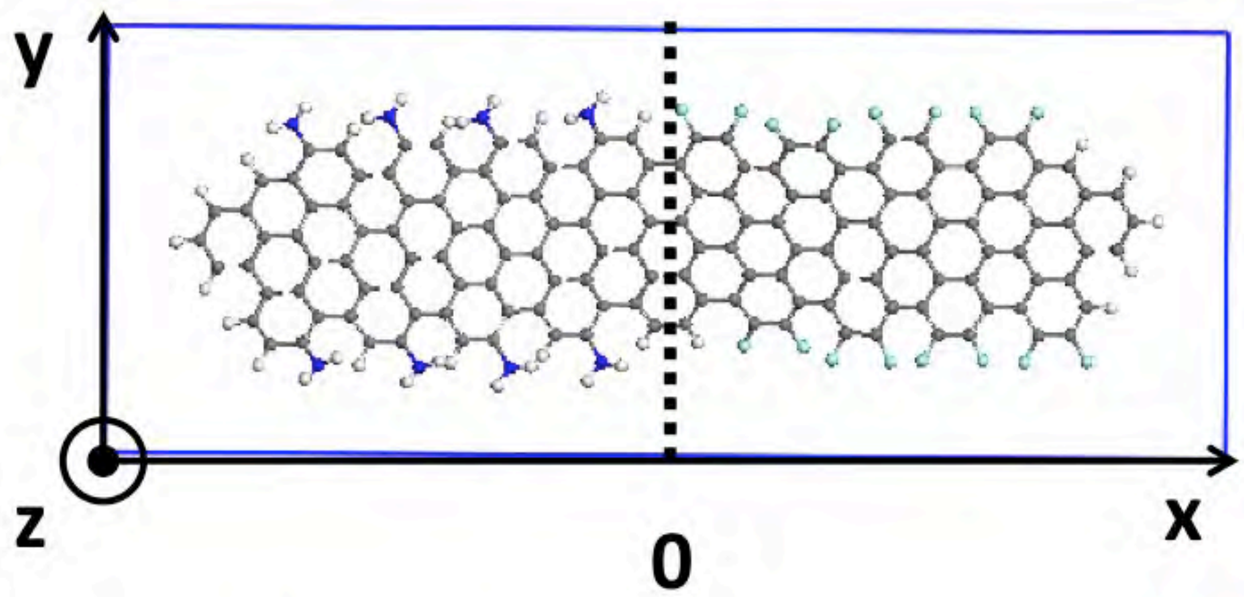
ELECTRON density

$$\rho_e^I(\mathbf{r}) = \sum_{\alpha\beta} |c_{\alpha\beta}^I \cdot \phi_\beta(\mathbf{r})|^2$$

LOCALIZATION

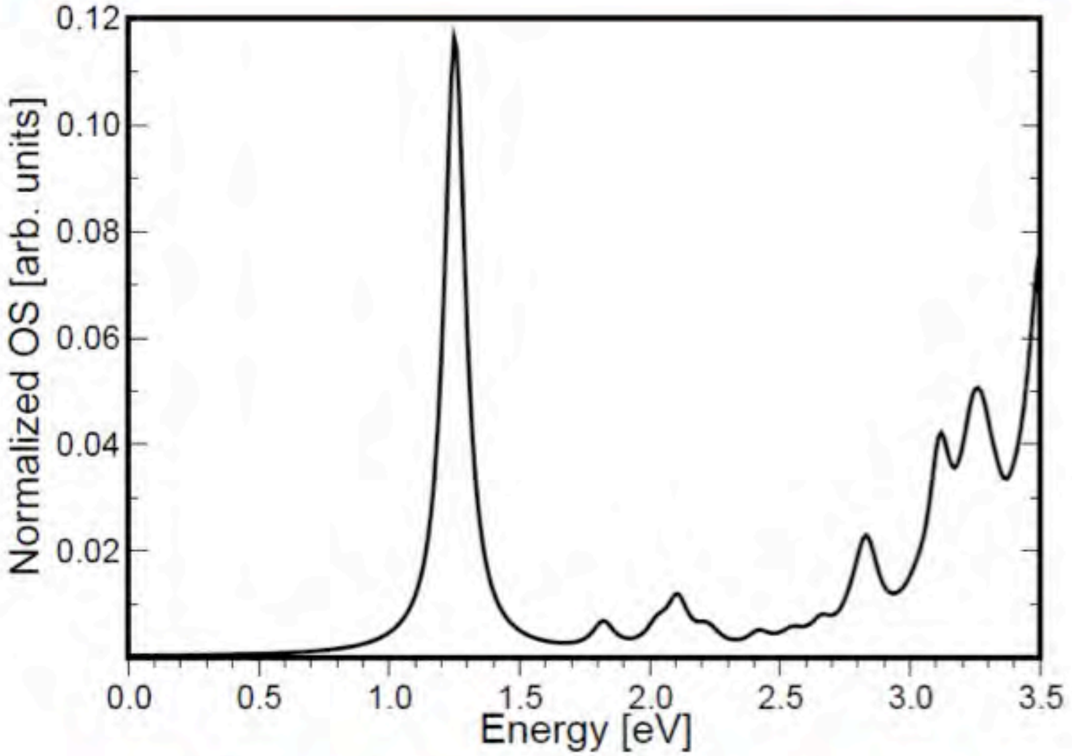
$$L_h = \frac{\sum_{y,z} \sum_{x \leq 0} \rho_h(x,y.z)}{\sum_{x,y,z} \rho_h(x,y.z)}$$

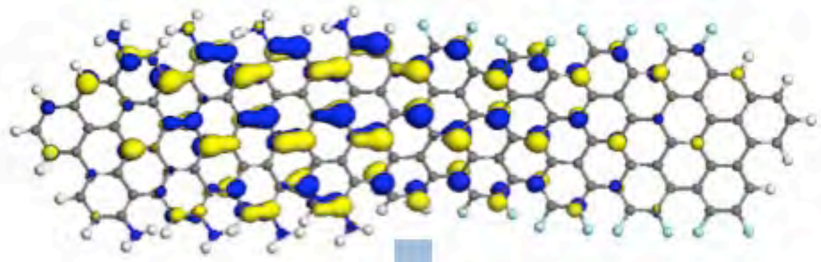
$$L_e = \frac{\sum_{y,z} \sum_{x \geq 0} \rho_e(x,y.z)}{\sum_{x,y,z} \rho_e(x,y.z)}$$



$50\% \leq L_{h/e} \leq 100\%$

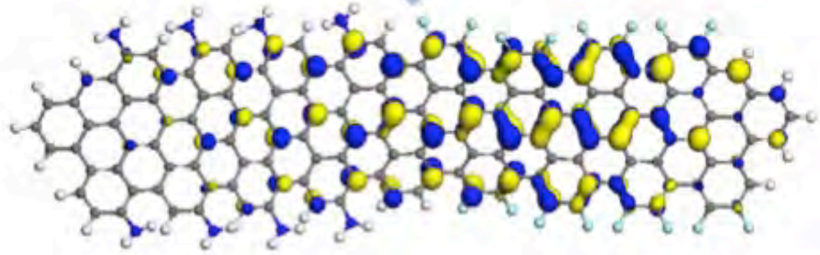
Optical Properties of NH_2//F



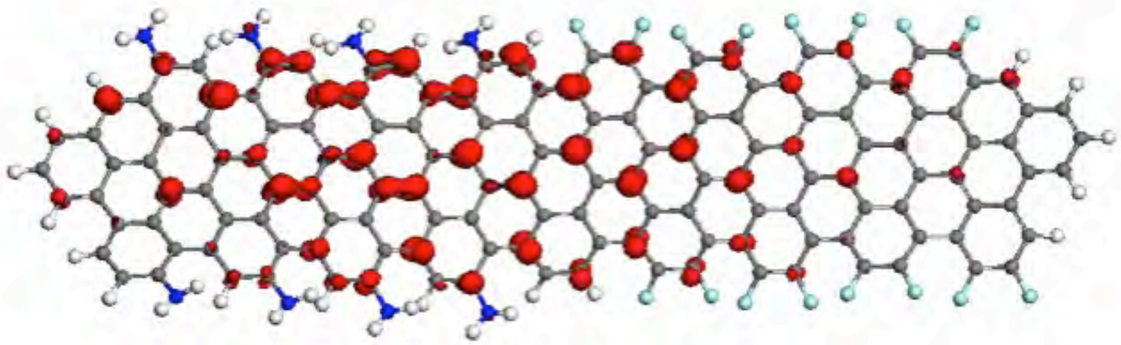


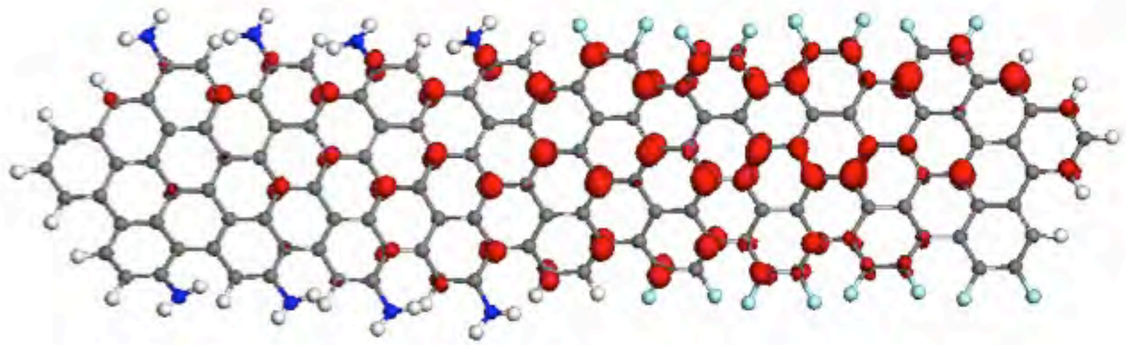
HOMO

(0.59)



