Barcelona Supercomputing Center
Centro Nacional de Supercomputación

# Structural, electronic and transport properties of distorted nanographenes by DFT methods (and some other works)

Blanca Biel
University of Granada

ugr | Universidad de Granada

# Outline

- Other RES projects:
  - SPM characterization of point-like defects in $MoS_2$ (STM and AFM)
  - $MoS_2$ capabilities as a selective gas sensor

- Distorted nanographenes:
  - NANOGRAPHOUT
  - State-of-the-art
  - Our approach
  - Results
  - What didn’t work /work in progress

# Nanoelectronics Research Group

- Simulation of Si- and 2D-based devices

→ Monte Carlo, Boltzmann, k·p, …

- Characterization of Si- and 2D-devices
- *Ab initio* calculations


- Dr. Blanca Biel
- Dr. César González

$MoS_2$-based devices (FETs, sensors)
SPM → defects and grain boundaries in 2D
Lateral 2D herostructures
Defects in nanographenes

siesta

VASP b-initio icnna ackage imulation

**FIREBALL**

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# SPM characterization of point-like defects in $MoS_2$

Dr. Yannick Dappe

Dr. César González

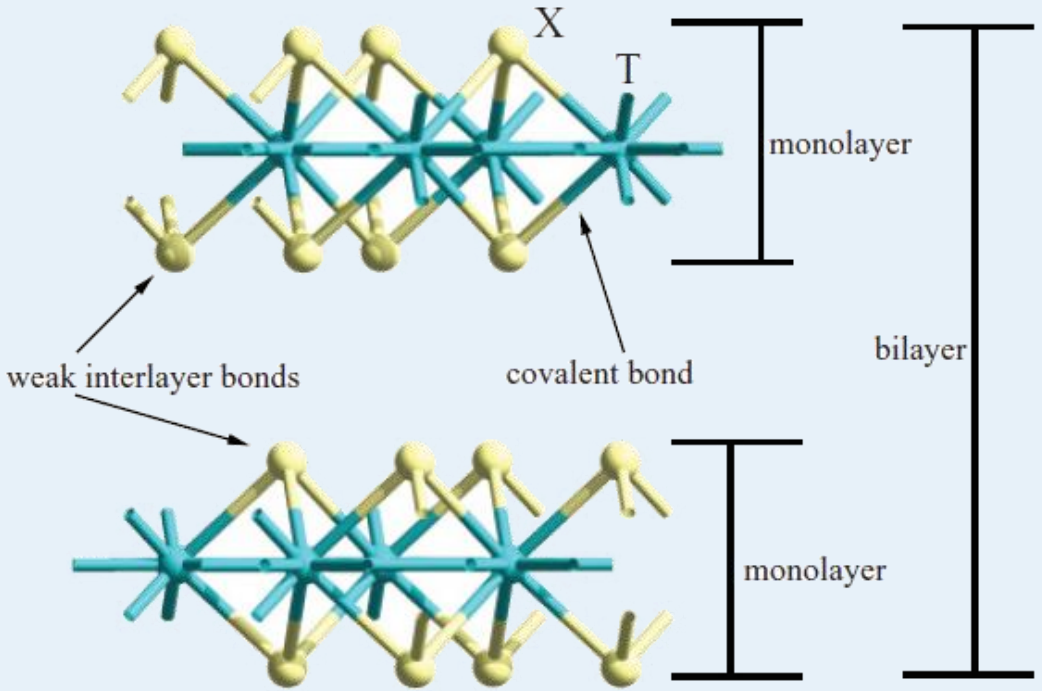
Universidad de Granada

# All about $MoS_2$

## Molybdenum disulfide ($MoS_2$)

- Well known in the **bulk** form as a dry lubricator
- a(Å) = 3.16, c(Å) = 12.294

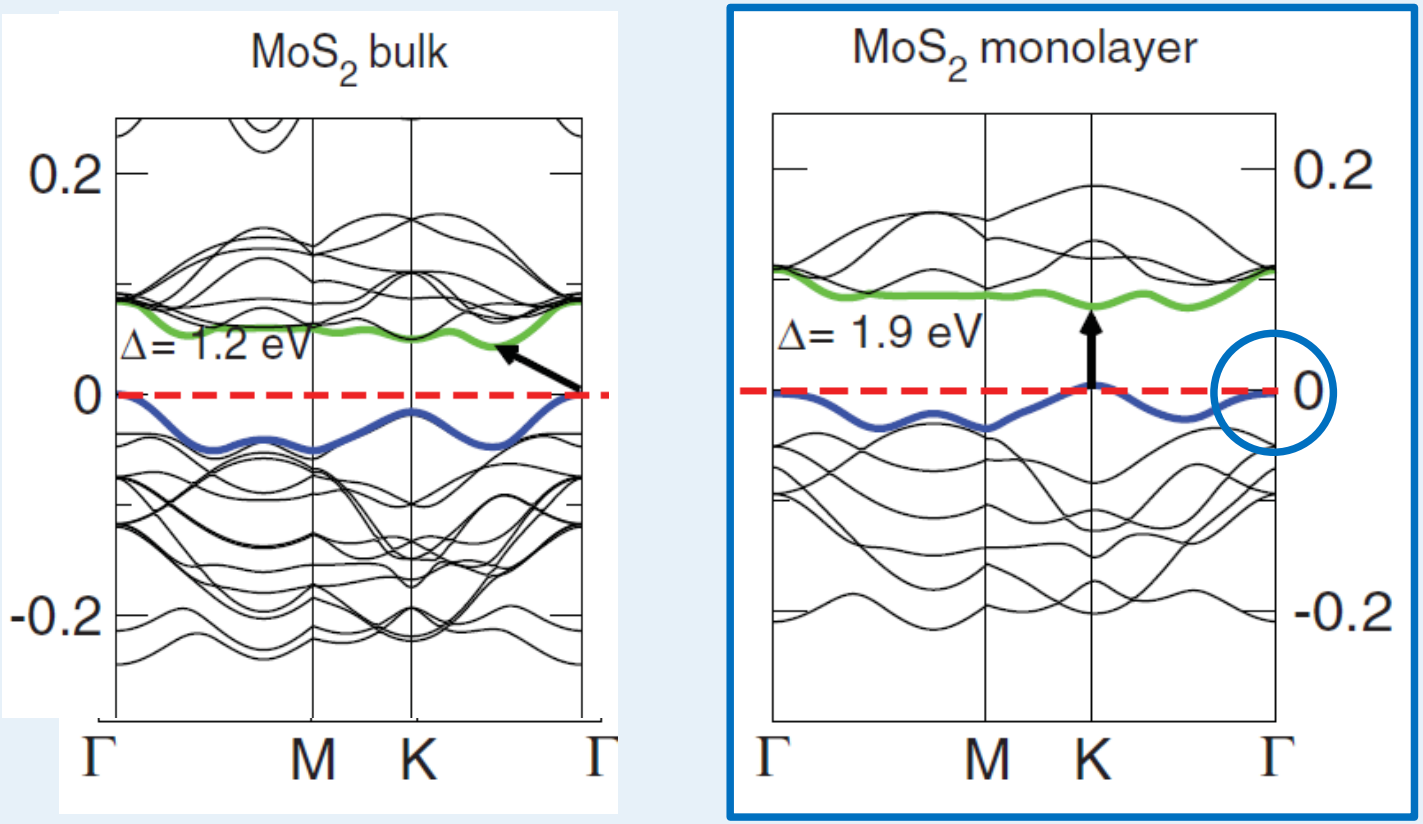
Kuc *et al.*, PHYSICAL REVIEW B **83**, 245213 (2011)



# $MoS_2$ single-layer

- Semiconductor with a **direct gap ~ 1.9 eV**

Kuc *et al*., PHYSICAL REVIEW B **83**, 245213 (2011)



# Motivation

ARTICLE

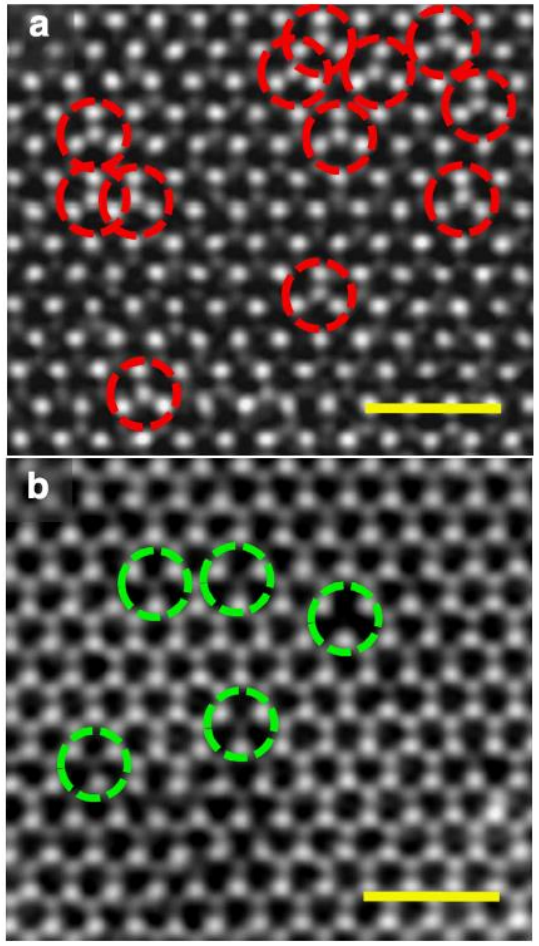
Received 31 Aug 2014 | Accepted 15 Jan 2015 | Published 19 Feb 2015

DOI: 10.1038/ncomms7293 OPEN

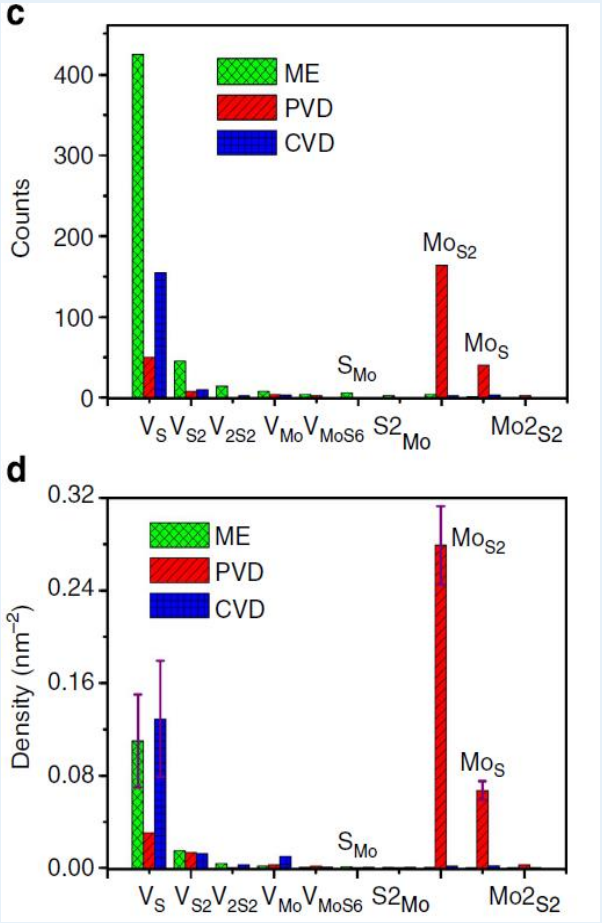
## Exploring atomic defects in molybdenum disulphide monolayers

Jinhua Hong[1,*], Zhixin Hu[2,*], Matt Probert[3], Kun Li[4], Danhui Lv[1], Xinan Yang[5], Lin Gu[5], Nannan Mao[6,7], Qingliang Feng[6], Liming Xie[6], Jin Zhang[7], Dianzhong Wu[8], Zhiyong Zhang[8], Chuanhong Jin[1], Wei Ji[2,9], Xixiang Zhang[4], Jun Yuan[1,3] & Ze Zhang[1]

- Most common defects:
  - PVD: antisites → vacS+Mo, vacS2+Mo
  - ME, CVD: vacS, vacS2
- Different impact on properties (tuning?!)
  → **sample characterization**




STEM-ADF image

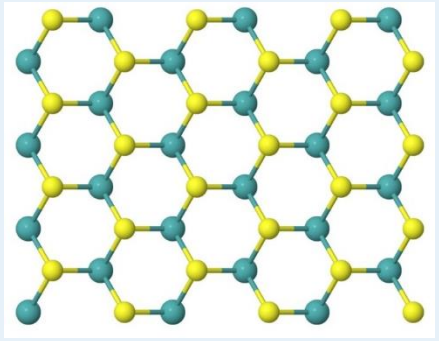


# Motivation

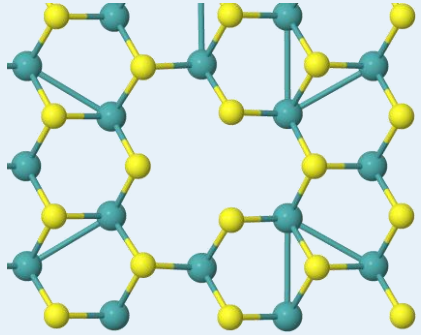
## Open questions…

- Do the STM images change with voltage or distance?
- Are geometrical or electronic effects predominant?
- How strong is the influence of the AFM tip?
- Can we identify or at least discriminate between certain defects by force spectroscopy?
- Can we transfer atoms from tip to simple and *vice-versa*? (doping, manipulation, …)