LUMO





HOLE (64%) **ELECTRON (65%)**

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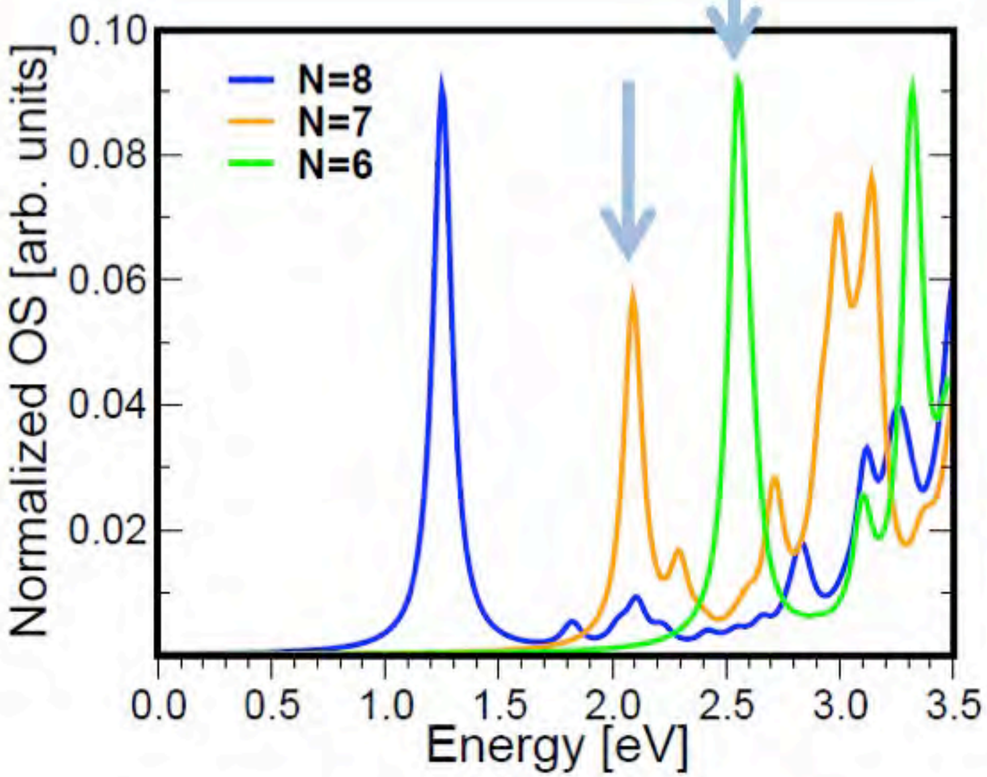
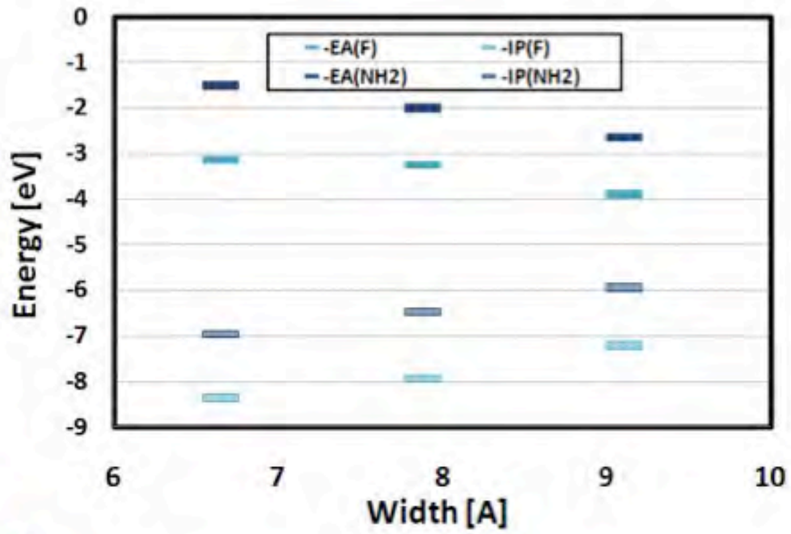
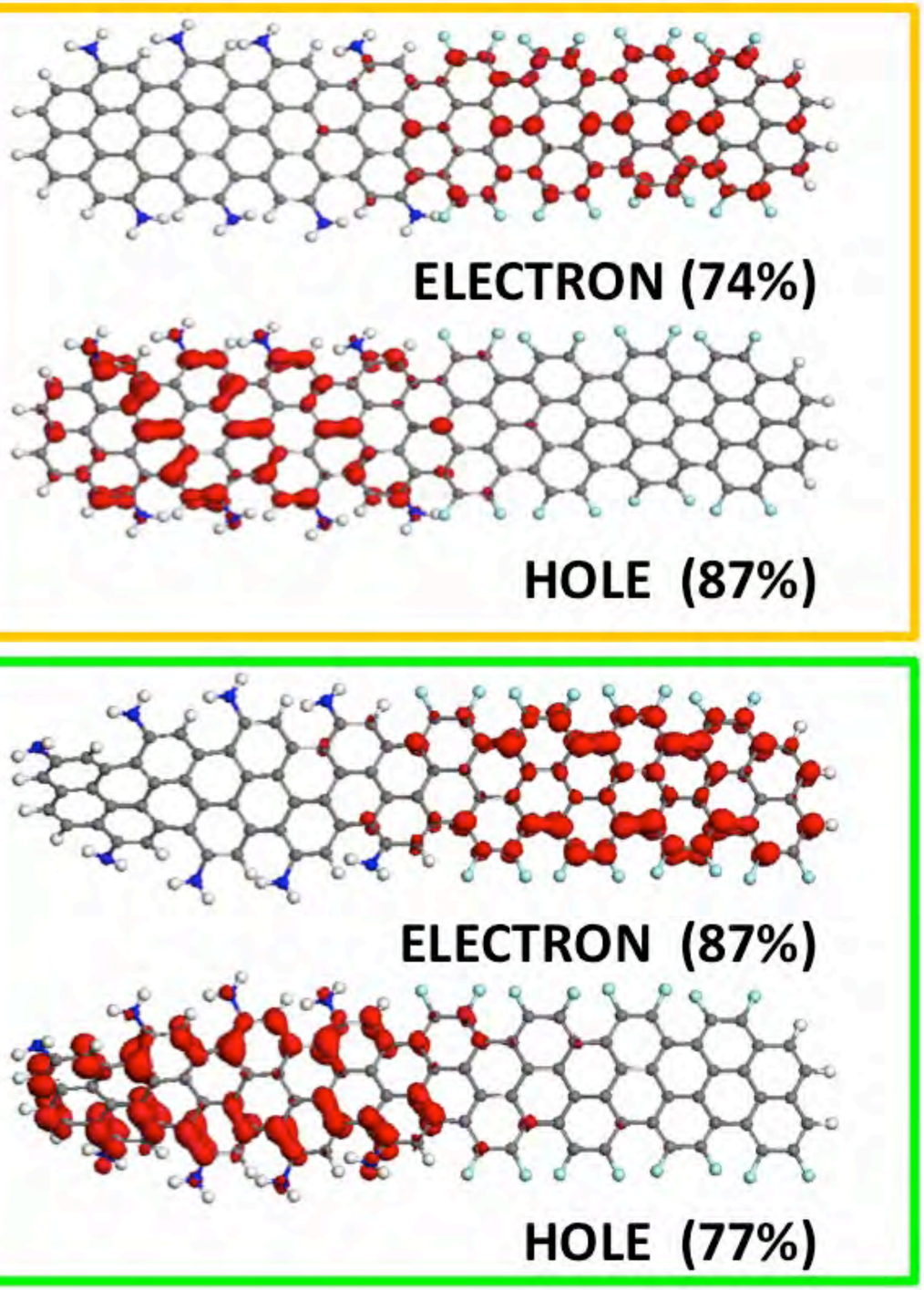
Width Modulation







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Conclusions

- **Gap offset tuned** upon **edge covalent functionalization**
- Design **all-graphene *type II* nano-junctions**
- **Localized Molecular Orbitals** close to the gap region
- **Large oscillator strength** and **charge transfer character** of the 1st optically active excitation
- **Tunability** upon **width modulation**

For support: *MAE – MIUR-FIRB ItalNanoNet – Fondazione Cassa di Risparmio di Modena - FAPESP and CNPq (Brazil)*

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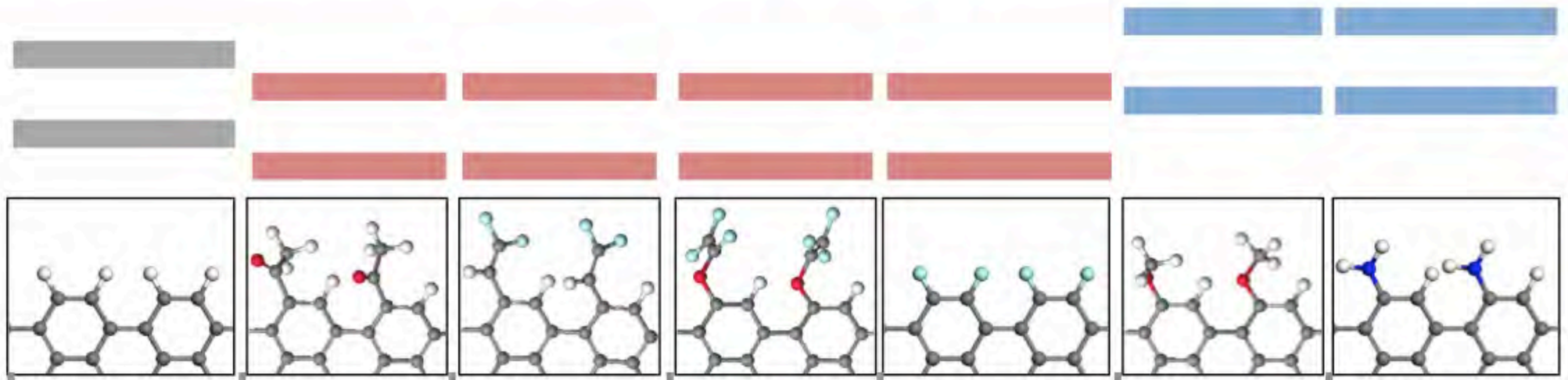
CINECA

THANK YOU!

SUPPLEMENTARY SLIDES

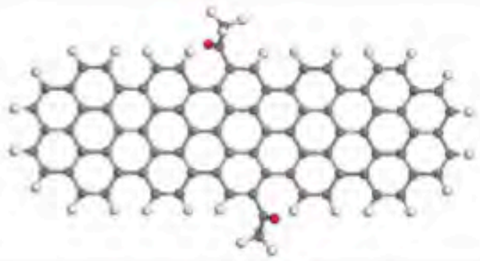
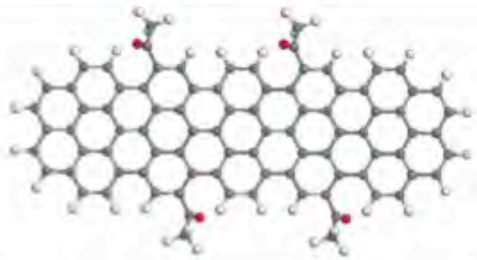
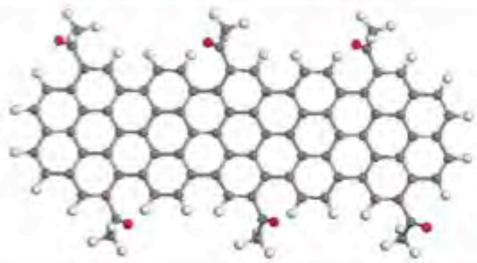
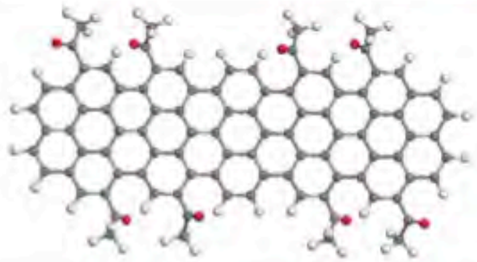
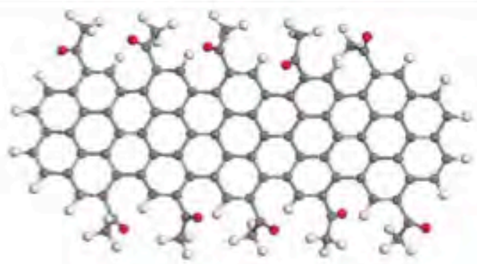
Functional Group Stability



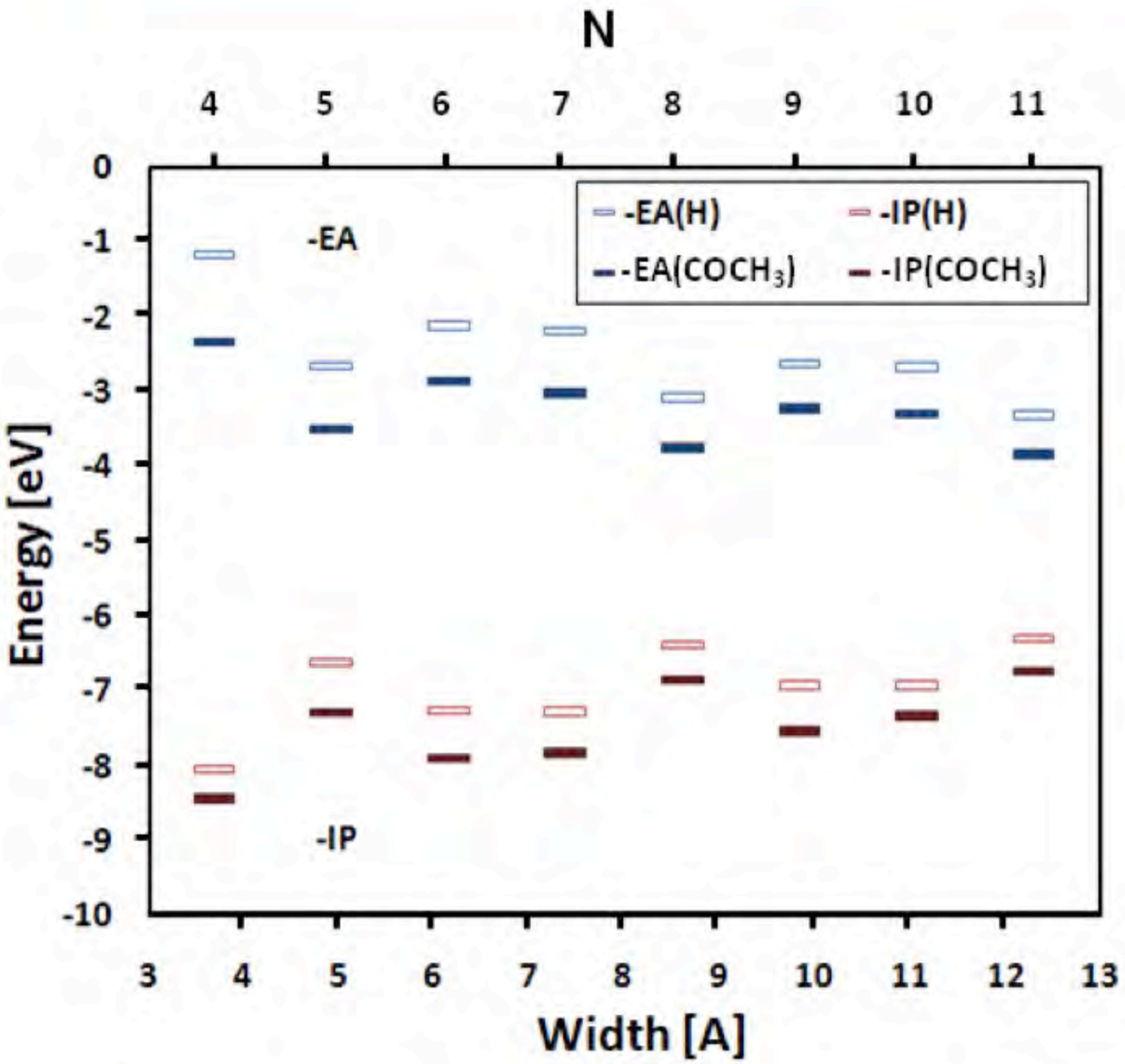
	H	$COCH_3$	$CH=CF_2$	$OCF=CF_2$	F	OCH_3	NH_2
E_G [eV]	5.13	4.86	4.65	4.74	4.69	4.75	4.47
-ΔEA [eV]	0.00	-0.69	-0.67	-0.70	-1.10	0.12	0.14
-ΔIP [eV]	0.00	-0.42	-0.19	-0.31	-0.67	0.50	0.79

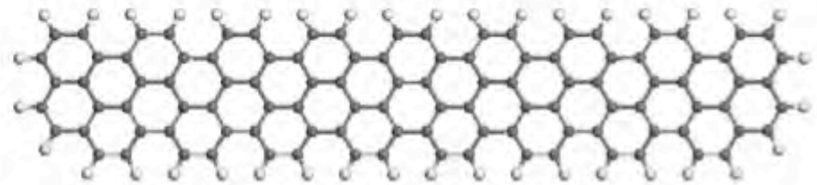
CNRNANO MODENA S3

Number of Groups Stability

		ΔEA [eV]	ΔIP [eV]	E_G [eV]
2		0.21	0.09	5.01
4		0.29	0.17	5.01
6		0.37	0.23	4.99
8		0.47	0.30	4.96
10		0.69	0.42	4.86

Flake Width Stability





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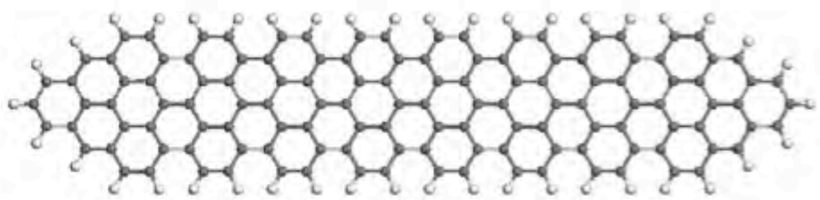

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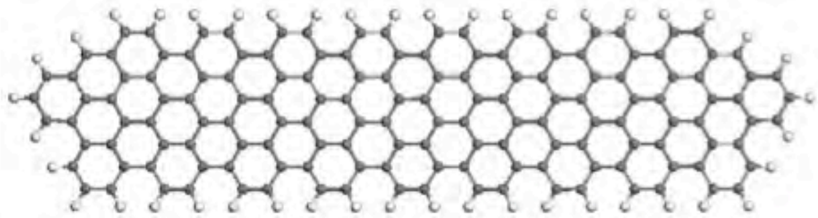

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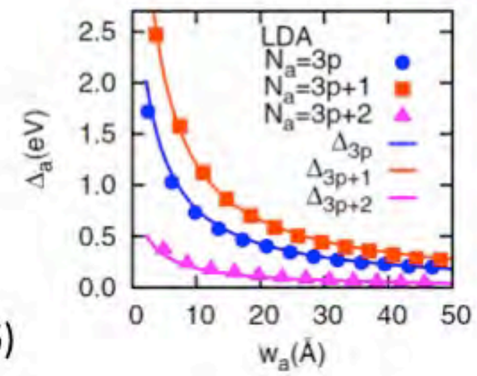
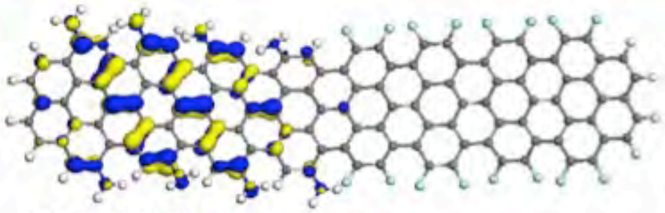
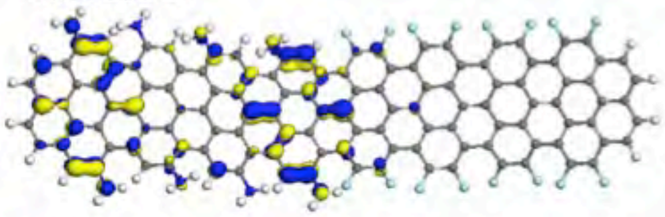