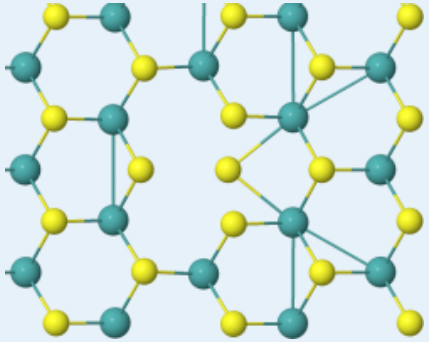
# Motivation: selected defects



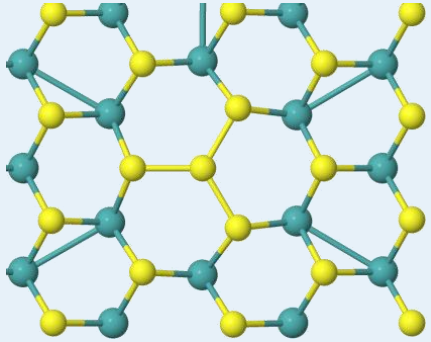
pristine



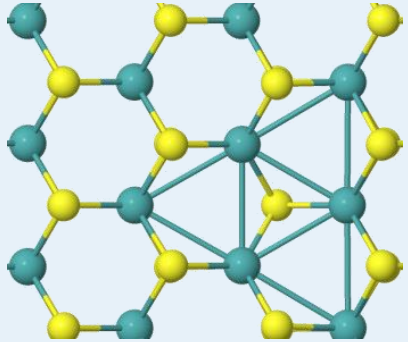
Mo vacancy



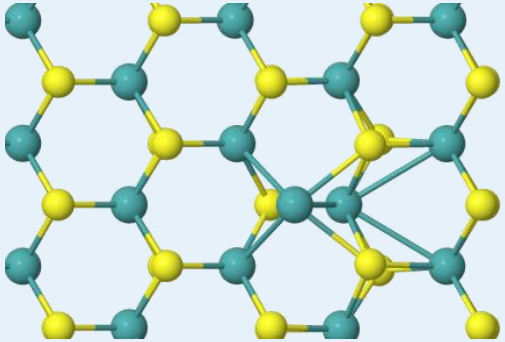
Mo vacancy+S



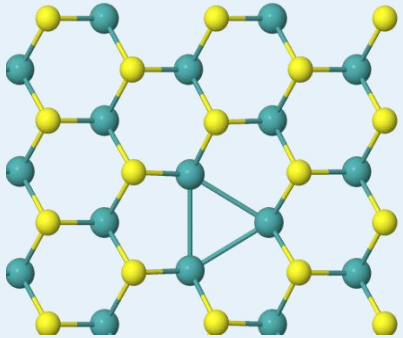
Mo vacancy+2S



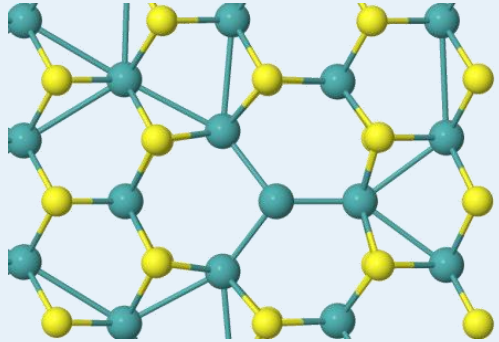
S vacancy



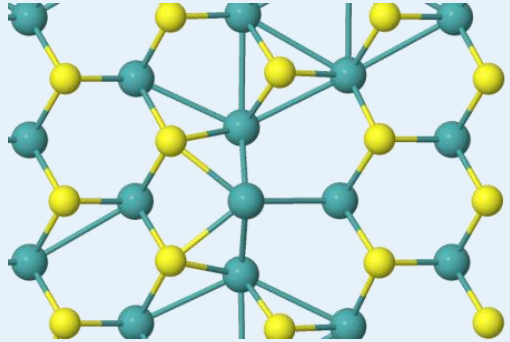
S vacancy+Mo



S di-vacancy



S di-vacancy+Mo



S di-vacancy+2Mo

# Motivation: selected defects

## Are all defects equivalent (in electronic terms)?

| | Clean | V-Mo | V-Mo+S | V-Mo+S2 | V-S | V-S+Mo | V-S2 | V-S2+Mo | V-S2+Mo2 |
|---|---|---|---|---|---|---|---|---|---|
| $E_g$(eV) | 1.70 | 0.64 | 0.60 | 1.25* | 1.0 | no gap | 0.80 | no gap | no gap |

# Motivation: selected defects

## Are all defects equivalent?

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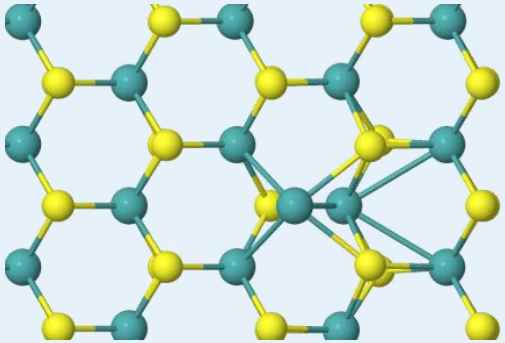
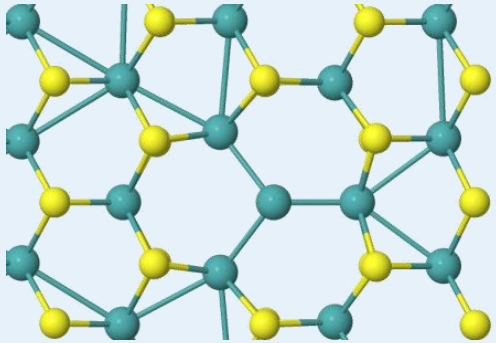
|---|---|---|---|---|---|---|---|---|---|
| $E_g$(eV) | 1.70 | 0.64 | 0.60 | 1.25* | 1.0 | no gap | 0.80 | no gap | no gap |

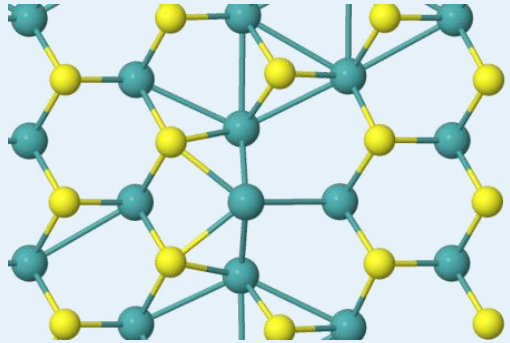
V-S+Mo



V-S2+Mo



V-S2+Mo2



# Methodology

- **Fully *ab initio***

- **STM**: combination of **DFT + Keldysh-NEGFs** formalism
  → **Fireball** (localized orbitals)

- **AFM**: **DFT** simulation of tip-sample interaction + **force extraction**
  → **VASP** (plane waves)

# Scanning Tunneling Microscopy simulations

IOP Publishing Nanotechnology

Nanotechnology 27 (2016) 105702 (12pp) doi:10.1088/0957-4484/27/10/105702

## Theoretical characterisation of point defects on a $MoS_2$ monolayer by scanning tunnelling microscopy

C González[1,2], B Biel[1] and Y J Dappe[2]

[1] Departamento de Electrónica y Tecnología de Computadores, Universidad de Granada, Campus de Fuente Nueva & CITIC, Campus de Aynadamar E-18071 Granada, Spain
[2] SPEC, CEA, CNRS, Université Paris-Saclay, CEA Saclay 91191 Gif-sur-Yvette Cedex, France

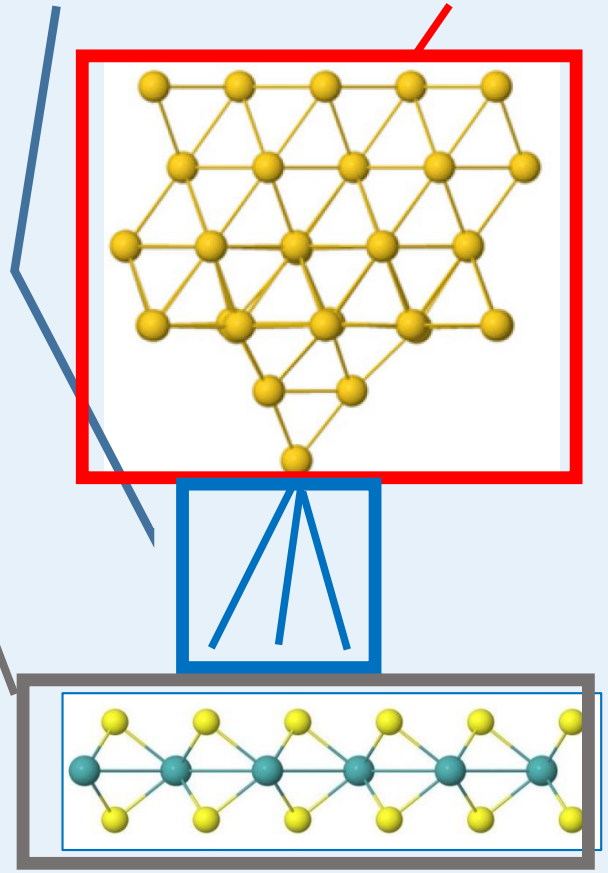
E-mail: cesar.gonzalez.pascual@gmail.es

# Theoretical STM model

$$J = \frac{4\pi e}{\hbar} \int_{E_F}^{E_F+eV} Tr\left[T_{TS}\,\rho_{SS}(E)\,D^{R}_{SS}\,T_{ST}\,\rho_{TT}(E-eV)\,D^{A}_{TT}\right]dE$$

$H = H_{Tip} + H_{interaction} + H_{sample}$

DFT-LDA FIREBALL code



Au(111) tip

- J. M. Blanco, F. Flores, and R. Perez, Prog. in Surf. Sci. **81**, 403 (2006)
- P. Jelinek *et al.*, Phys. Rev. B 71 (2005) 235101

$MoS_2$: one 6x4 single layer

- Keldysh-Green's functions formalism

# STM simulations

- **STM images:**

Determination of atom/defect position ➔ geometric effects should dominate (in principle)

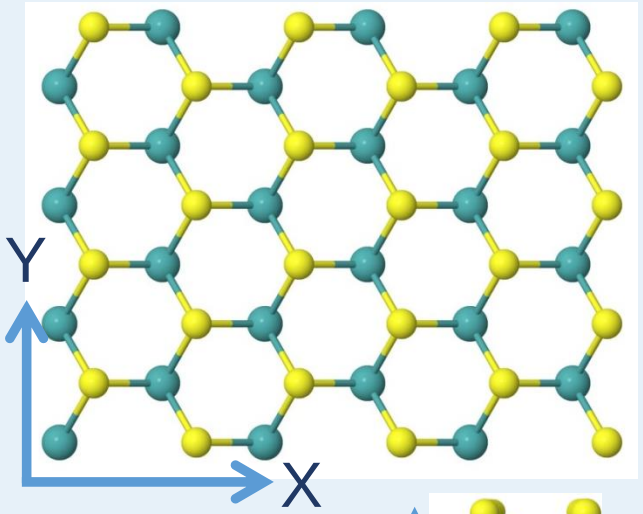
- **bright protrusión ←→ atom closer to tip**
- **dark holes ←→ atom far from tip**

- **BUT (some systems): actual interplay between geometrical and electronic effects**

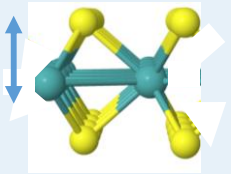
# STM simulation of pristine $MoS_2$ monolayer