Y. Son *et al.*, PRL **97**, 216803 (2006)

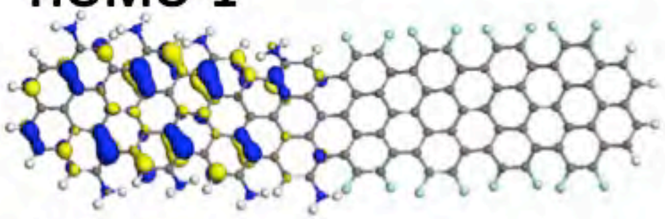
Width Modulation



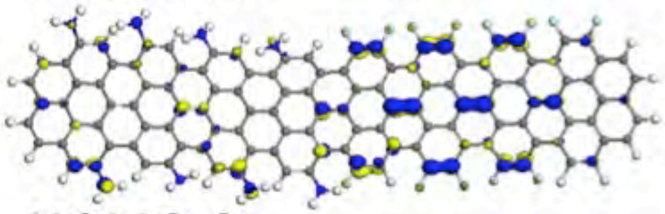
HOMO



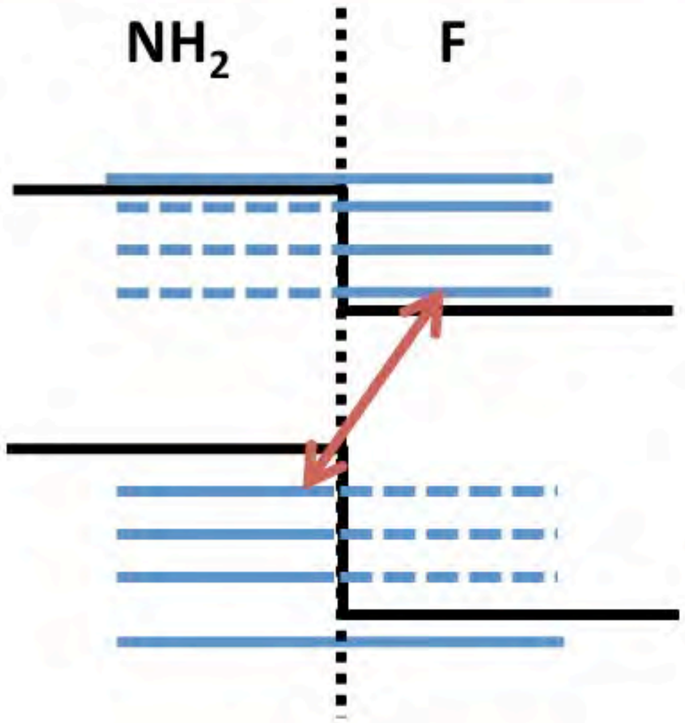
HOMO-1

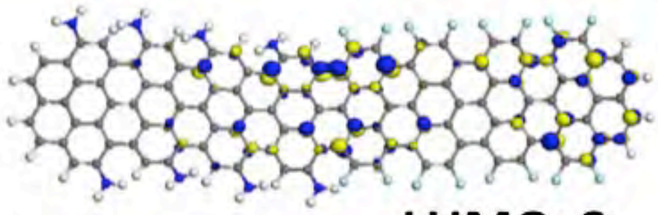


HOMO-2

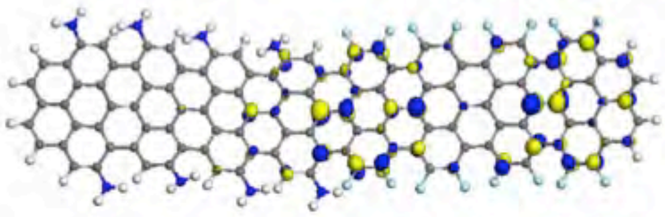


HOMO-3





LUMO+3



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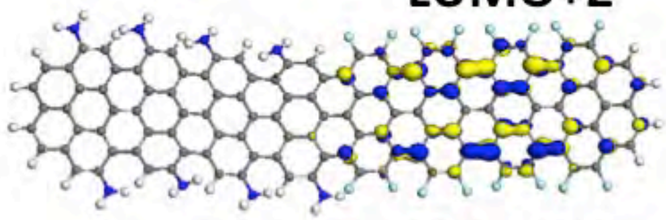
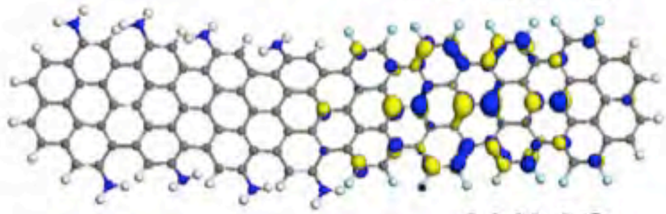
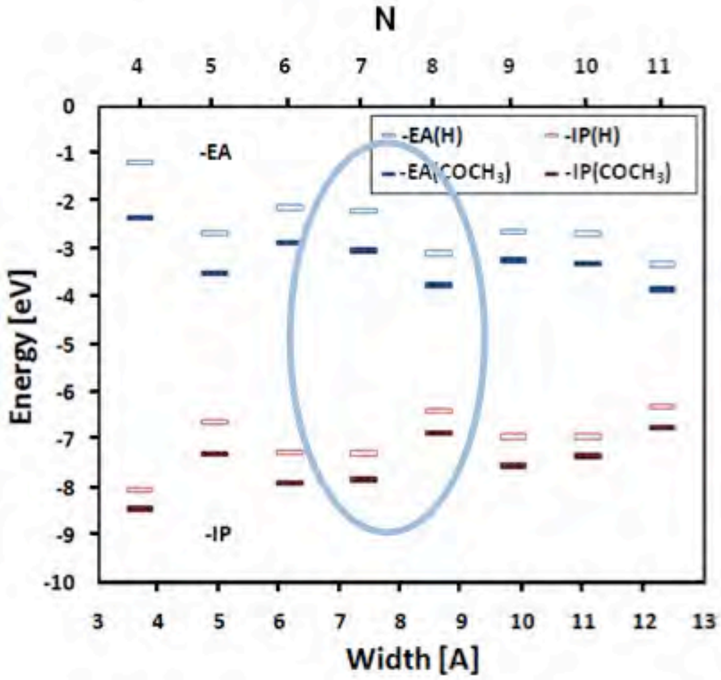


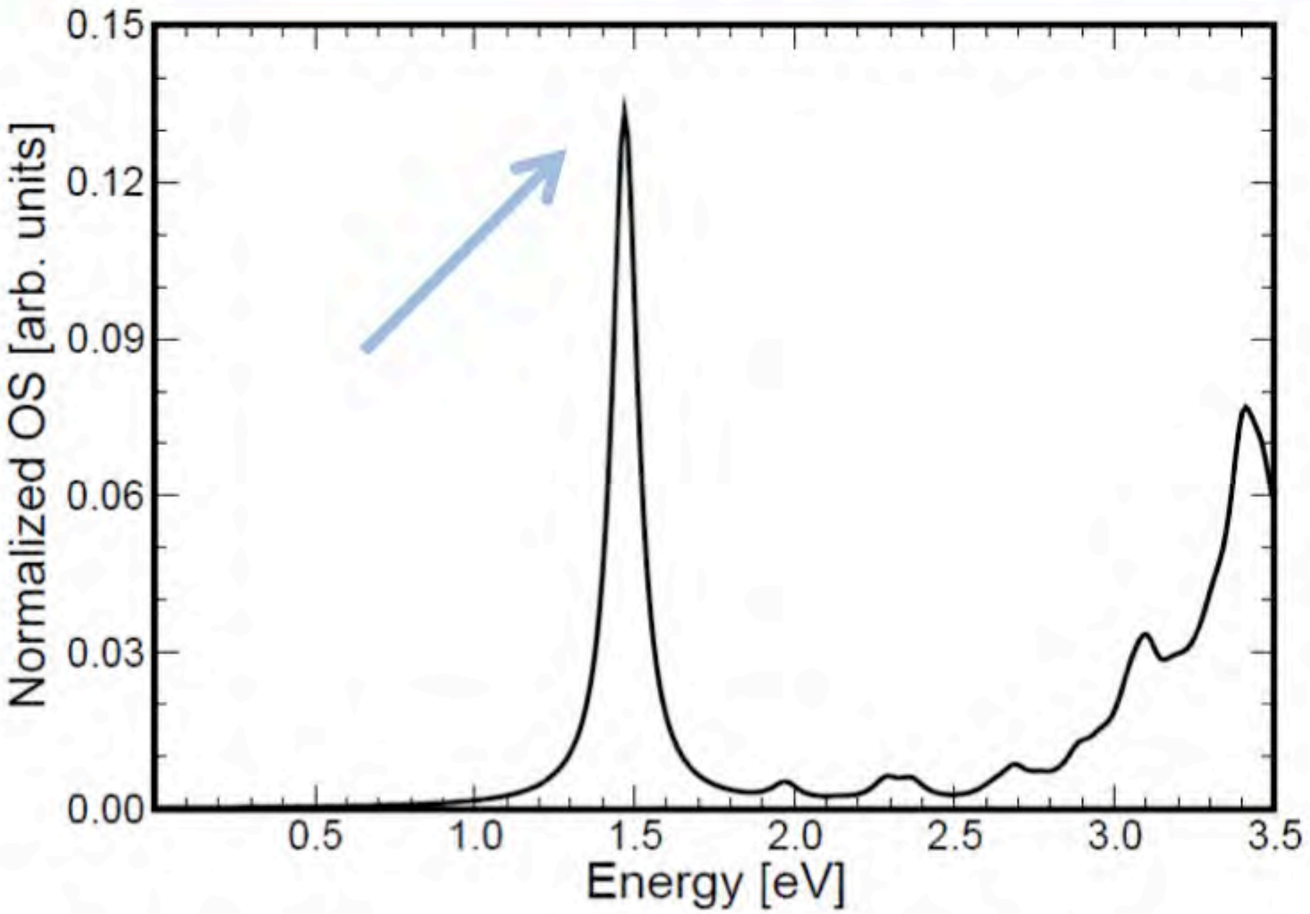
LUMO+1

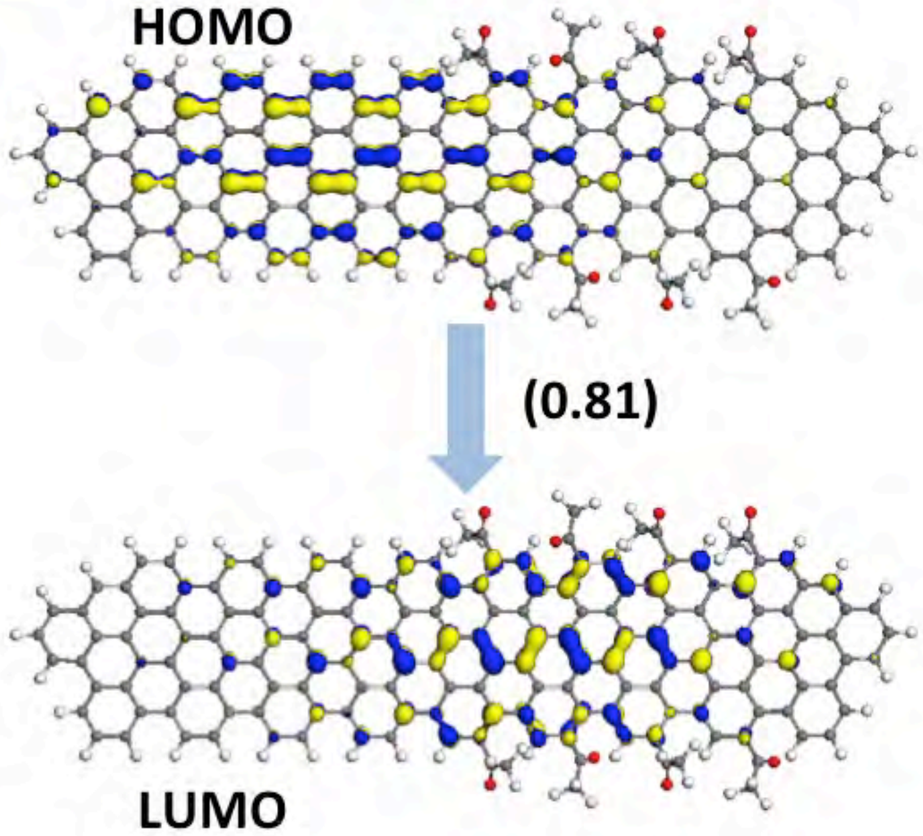


LUMO

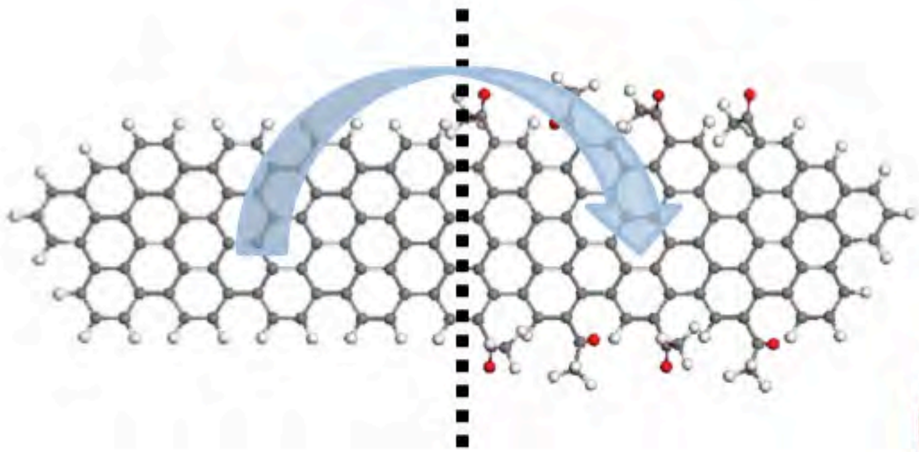


Optical Properties of H//$COCH_3$

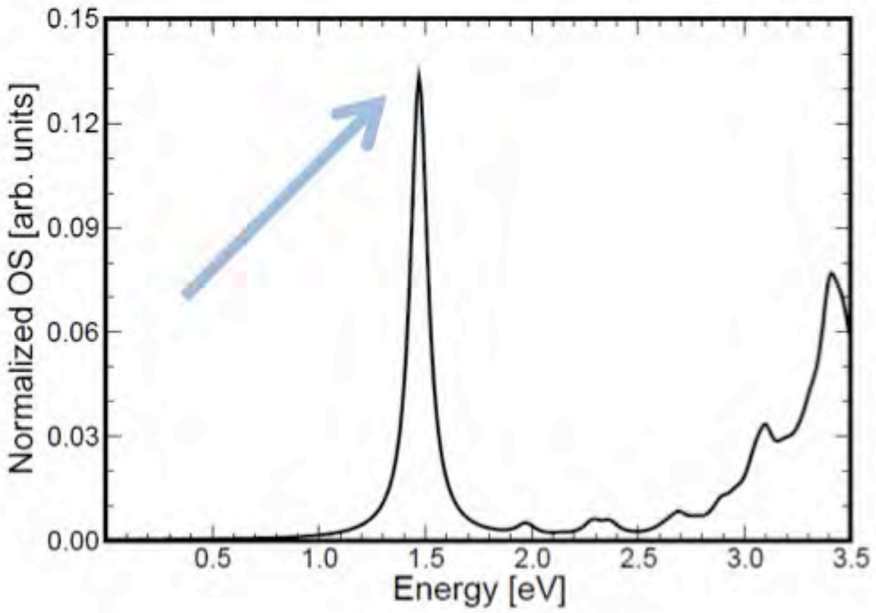


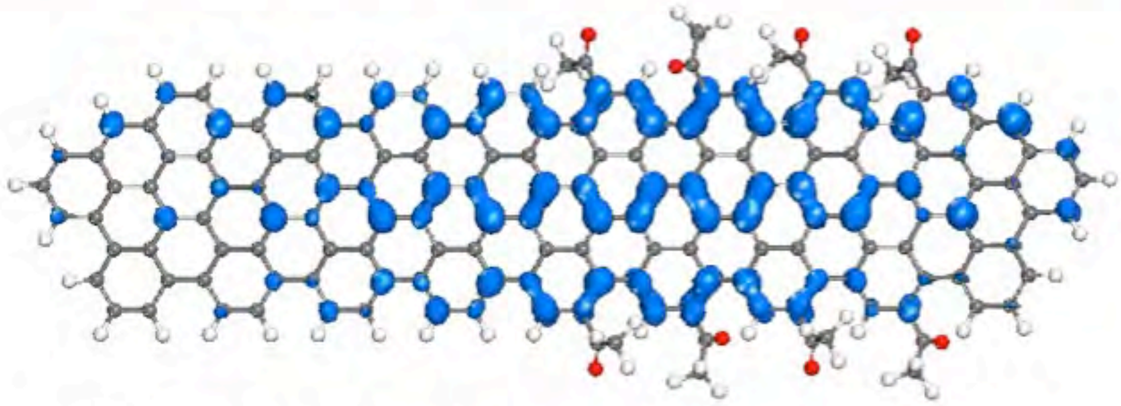


Charge Transfer Character?

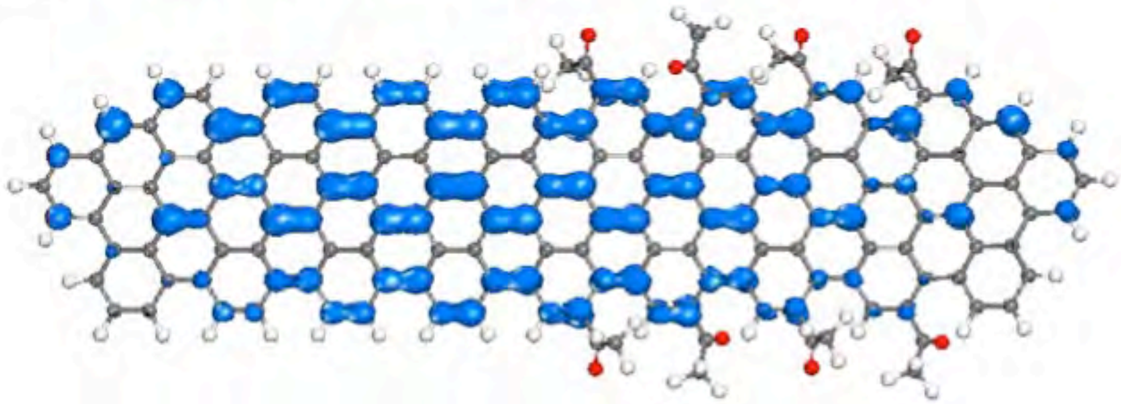