## Pristine $MoS_2$ monolayer:

Top view

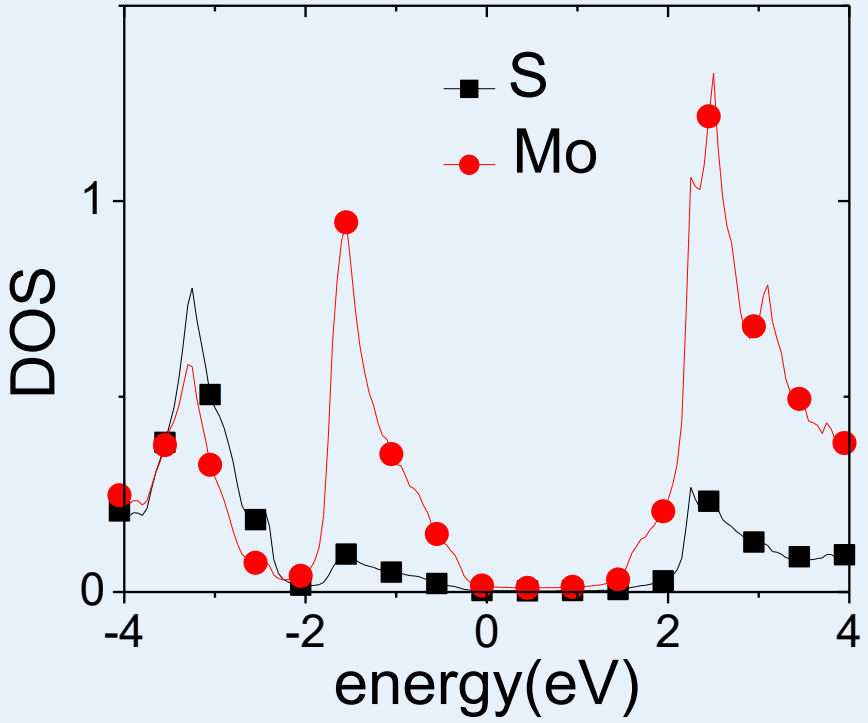



Lateral view 1.51 Å



S atoms

Mo atoms




S atoms 1.51 Å higher than Mo **BUT** Mo contribution to DOS larger than S's for empty states

**predomination of geometry or electronic effects?**

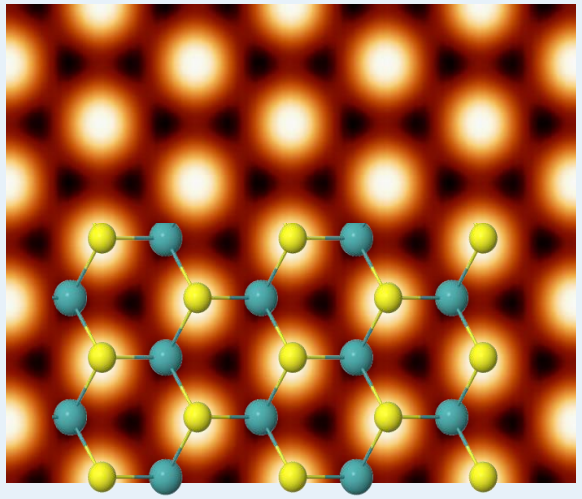
# STM simulation of pristine $MoS_2$ monolayer

## Clean monolayer:

(WSxM software)

- Constant height mode
- 4.0 Å, **4.5 Å**, 5.0 Å
- No alterations with distance
- Voltage range ~ -2V – 3.4V

**V = -0.1 (occupied states)**

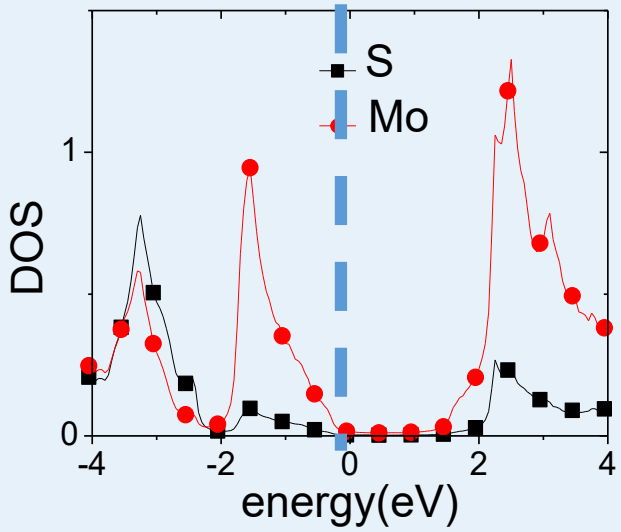


**Triangular pattern**

**STM simulated images**

S atoms

Mo atoms



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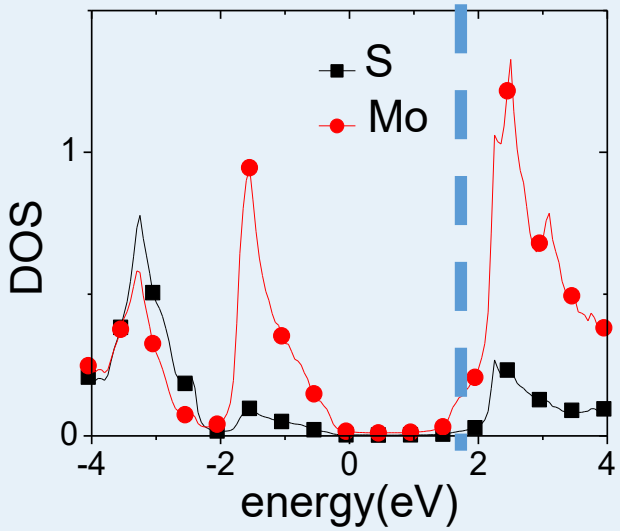


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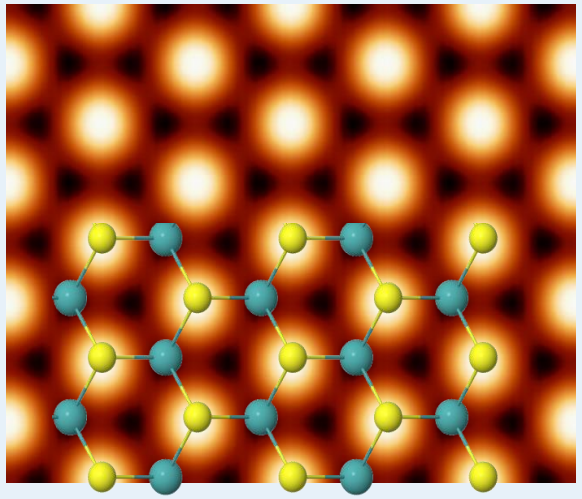
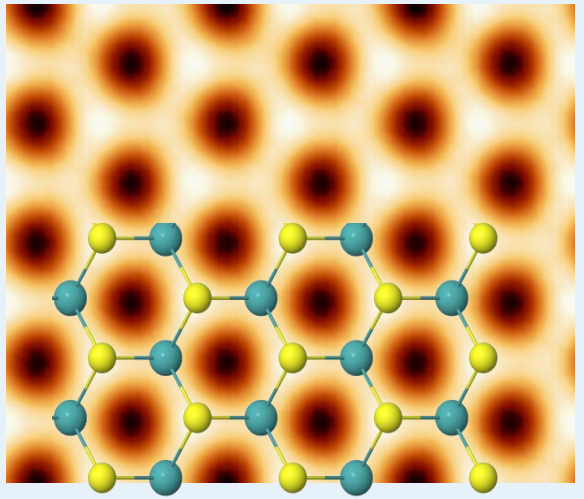


**Triangular pattern**

**V = +1.9 (empty states)**



**Asymmetric hexagonal pattern**

**STM simulated images**

S atoms

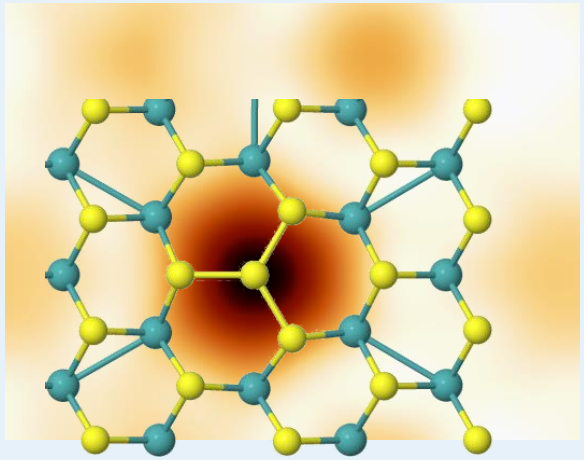
Mo atoms

**Geometry effects**

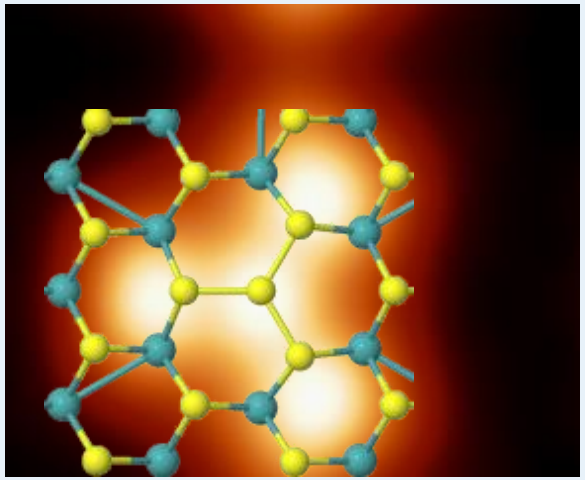
**DOS compensation**

# STM simulation of atomic defects in $MoS_2$

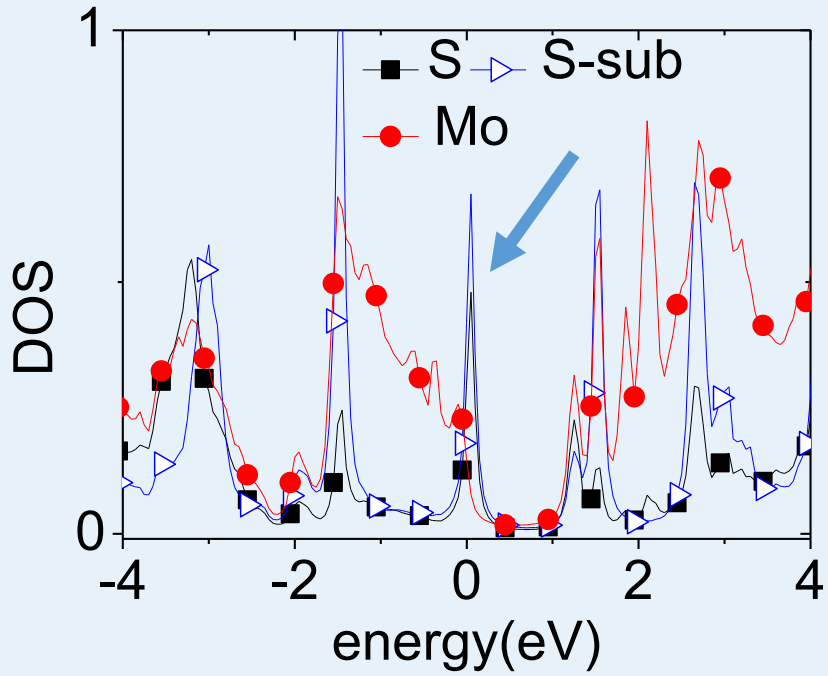
## Mo monovacancy with 2 substitutional S:



V= + 1.9



V= + 0.5




- 2 subs-S no connected to Mo atoms but to S atoms:

→ sharp peak in DOS

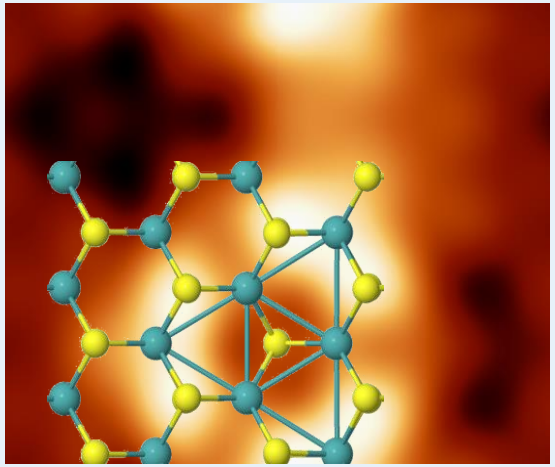
→ bright at low V

**Strong dependence on applied voltage**

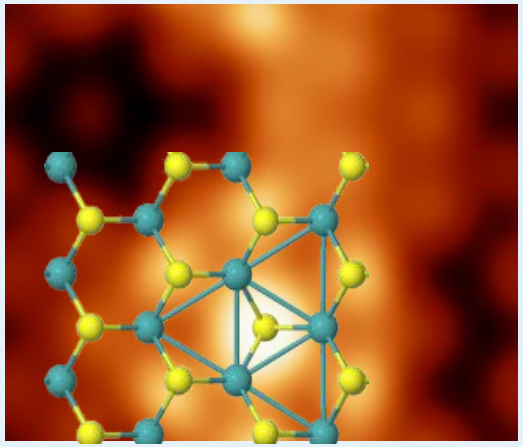
# STM simulation of atomic defects in $MoS_2$