Hole/Electron in $H//COCH_3$





ELECTRON (60%)



HOLE (56%)

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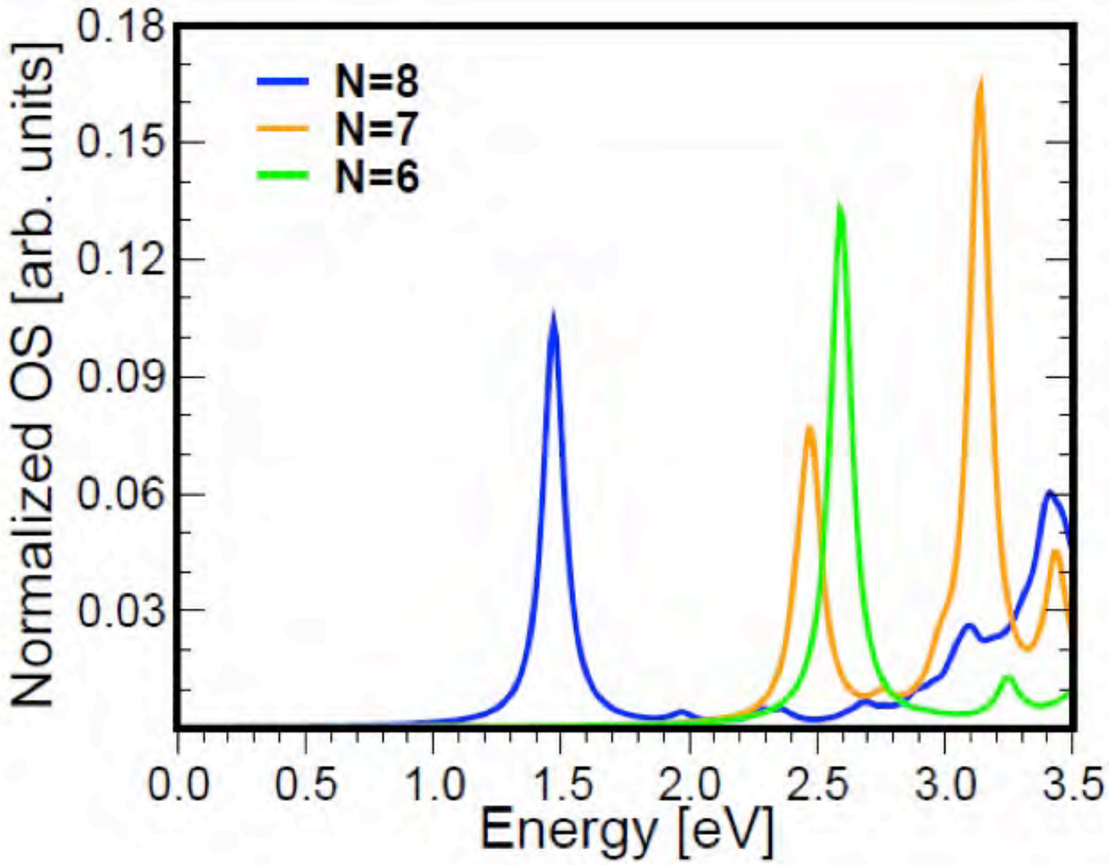
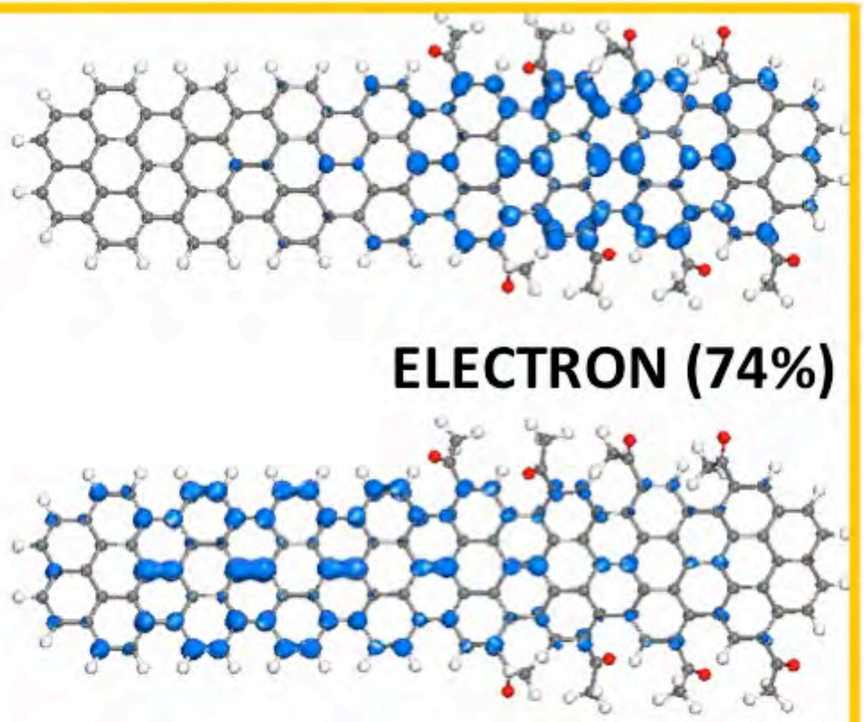
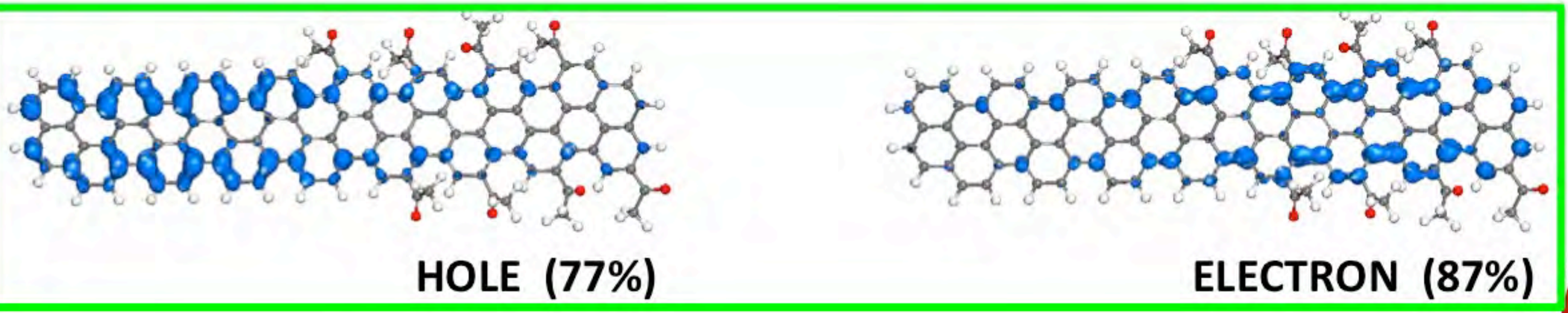
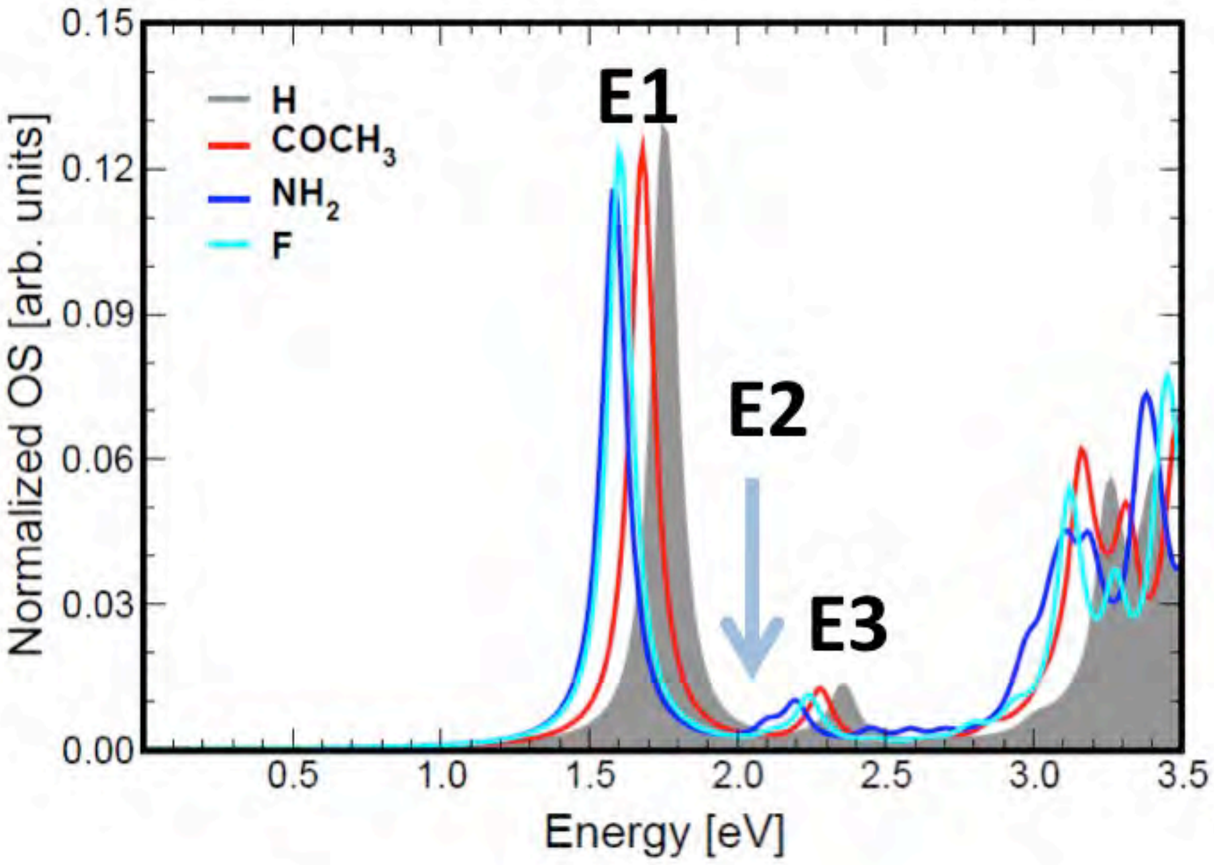
Width Modulation (H//$COCH_3$)

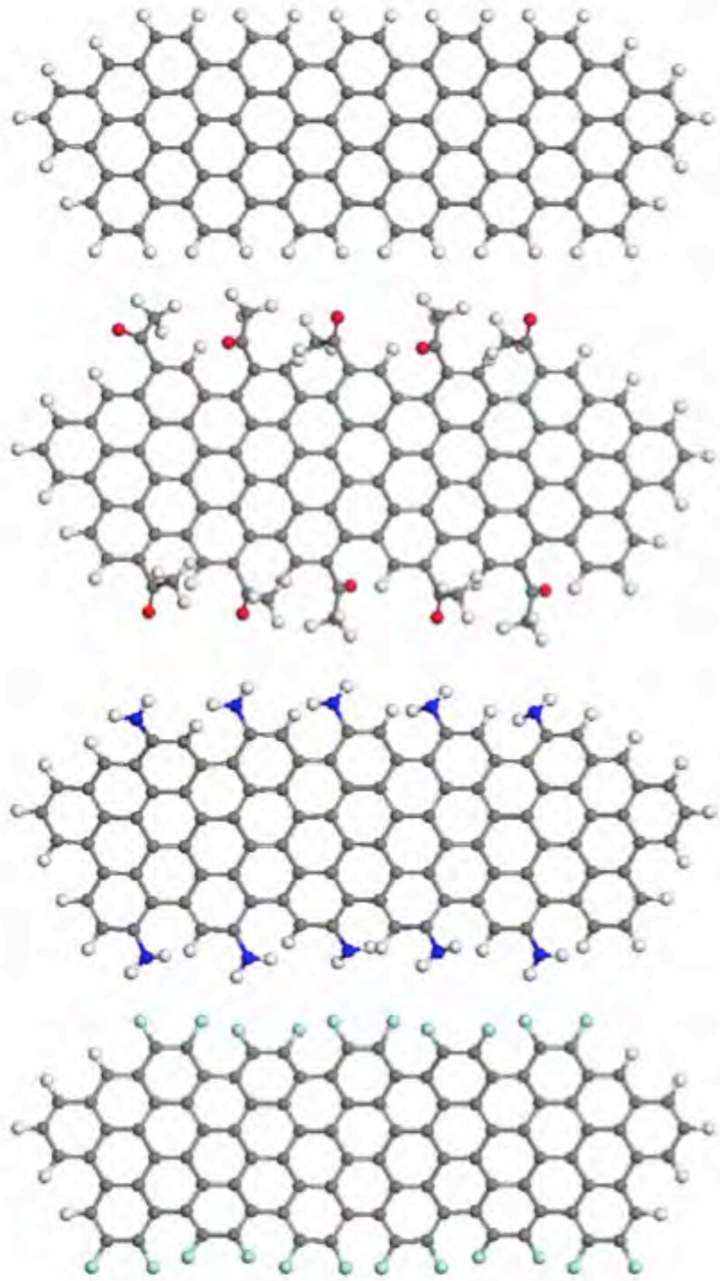






UV-Vis Spectra of Graphene Flakes

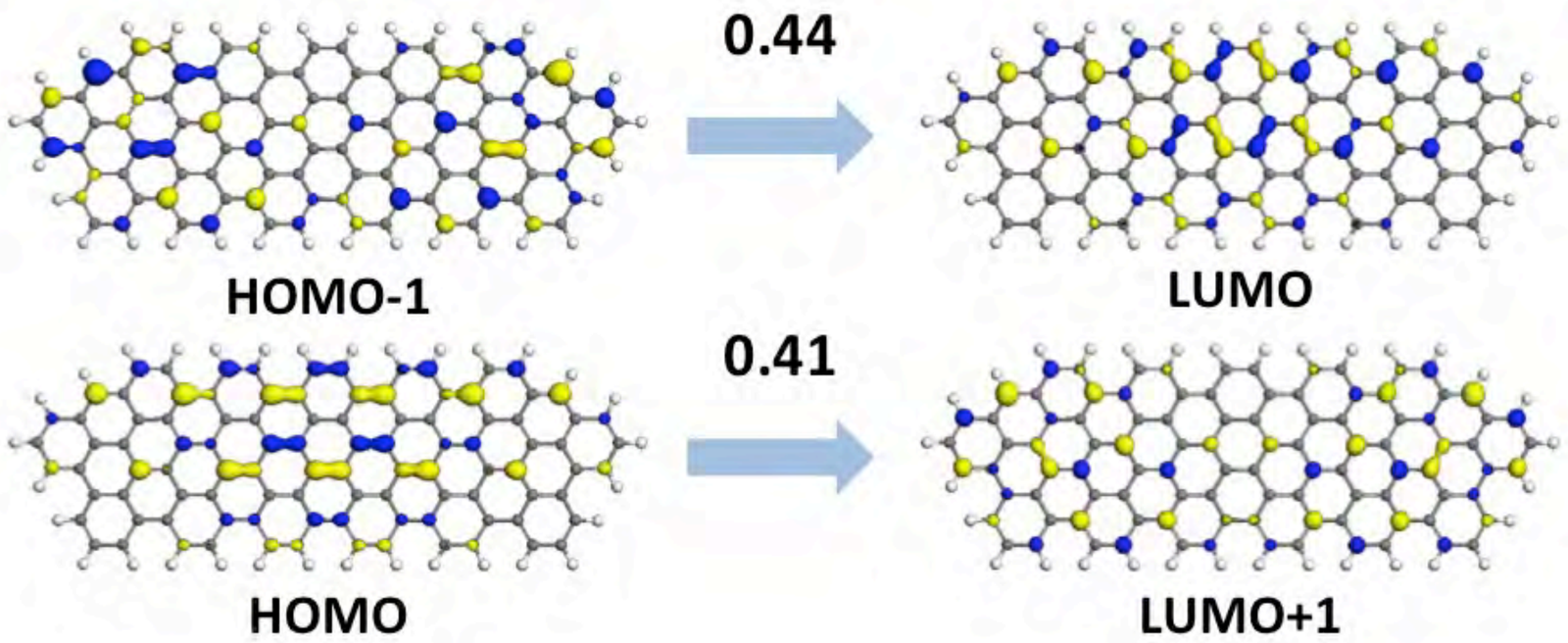




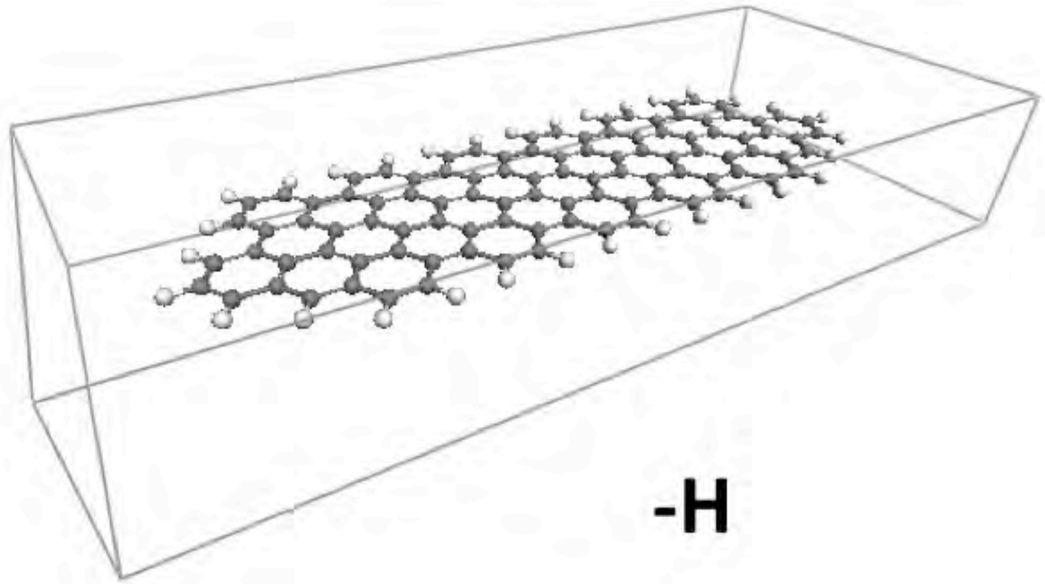
Optically Active Excitations

E1

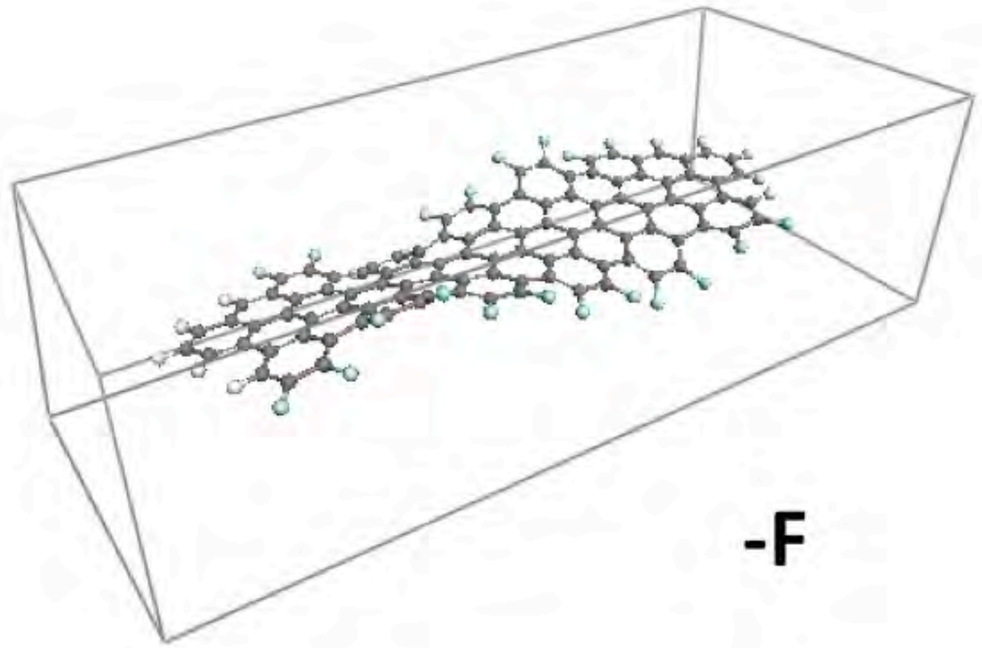
E3



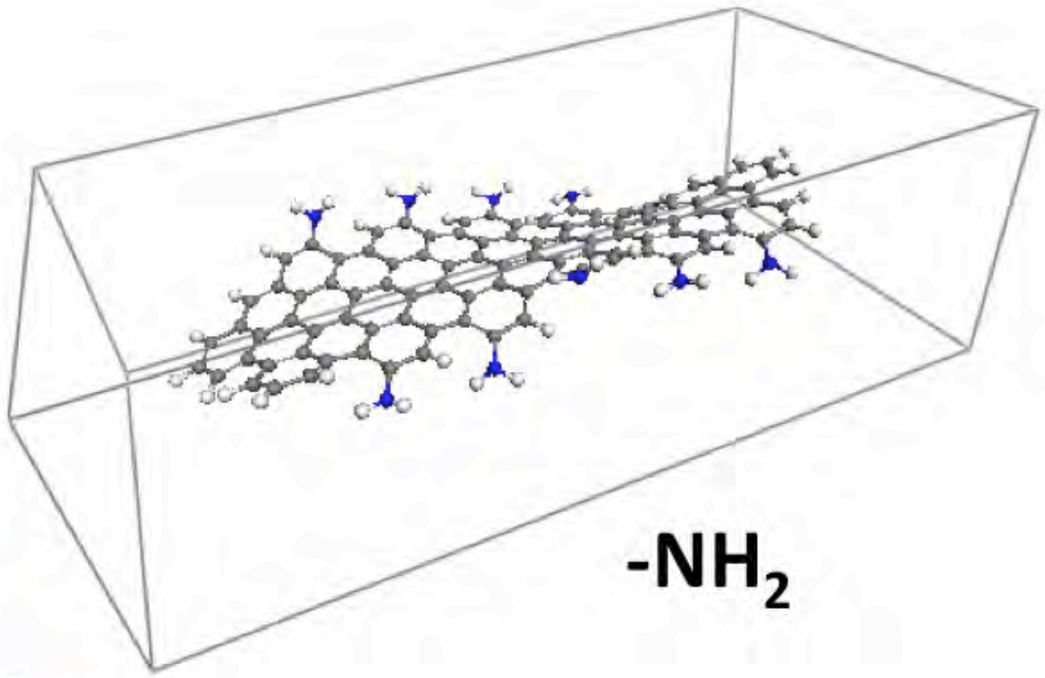
Graphene nanoflakes: perspective view



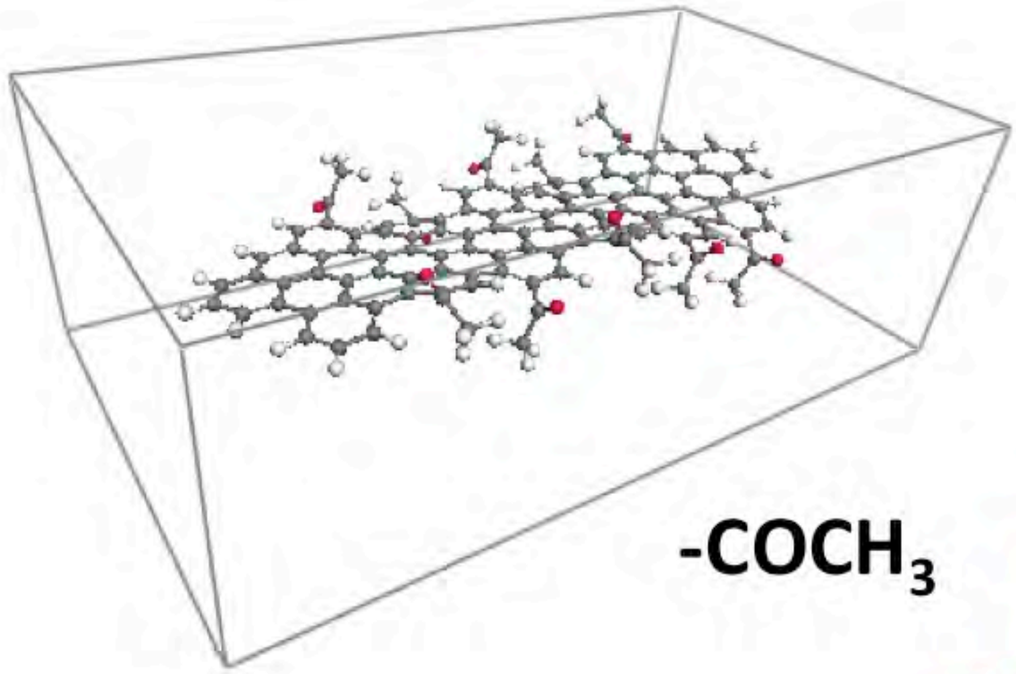
-H



-F

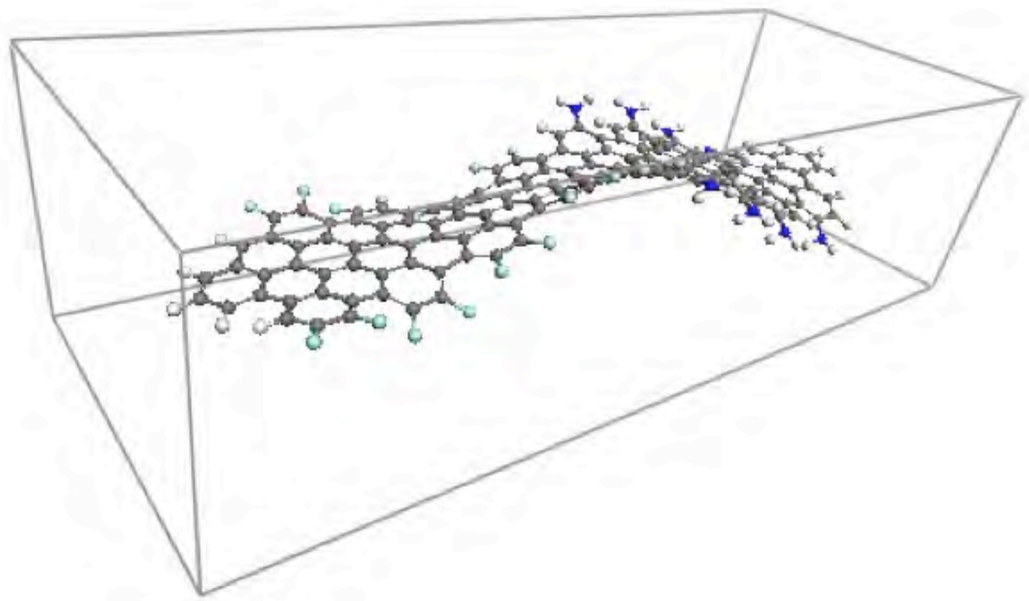


$-NH_2$

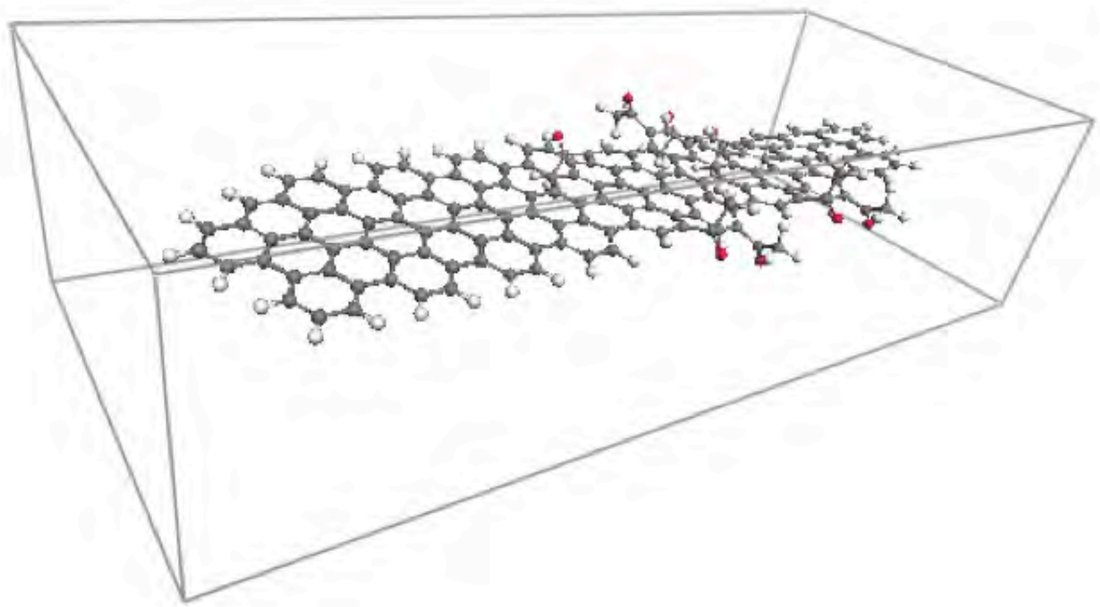


$-COCH_3$

Graphene nanojunctions: perspective view



$NH_2//F$



$H//COCH_3$

Hartree-Fock Hamiltonian

Hartree-Fock Hamiltonian

$$E = \sum_{i=1}^{N_{\text{elec}}} h_i + \frac{1}{2} \sum_{i=1}^{N_{\text{elec}}} \sum_{j=1}^{N_{\text{elec}}} (J_{ij} - K_{ij}) + V_{\text{nn}}$$