## S monovacancy:

V= + 1.9

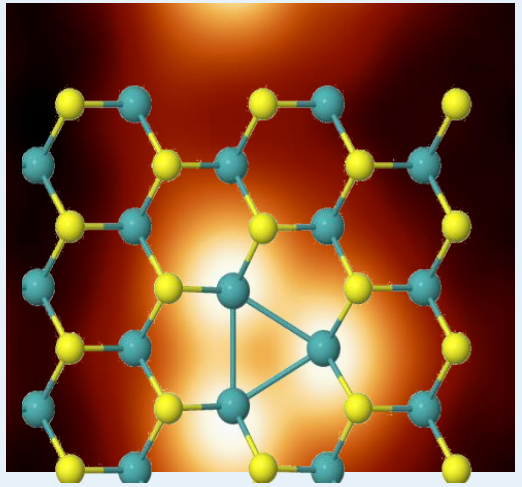


V= + 1

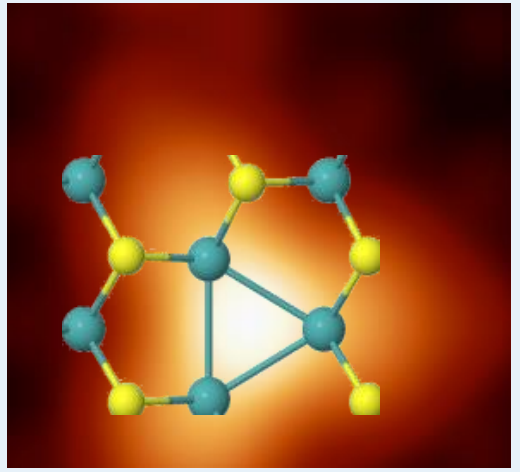


## S divacancy:

V= + 1.9



V= - 1.0



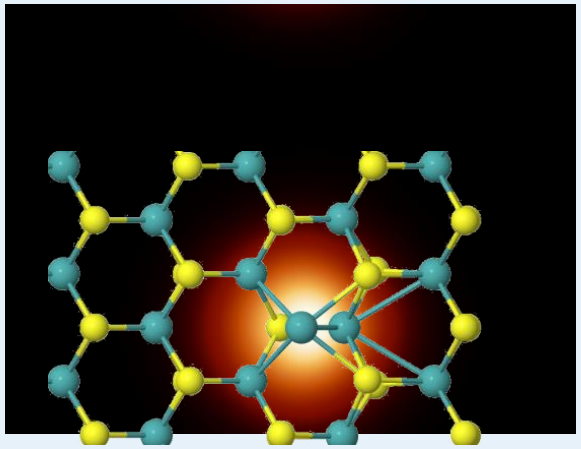
**Dependence on applied voltage**
**→ contrast change**
**(dark hole or bright protrusión)**

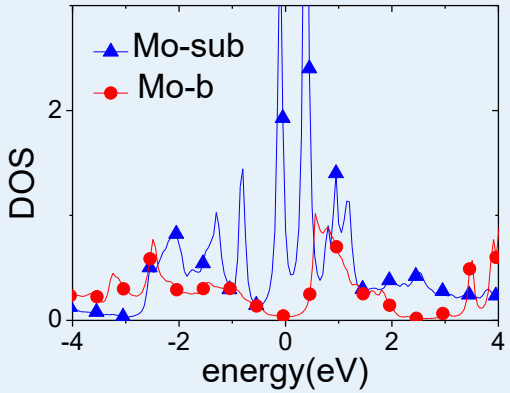
For **S or Mo vacancies** and
**S substitutionals** in the Mo vacancy

# STM simulation of atomic defects in $MoS_2$

## S monovacancy with substitutional Mo:

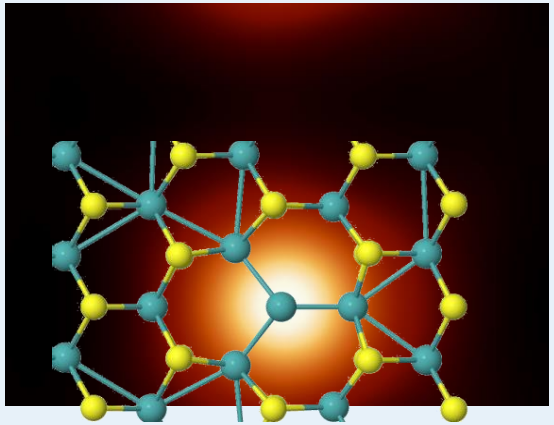
V= + 1.9

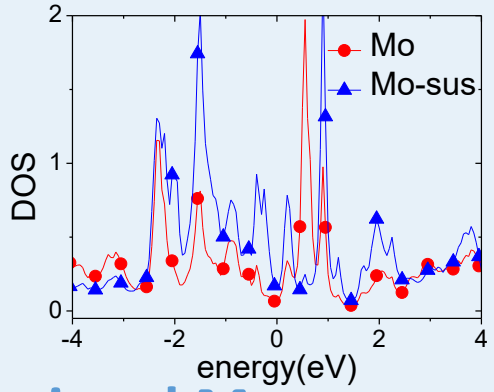





## S divacancy with substitutional Mo:

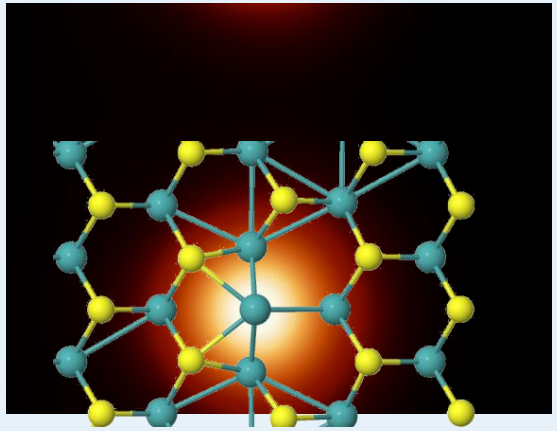
V= + 1.9

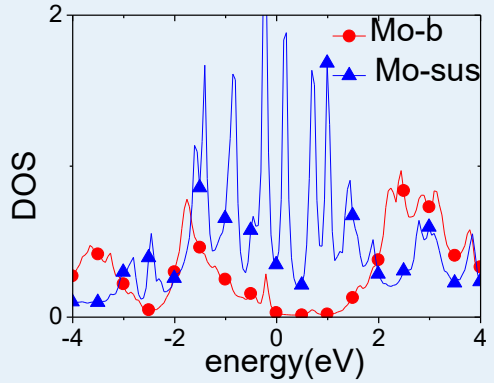





## S divacancy with 2 substitutional Mo:

V= + 1.9






**Bright protrusión**
(regardless of voltaje)

One or two **Mo atoms in an empty S** site
("metallic" defects)

# STM simulations: conclusions

- **Geometry effects** dominate in the STM imaging of S atoms for the **pristine** monolayer

- **Defects:**
  - Vacancies and S substitutionals in the Mo vacancy
    → imaged as **large protrusions or dark holes**, depending on the applied voltage
  - One or two Mo atoms in an empty S site (‘**metallic defects**’)
    → **bright protrusion** independently of the applied bias.

González *et al*. Nanotechnology **27** 105702 (2016)

# Atomic Force Microscopy simulations

THE JOURNAL OF PHYSICAL CHEMISTRY C



Article

## Reactivity Enhancement and Fingerprints of Point Defects on a MoS Monolayer Assessed by *ab initio* Atomic Force Microscopy

Cesar Gonzalez, Yannick J. Dappe, and Blanca Biel

*J. Phys. Chem. C*, **Just Accepted Manuscript** • DOI: 10.1021/acs.jpcc.6b05998 • Publication Date (Web): 30 Jun 2016

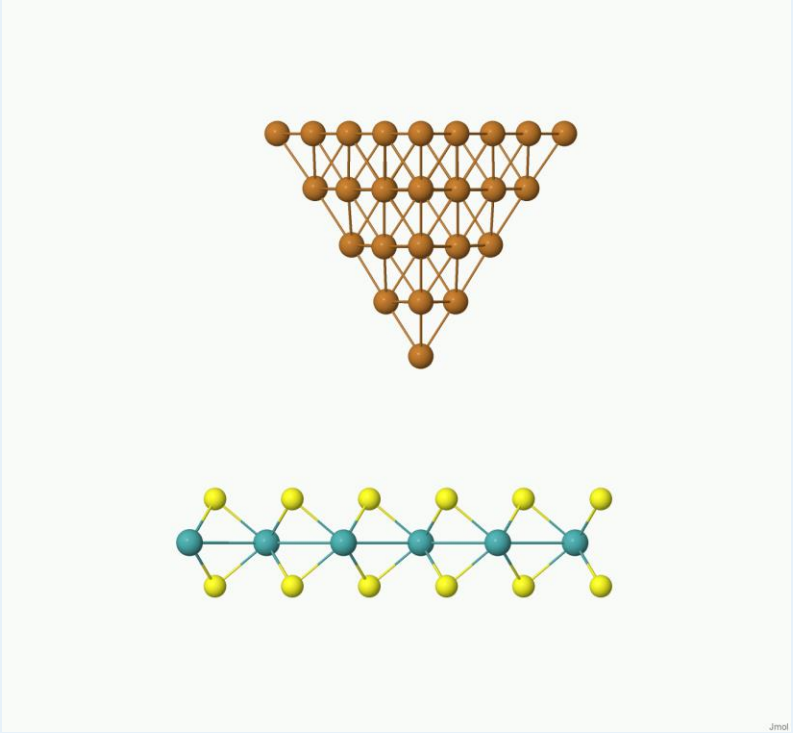


**Just Accepted**

# Theoretical AFM model

**DFT calculations**: VASP code

- Initial distance: 5 Å
- Steps of 0.25 Å
- Relaxation of whole system in each step
- Range: 2 Å - 5 Å



$$\Delta f = \frac{f_0}{2\pi k A_0} \int_0^{2\pi} F_{TS}\left[d + A_0 + A_0 \cos\varphi\right] \cos\varphi \, d\varphi$$

nc-AFM (FM-AFM)

R. García and R. Pérez Surf. Sci. Rep. 47 (2002) 197

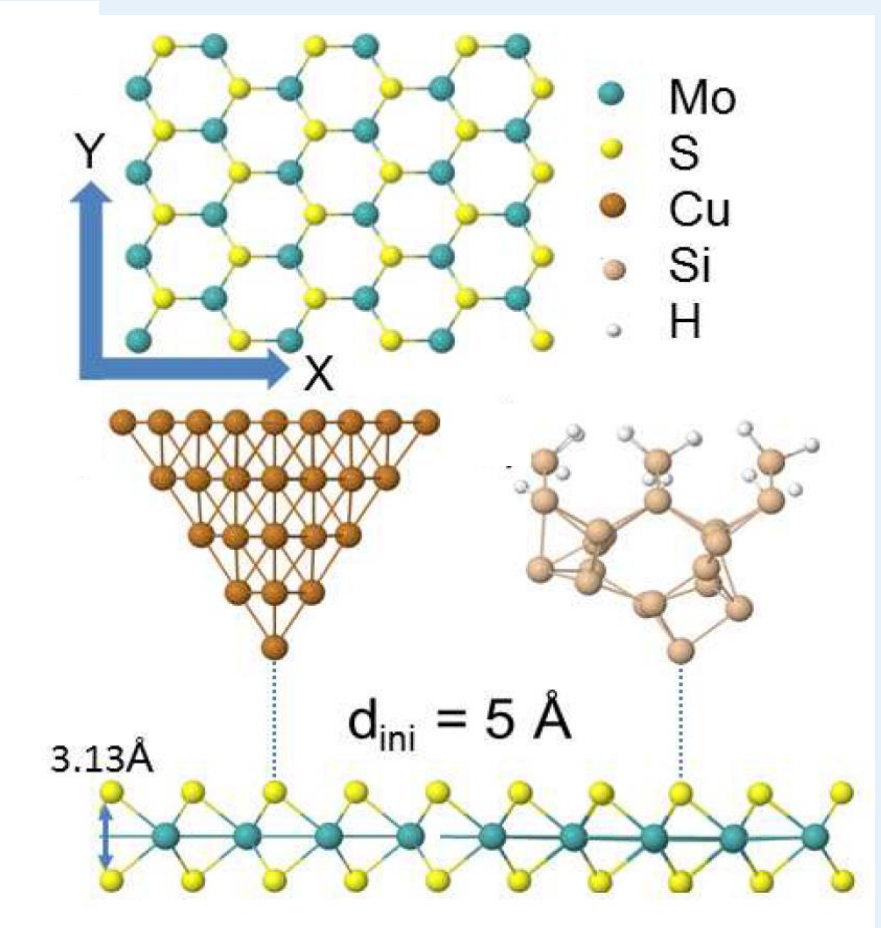
# Theoretical AFM model

**DFT calculations**: VASP code

- Two tips:
  - Cu (very reactive)
  - Si (less reactive)

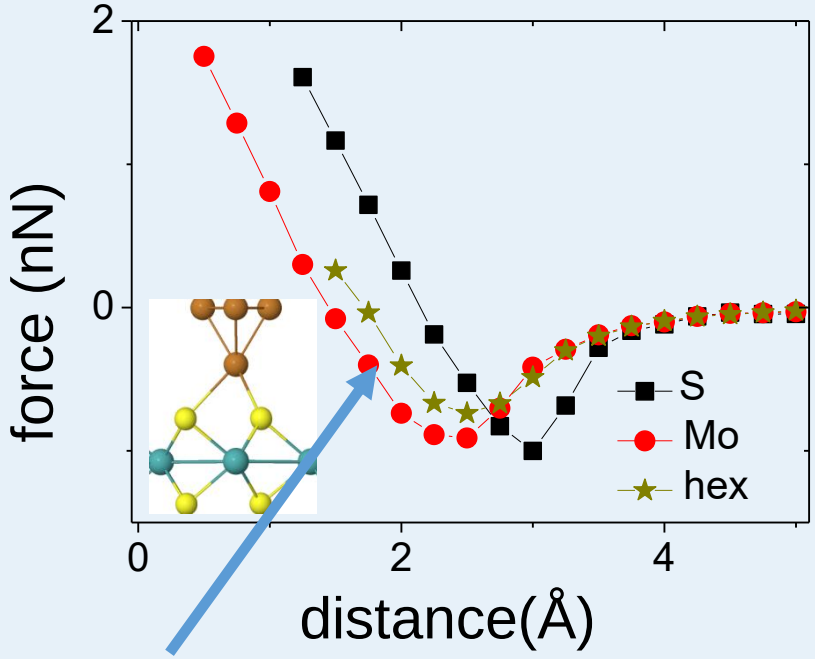
- Analysis of tip-sample force interaction curves
  - Most attractive point ➔ force minimum value
  - Type of interaction ➔ tip-sample distance at minimum force

- Comparison of force curves → discrimination between defects?



# AFM simulations of pristine $MoS_2$ monolayer

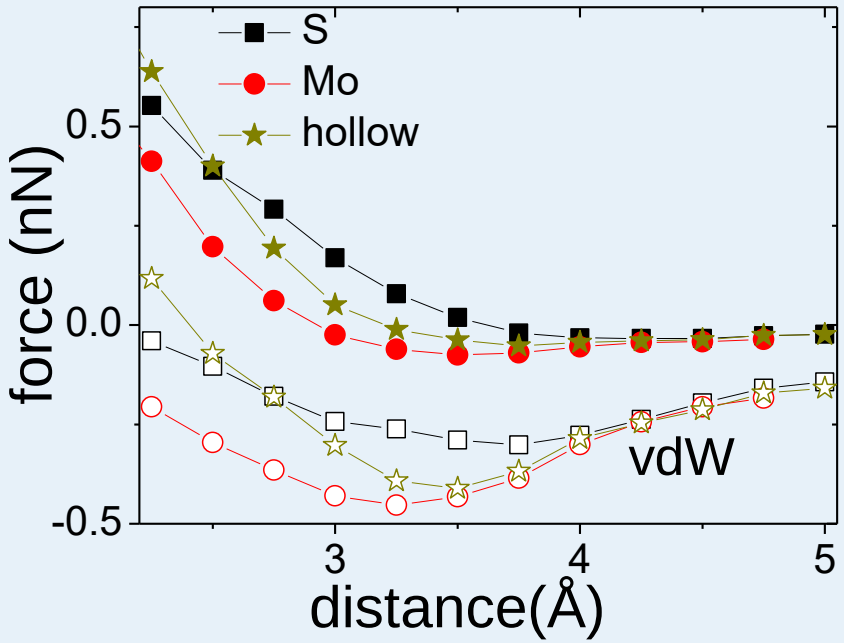
## Cu tip




- Most attractive point for the Cu tip: over a S atom
- Mo force minimum at a shorter distance than over S (interaction with neighboring S atoms!)

➔ contrast change between Mo and S with distance

## Si tip

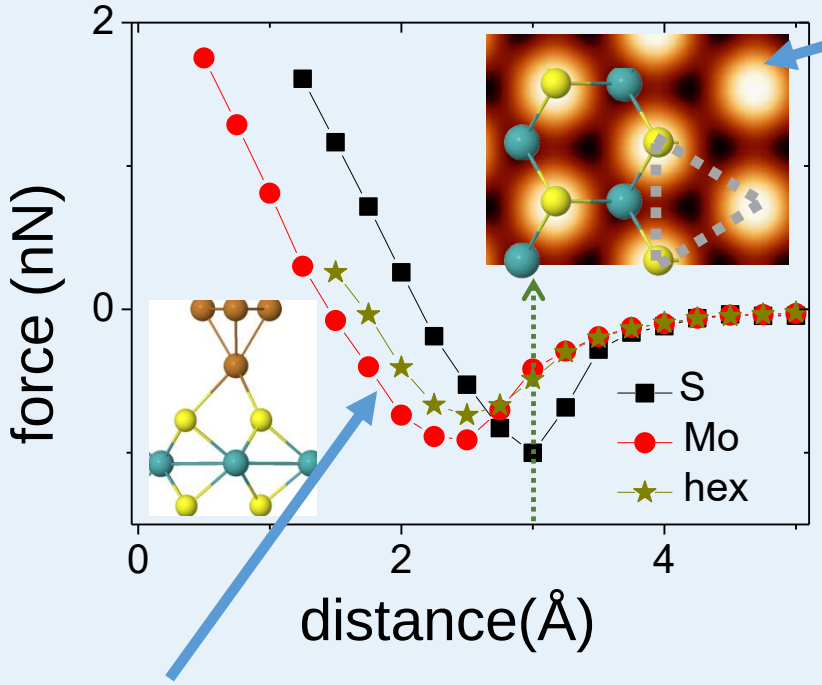



- Most attractive point for the Si tip: over a Mo atom
- Need to introduce vdW interaction to get attractive forces

# AFM simulations of pristine $MoS_2$ monolayer

Expected nc-AFM images obtained at 3 Å

## Cu tip



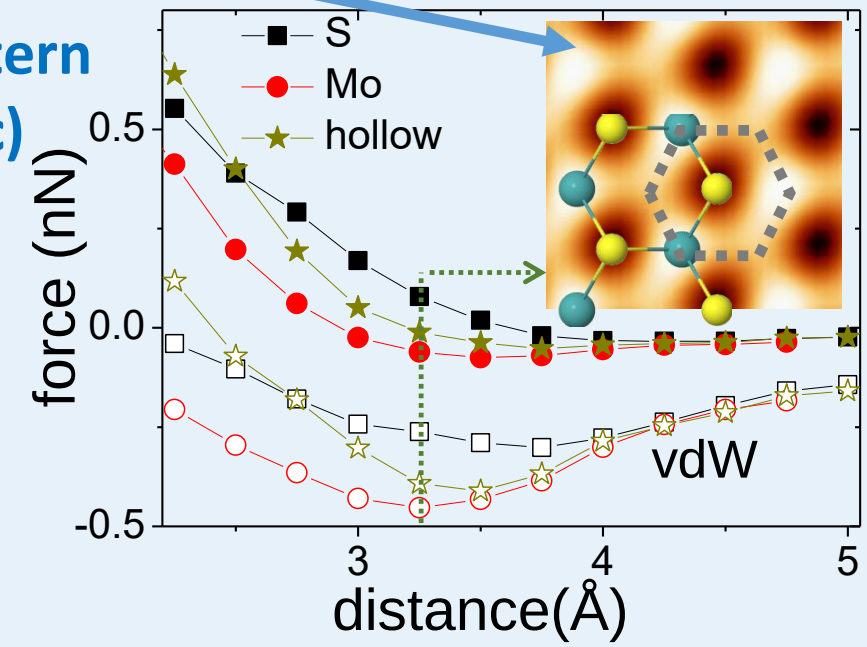

**Triangular pattern**

- Most attractive point for the Cu tip: over a S atom
- Mo force minimum at a shorter distance than over S (interaction with neighboring S atoms!)

➔ contrast change between Mo and S with distance

**Hexagonal pattern (asymmetric)**

## Si tip

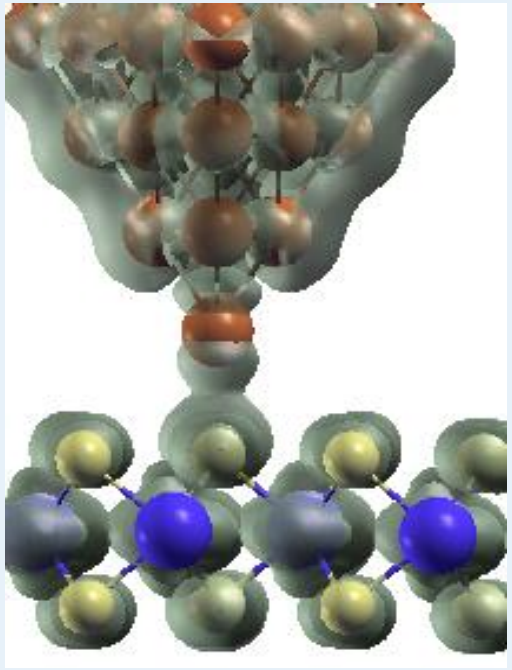



- Most attractive point for the Si tip: over a Mo atom
- Need to introduce vdW interaction to get attractive forces

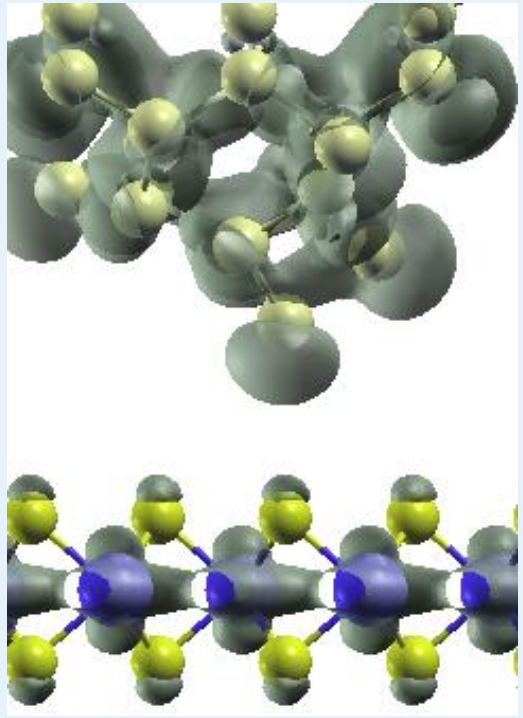
# AFM simulations of pristine $MoS_2$ monolayer

- **Tip interaction** → analysis of charge density:
  - Bond between Cu tip and S atom
  - No bond between Si tip and S atom

→ **Cu tip more reactive**



Most attractive point for a Cu tip approaching a S atom

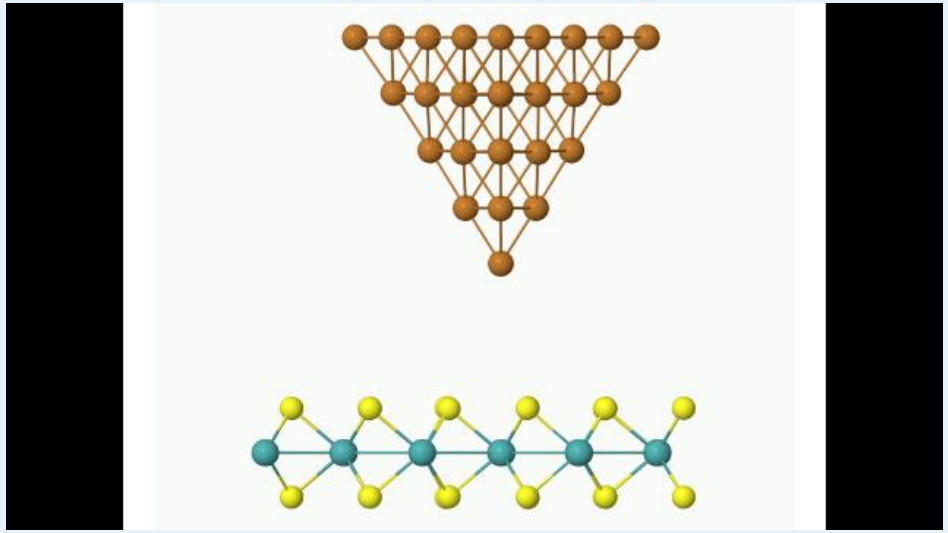


Most attractive point for a Si tip approaching a S atom

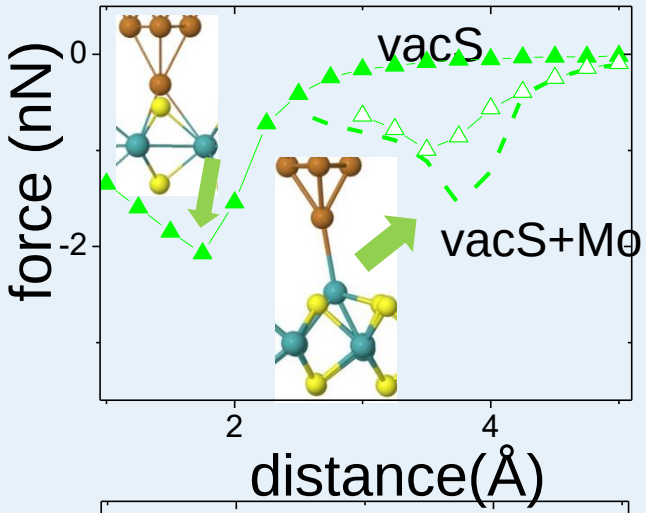
# AFM simulations of atomic defects in $MoS_2$