$$\mathbf{h}_i = -\tfrac{1}{2}\nabla_i^2 - \sum_a^{N_{\text{nuclei}}} \frac{Z_a}{|\mathbf{R}_a - \mathbf{r}_i|}$$

$$J_{ij} = \int \psi_i^*(1)\psi_j^*(2)\left(\frac{1}{r_{12}}\right)\psi_i(1)\psi_j(2)\,dv_1\,dv_2$$ Coulomb Integral

$$K_{ij} = \int \psi_i^*(1)\psi_j^*(2)\left(\frac{1}{r_{12}}\right)\psi_i(2)\psi_j(1)\,dv_1\,dv_2$$ Exchange Integral

Total Wave Function

$$\Phi_{\text{SD}} = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_1(1) & \phi_2(1) & \cdots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \cdots & \phi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(N) & \phi_2(N) & \cdots & \phi_N(N) \end{vmatrix} \quad ; \quad \langle \phi_i | \phi_j \rangle = \delta_{ij}$$

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F. Jensen *Introduction to Computational Chemistry*, Wiley 2nd ed. (2007)

E. Lewars *Computational Chemistry*, Kluwer (2004)

LCAO and Roothaan-Hall Equations

LCAO expansion of MOs

$$\phi_i = \sum_{\alpha}^{M_{\text{basis}}} c_{\alpha i}\chi_\alpha$$

$$\mathbf{F}_i \sum_{\alpha}^{M_{\text{basis}}} c_{\alpha i}\chi_\alpha = \varepsilon_i \sum_{\alpha}^{M_{\text{basis}}} c_{\alpha i}\chi_\alpha \quad \Rightarrow \quad \mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon}$$

Roothaan-Hall Equations

$$F_{\alpha\beta} = \langle \chi_\alpha | \mathbf{F} | \chi_\beta \rangle$$

$$S_{\alpha\beta} = \langle \chi_\alpha | \chi_\beta \rangle$$

OVERLAP

$$\mathbf{F}_i = \mathbf{h}_i + \sum_{j}^{N_{\text{elec}}} (\mathbf{J}_j - \mathbf{K}_j)$$

Fock operator

$\mathbf{g}$

$$\langle \chi_\alpha | \mathbf{h} | \chi_\beta \rangle = \int \chi_\alpha(1)(-\tfrac{1}{2}\nabla^2)\chi_\beta(1)\mathrm{d}\mathbf{r}_1 + \sum_{a}^{N_{\text{nuclei}}} \int \chi_\alpha(1)\left(\frac{Z_a}{|\mathbf{R}_a - \mathbf{r}_1|}\right)\chi_\beta(1)\mathrm{d}\mathbf{r}_1$$

$$\langle \chi_\alpha\chi_\gamma | \mathbf{g} | \chi_\beta\chi_\delta \rangle = \int \chi_\alpha(1)\chi_\gamma(2)\left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\right)\chi_\beta(1)\chi_\delta(2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2$$

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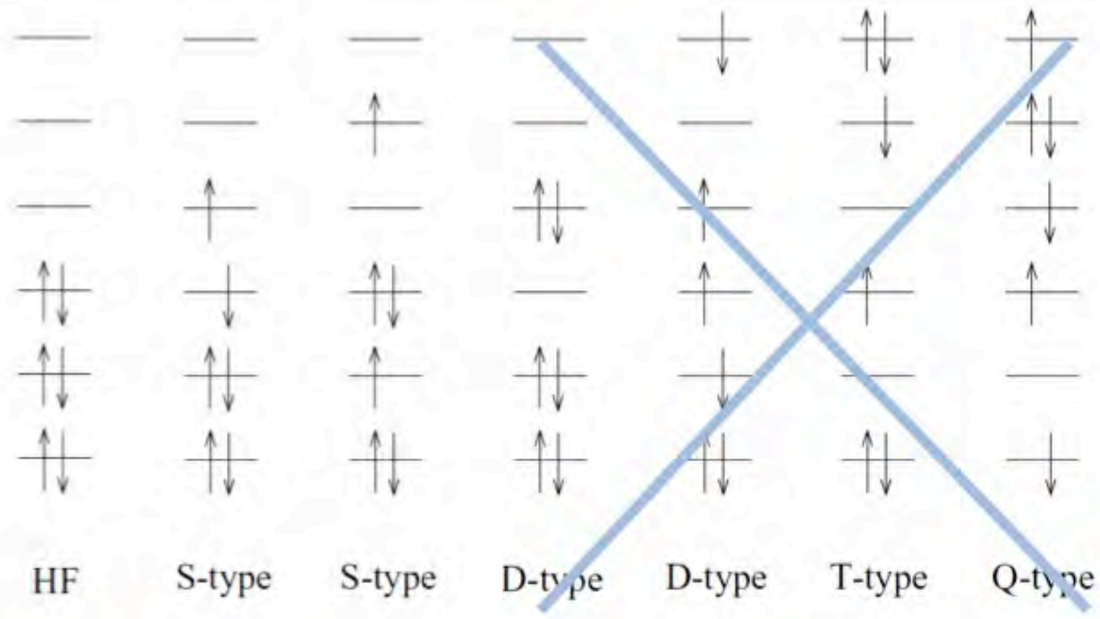
Configuration Interaction

only Single excitations included (**CIS**)



$$\Psi_{\mathrm{CI}} = a_0\Phi_{\mathrm{HF}} + \sum_{\mathrm{S}} a_{\mathrm{S}}\Phi_{\mathrm{S}} + \sum_{\mathrm{D}} a_{\mathrm{D}}\Phi_{\mathrm{D}} + \sum_{\mathrm{T}} a_{\mathrm{T}}\Phi_{\mathrm{T}} + \cdots = \sum_{i=0} a_i\Phi_i$$

$$\langle \Phi_0 | \mathbf{H} | \Phi_i^a \rangle = \langle \phi_i | \mathbf{h} | \phi_a \rangle + \sum_j \left(\langle \phi_i \phi_j | \phi_a \phi_j \rangle - \langle \phi_i \phi_j | \phi_j \phi_a \rangle \right)$$

Occupied MO

Virtual MO

$$\mathbf{F}\phi_a = \varepsilon_a \phi_a$$

$$\langle \phi_i | \mathbf{F} | \phi_a \rangle = \varepsilon_a \langle \phi_i | \phi_a \rangle = \varepsilon_a \delta_{ia}$$

CNRNANO MODENA

Semi-empirical Methods

- Only Valence Electrons included in the Basis Set (CORE = nuclei + core electrons);
- Atomic Orbitals (usually Slater type) as Basis Set;
- One- and Two-Electron Integrals parameterized;
- Overlap Matrix → Unit Matrix $S_{\mu\nu} = \langle \mu | \nu \rangle = \delta_{\mu\nu}\delta_{\mathrm{AB}}$

AM1

- Specifically parameterized to evaluate EA and IP;
- Parameterization referring to the nature of single atoms;
- Parameterized terms:
  - One-electron integrals

$$h_{\mu\nu} = \langle \mu_A | \mathbf{h} | \nu_B \rangle = \delta_{\mu\nu} U_\mu - \sum_{a \neq A}^{N_{\text{nuclei}}} Z'_a \langle \mu_A \mu_A | \nu_A \nu_A \rangle$$

$$\langle \mu_A | \mathbf{h} | \nu_B \rangle = \tfrac{1}{2} S_{\mu\nu} (\beta_\mu + \beta_\nu)$$

  - 27 types of Two-electron integrals
    - 5 types of one-center

$$\langle ss|ss\rangle = G_{ss}$$
$$\langle sp|sp\rangle = G_{sp}$$
$$\langle ss|pp\rangle = H_{sp}$$
$$\langle pp|pp\rangle = G_{pp}$$
$$\langle pp'|pp'\rangle = G_{p2}$$

    - 22 types of two-center (as interactions between multipoles)
  - Core-core repulsion

$$V_{\text{nn}}^{\text{AM1}}(\text{A},\text{B}) = V_{\text{nn}}^{\text{MNDO}}(\text{A},\text{B}) + \frac{Z'_A Z'_B}{R_{AB}} \sum_k \left(a_{kA} e^{-b_{kA}(R_{AB}-c_{kA})^2} + a_{kB} e^{-b_{kB}(R_{AB}-c_{kB})^2} \right)$$

- Parameters are taken from experimental values (8 out of 13 parameters are fitted).

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ZINDO

- Specifically parameterized for spectroscopy;
- Parameterized terms:
  - One-electron integrals:

$$\langle \mu_A | \mathbf{h} | \mu_A \rangle = \langle \mu_A | -\tfrac{1}{2}\nabla^2 - \mathbf{V}_A | \mu_A \rangle - \sum_{a \neq A}^{N_{\text{nuclei}}} \langle \mu_A | \mathbf{V}_a | \mu_A \rangle$$

$$\langle \mu_A | \mathbf{h} | \nu_A \rangle = -\delta_{\mu\nu} \sum_{a \neq A}^{N_{\text{nuclei}}} \langle \mu_A | \mathbf{V}_a | \mu_A \rangle$$

  - Two-electron integrals:

$$\langle \mu_A \nu_B | \lambda_C \sigma_D \rangle = \delta_{AC}\delta_{BD}\delta_{\mu\lambda}\delta_{\nu\sigma} \langle \mu_A \nu_B | \mu_A \nu_B \rangle$$

$$\langle \mu_A \nu_A | \mu_A \nu_A \rangle = \langle \mu_A \mu_A | \mu_A \mu_A \rangle = \gamma_{AA}$$

$$\langle \mu_A \nu_B | \mu_A \nu_B \rangle = \gamma_{AB}$$

see e.g.

$$J_{ik} = \frac{1}{R_{ik} + 2(J_{ii} + J_{kk})^{-1}}$$ Mataga-Nishimoto

$$J_{ik} = \frac{1}{[R_{ik}^2 + (1/J_{ii} + 1/J_{kk})^2/4]^{1/2}}$$ Ohno-Klopman

CNRNANO MODENA S3