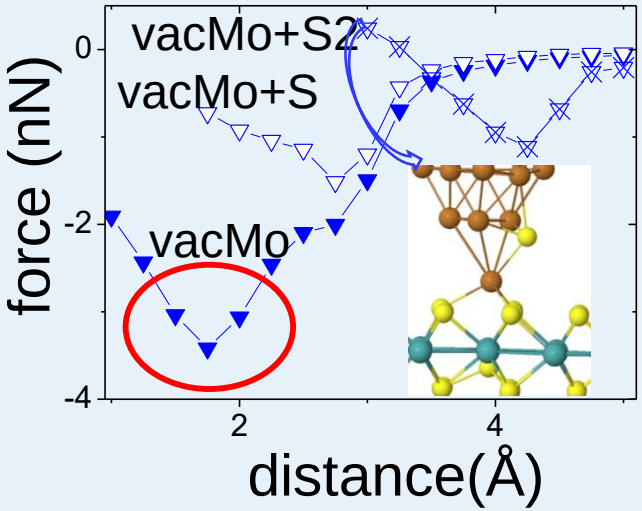
## Cu tip:

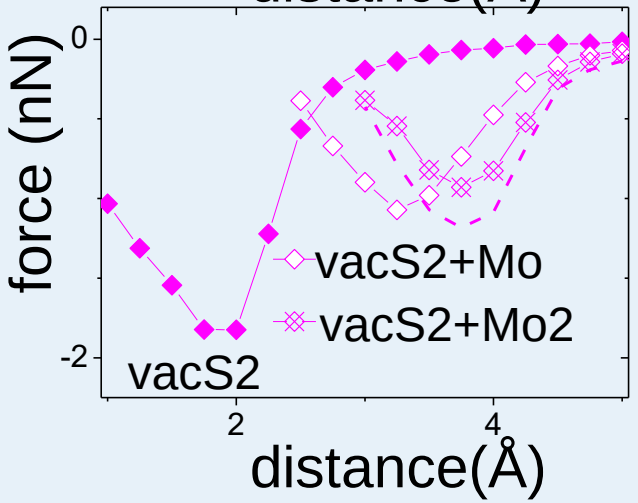
- Most attractive force → over a **Mo vacancy**

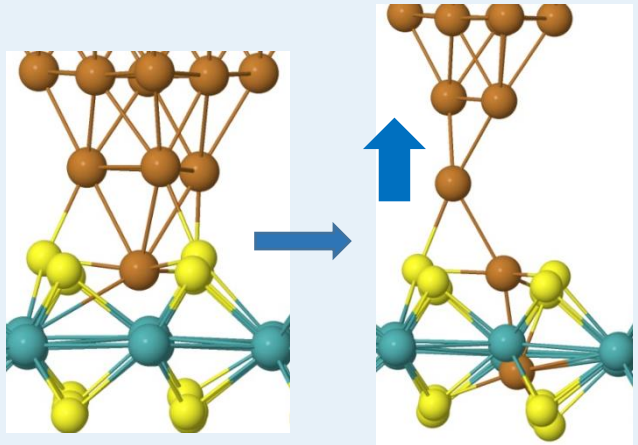


Capture of apex atoms



# AFM simulations of atomic defects in $MoS_2$

## Cu tip:

| tipCu | $F_m$(nN) | $d_m$(Å) | $\Delta h_{Cu}$(Å) | $\Delta h_{Mo/S}$(Å) | $\Delta Chg_{Cu}(e)$ |
|---|---|---|---|---|---|
| vacMo | -3.42 | 1.75 | -0.90 | - | -0.55 |
| vacS | -2.07 | 1.75 | -0.63 | - | -0.34 |
| vacS2 | -1.85 | 1.75 | -0.63 | - | -0.33 |
| Mo | -0.88 | 2.50 | -0.20 | +0.18 | -0.11 |
| vacMo+S | -1.56 | 2.75 | -0.33 | +0.09 | -0.33 |
| vacS2+Mo | -1.07 | 3.00 | -0.15 | +1.30 | -0.39 |
| S | -1.00 | 3.00 | -0.25 | +0.38 | -0.12 |
| vacS+Mo | -1.01(-1.51) | 3.50(3.75) | -0.22 | +0.46 | -0.39 |
| vacS2+Mo2 | -0.93(-1.18) | 3.75(3.75) | -0.26 | +0.34 | -0.28 |
| vacMo+S2 | -1.11 | 4.25 | -0.29 | +0.27 | -0.23 |

The monolayer is more semiconducting than the metallic tip

➔ significant charge transfer takes place from the tip to the substrate

# AFM simulations of atomic defects in $MoS_2$

## Si tip:

| tipSi | $F_m$(nN) | $d_m$(Å) | $\Delta h_{Si}$(Å) | $\Delta h_{Mo/S}$(Å) | $\Delta Chg_{Si}(e)$ |
|---|---|---|---|---|---|
| vacS2+Mo2 | -1.80(-2.55) | 4.00 | -0.60 | +0.60 | +0.49 |
| vacS+Mo | -1.55(-2.17) | 4.00 | -0.60 | +0.49 | +0.39 |
| S | -0.03 | 4.00 | -0.00 | +0.00 | +0.03 |
| vacMo+S2 | -0.11 | 3.75 | -0.01 | -0.00 | +0.14 |
| vacS2+Mo | -1.36 | 3.50 | -0.25 | +1.32 | +0.20 |
| Mo | -0.07 | 3.50 | -0.01 | +0.00 | +0.06 |
| vacMo | -0.80 | 2.50 | -1.20 | - | +0.68 |
| vacMo+S | -0.81 | 2.25 | -0.78 | -0.28 | +0.47 |
| vacS2 | -1.05 | 1.75 | -1.03 | - | +0.48 |
| vacS | -0.86 | 1.50 | -1.03 | - | +0.46 |

The monolayer is more metallic than the **semiconducting tip**

➔ significant charge transfer takes place from the substrate to the tip

# How to interpret the information?

| tipCu | $F_m$(nN) | $d_m$(Å) |
|---|---|---|
| vacMo | -3.42 | 1.75 |
| vacS | -2.07 | 1.75 |
| vacS2 | -1.85 | 1.75 |
| Mo | -0.88 | 2.50 |
| vacMo+S | -1.56 | 2.75 |
| vacS2+Mo | -1.07 | 3.00 |
| S | -1.00 | 3.00 |
| vacS+Mo | -1.01(-1.51) | 3.50(3.75) |
| vacS2+Mo2 | -0.93(-1.18) | 3.75(3.75) |
| vacMo+S2 | -1.11 | 4.25 |

- **@ 3 Å : pristine S**

**BUT**: vacMo force ~2nN @ 3 Å
➔ competing with 'pristine' S !
**Need to check for force curve !**

| tipSi | $F_m$(nN) | $d_m$(Å) |
|---|---|---|
| vacS2+Mo2 | -1.80(-2.55) | 4.00 |
| vacS+Mo | -1.55(-2.17) | 4.00 |
| S | -0.03 | 4.00 |
| vacMo+S2 | -0.11 | 3.75 |
| vacS2+Mo | -1.36 | 3.50 |
| Mo | -0.07 | 3.50 |
| vacMo | -0.80 | 2.50 |
| vacMo+S | -0.81 | 2.25 |
| vacS2 | -1.05 | 1.75 |
| vacS | -0.86 | 1.50 |

- **S network deduced** from:

- vacS position at short distances
- vacS+Mo, vacS2+Mo2 at large distances

# AFM simulations: conclusions

- Characterization of all **features** (S and Mo atoms, their vacancies and the corresponding antisites) by force minimum and tip-sample distance

- Great reactivity **enhancement** in the $MoS_2$ monolayer in the presence of defects

➔**metal-semiconductor junction formed between the tip and the $MoS_2$ substrate**

- Atoms transference from/to tip-sample ➔ tool to **locally modify the electronic environment**

# $MoS_2$ capabilities as a selective gas sensor



**Sibel Özkaya**
University of Aksaray


**Pablo Pou**
Autonomous University of Madrid

# Why do we need another 2D material?

NANO LETTERS

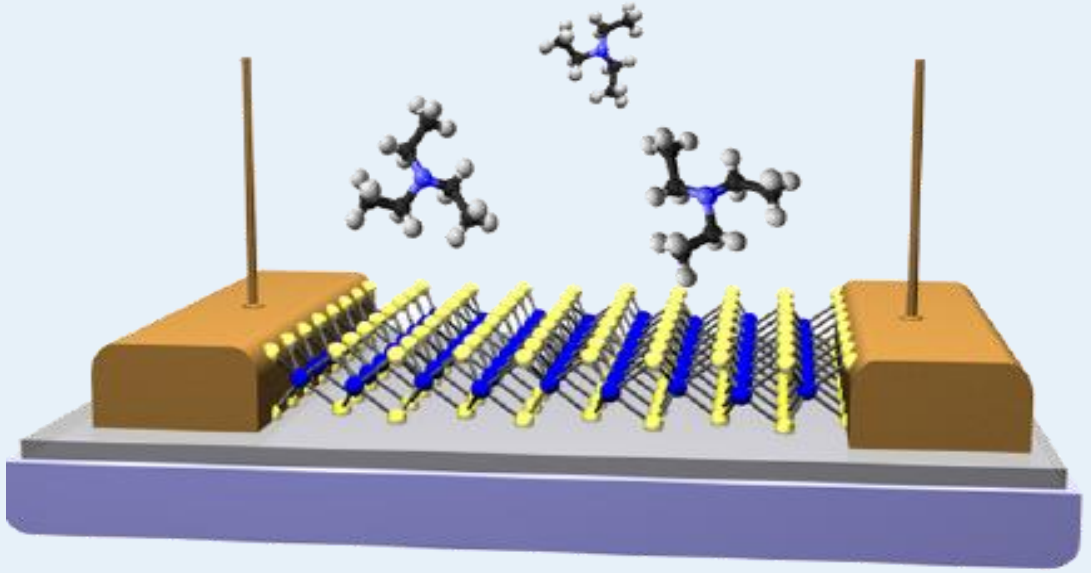
Letter

pubs.acs.org/NanoLett

## Chemical Vapor Sensing with Monolayer $MoS_2$

F. K. Perkins,*,† A. L. Friedman,† E. Cobas,‡ P. M. Campbell, G. G. Jernigan, and B. T. Jonker*

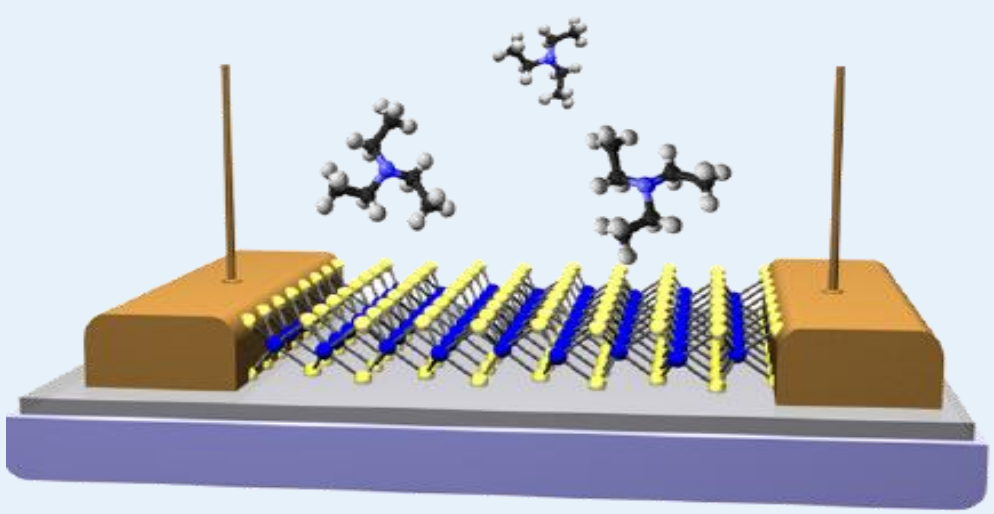
Naval Research Laboratory, Washington, District of Columbia 20375, United States

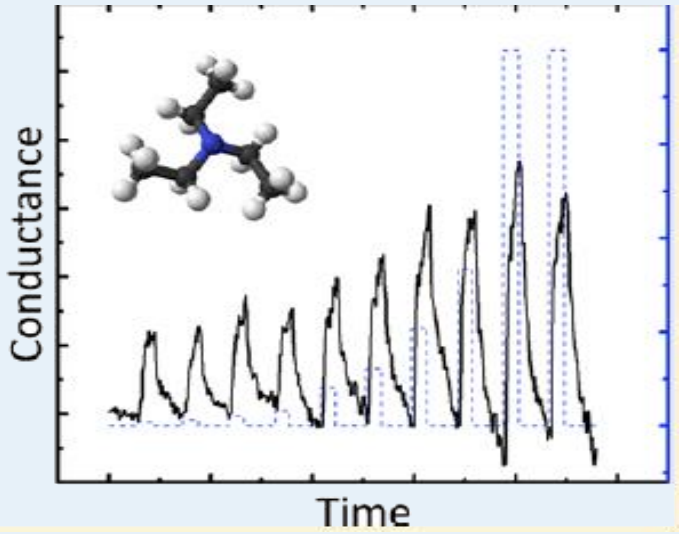


- $MoS_2$-, graphene- and CNTs-based FETs
- Exposure to several gas species
- Conductance measurements

# Why do we need another 2D material?

- **Single monolayer $MoS_2$** functions effectively as a chemical sensor
- Sensitive **transduction of transient surface physisorption events to the conductance** of the monolayer channel
- **Highly selective reactivity to a range of analytes - unlike graphene!**





# Why do we need another 2D material?

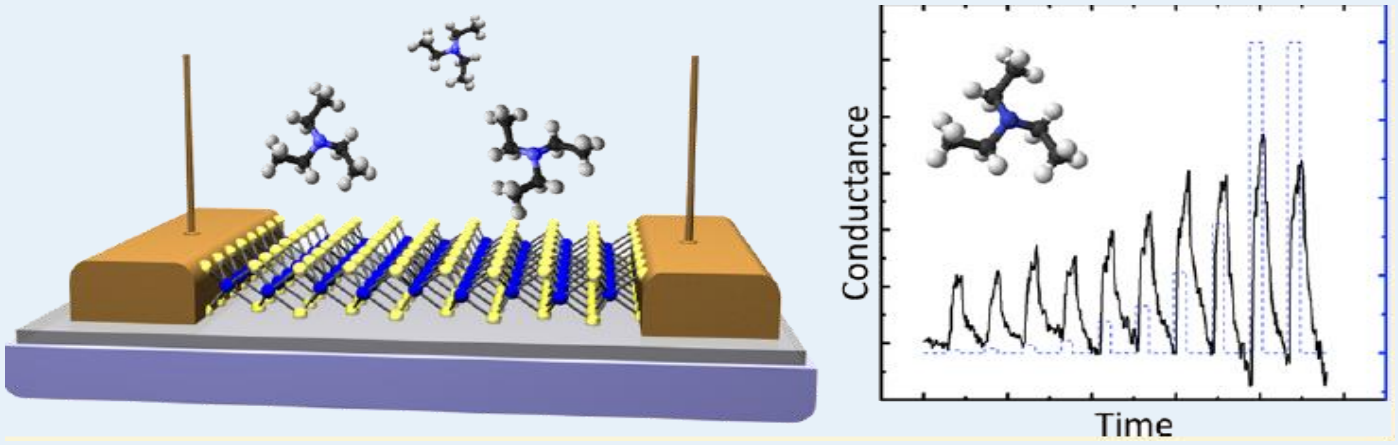
**Response to chemical character:**

- **Strong electron donors: pronounced response** (conductivity increases abruptly)

→ **triethylamine (TEA)**

- **Electron acceptors: no measurable change** in conductance

→ **nitromethane (NM)**



# Methodology

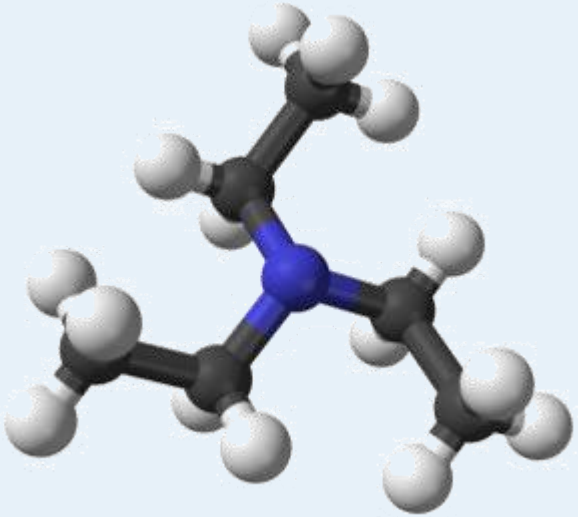

http://departments.icmab.es/leem/siesta/

- Density Functional theory (DFT) -based code
- Strictly localized pseudoatomic orbitals
- Norm-conserving pseupotentials
- **PBE + KBM van der Waals** functional
  - Transport formalism (NEGFs) → **TRANSIESTA**

# Adsorbates

## triethylamine (TEA)

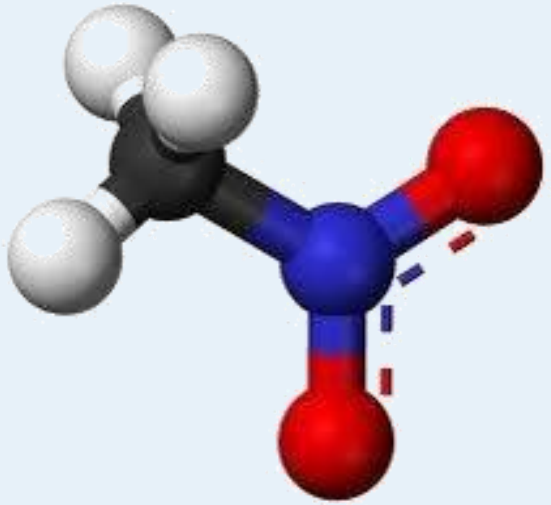
$N(CH_2– CH_3)_3$



**HOMO-LUMO** gap (PBE): **6.24 eV**
**electron donor**

## nitromethane (NM)

$CH_3NO_2$

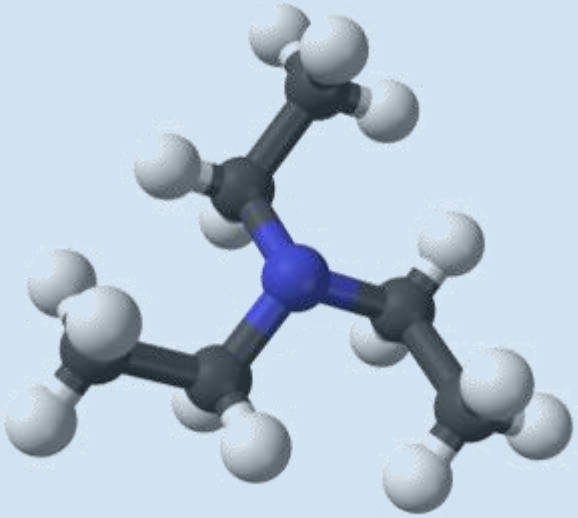


**HOMO-LUMO** gap (PBE): **3.57 eV**
**electron acceptor**

# Adsorbates

## triethylamine (TEA)

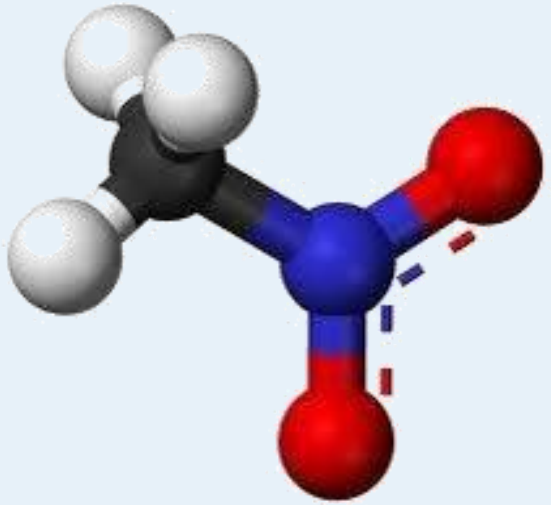
$N(CH_2– CH_3)_3$



**HOMO-LUMO** gap (PBE): **6.24 eV**
**electron donor**

## nitromethane (NM)

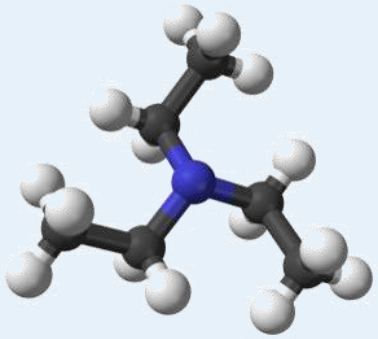
$CH_3NO_2$

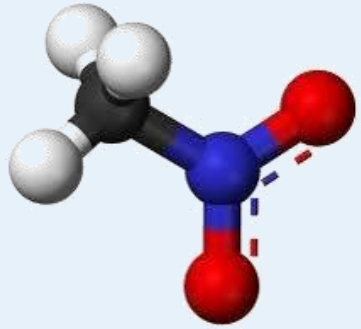


**HOMO-LUMO** gap (PBE): **3.57 eV**
**electron acceptor**

# Potential Energy Surface (PES)

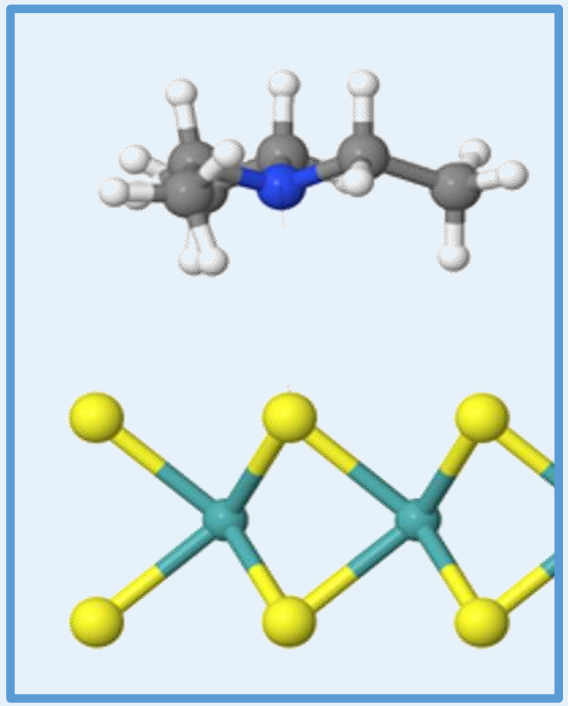
- Determination of adsorption energies map (PES) for 14 configurations
- Convergence in supercell size up to 5x5 → no significant changes in adsorption energies
- 3x3 supercell, ~ 20 Å vacuum in confinement direction
- Standard DZP basis
- PBE+KBM functionals
- Initial distance to surface: 1 – 5 Å

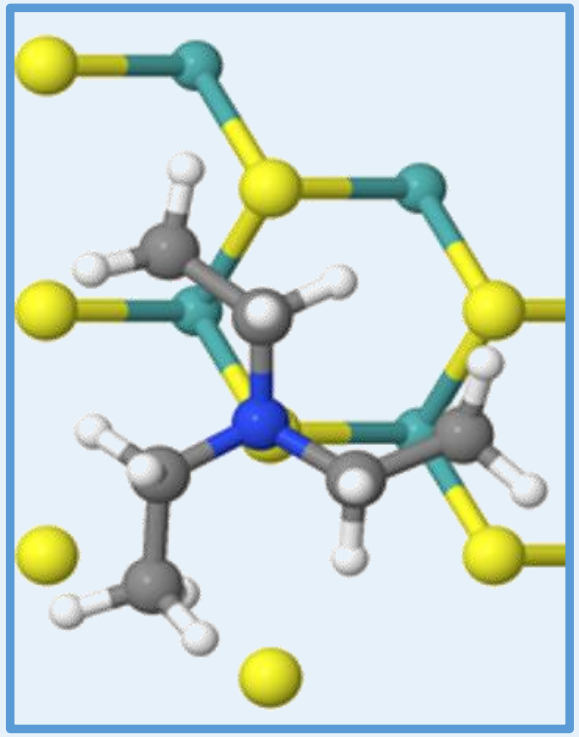




# Triethylamine

Most strongly absorbed:

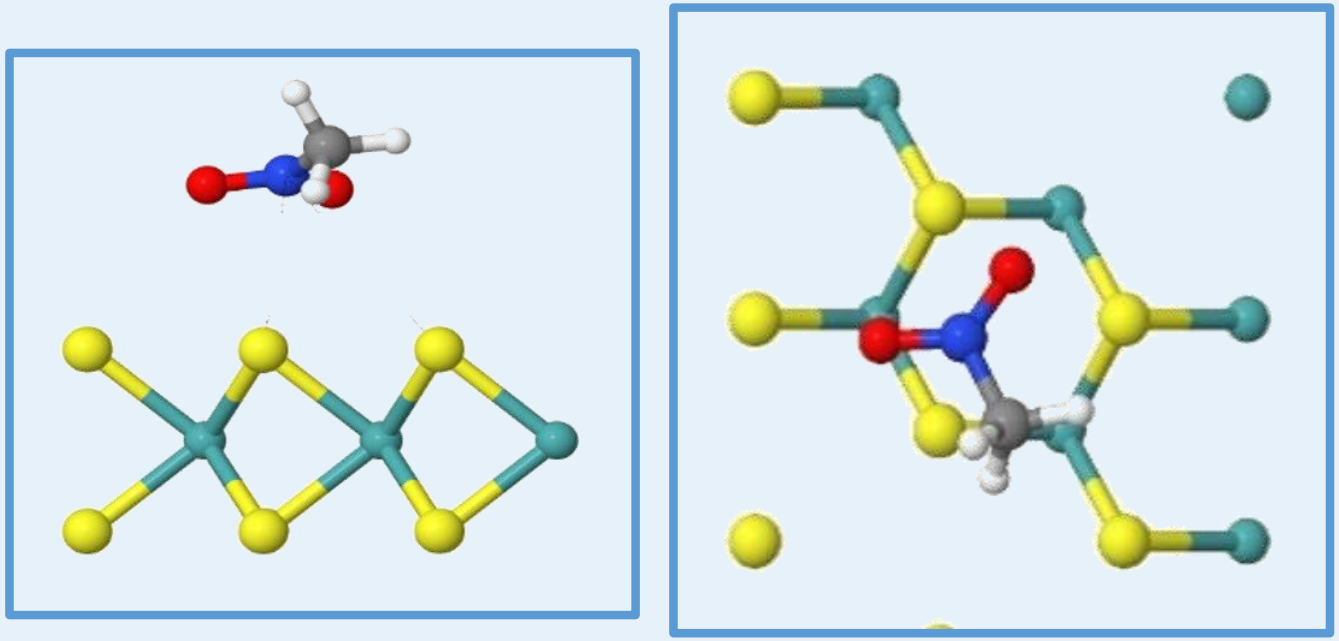




- vdW-KBM functional
  - Equilibrium distance: 3.17 Å, adsorption energy: 1.126 eV ?

# Nitromethane

Most strongly absorbed:



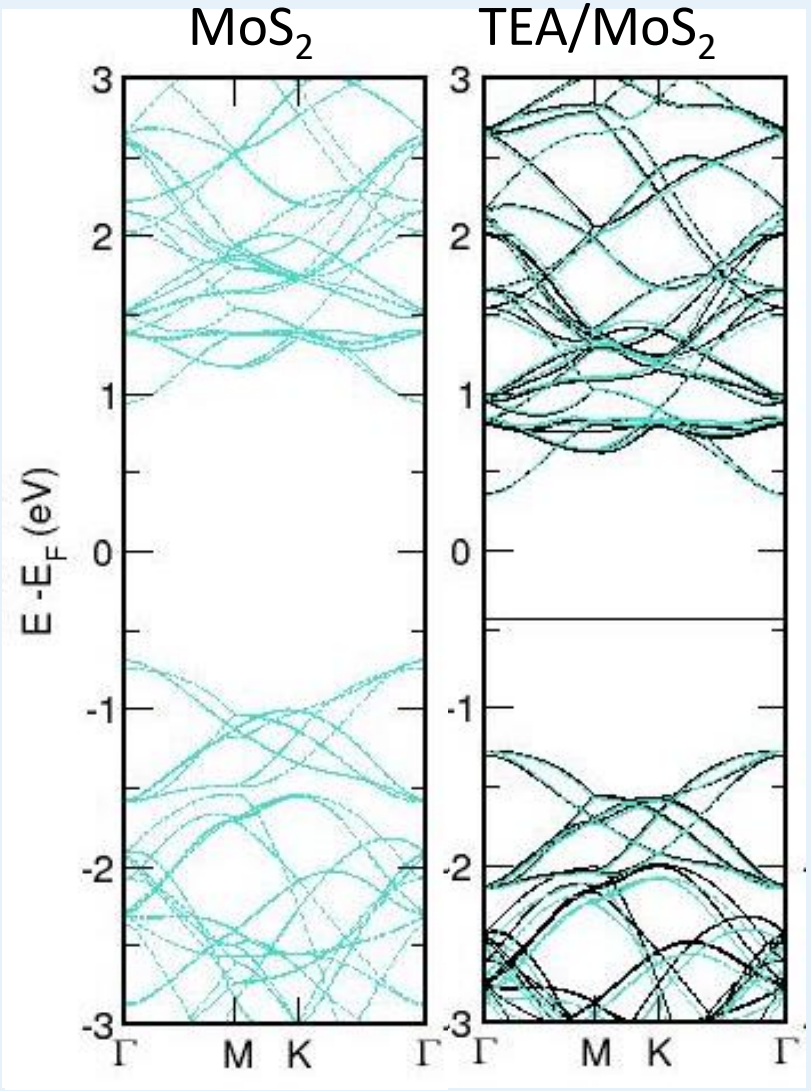
- vdW-KBM functional

  - Equilibrium distance: 2.85 Å, adsorption energy: 0.79 eV ?

➔ **Basis too short/incomplete ?!**

# $TEA/MoS_2$ bandstructure

- **Same behaviour** regardless of orientation with respect to substrate

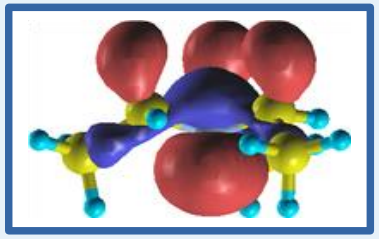



**TEA bandstructure**

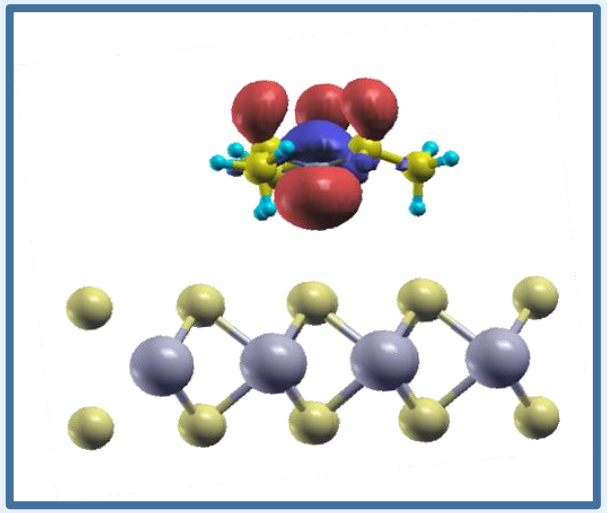
# $TEA/MoS_2$ bandstructure

- **Same behaviour** regardless of orientation with respect to substrate

- Molecule HOMO level



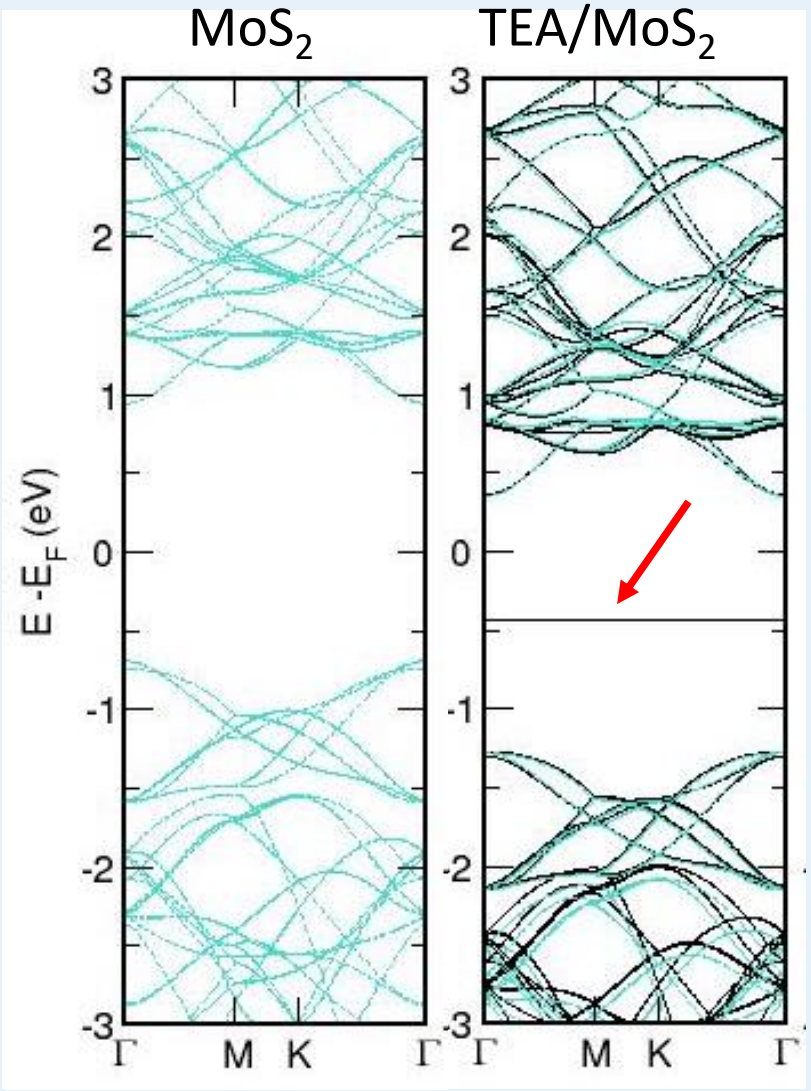
TEA HOMO level



$TEA/MoS_2$ midgap level

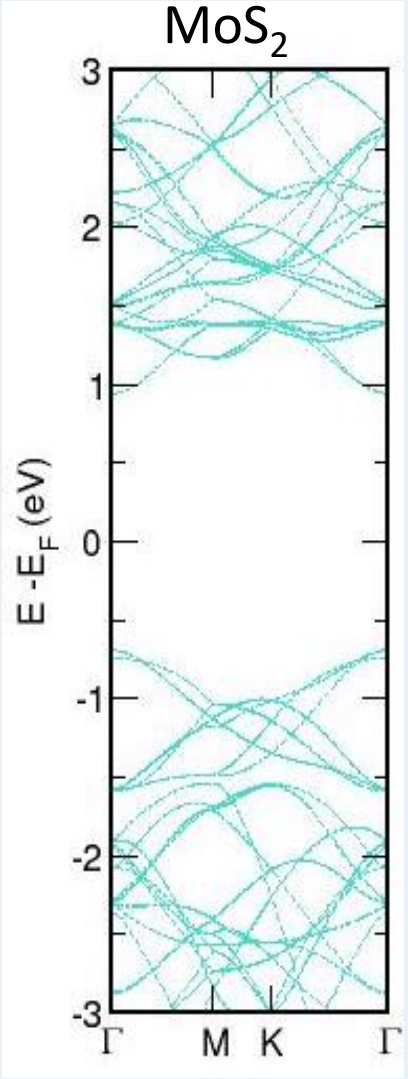
- filled → **donor state**

➔ **Electron doping of $MoS_2$ by TEA**




**TEA bandstructure**

# Is it the same for NM?



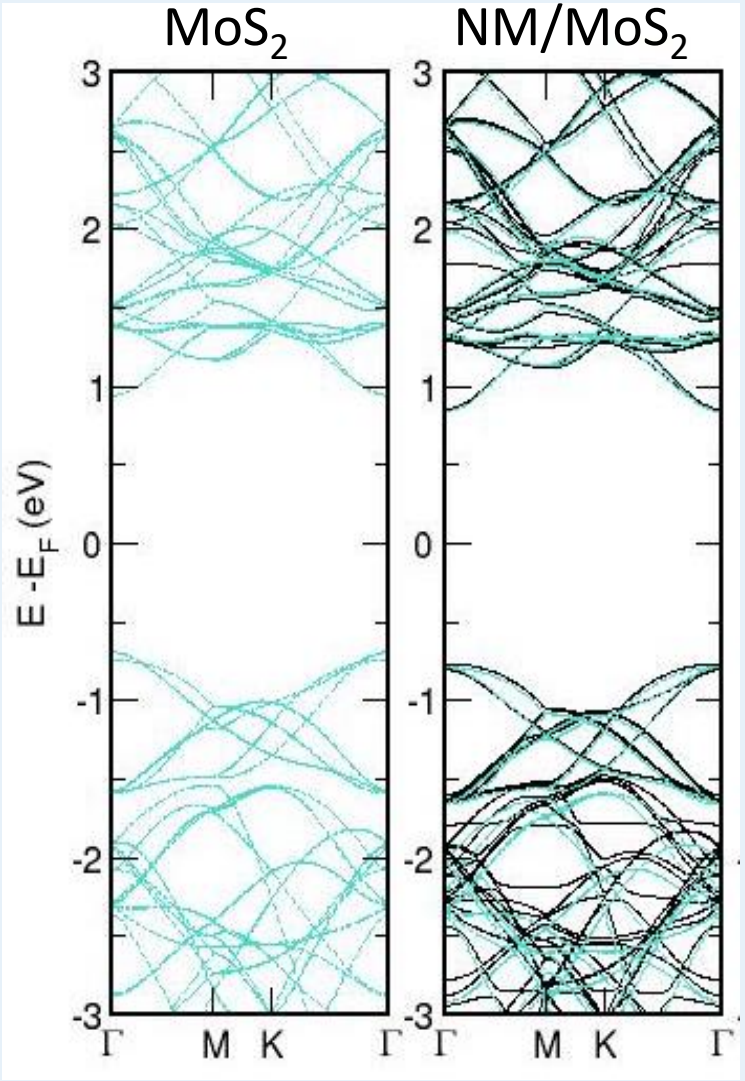
# Is it the same for NM?

- **Same behaviour** regardless of orientation with respect to substrate

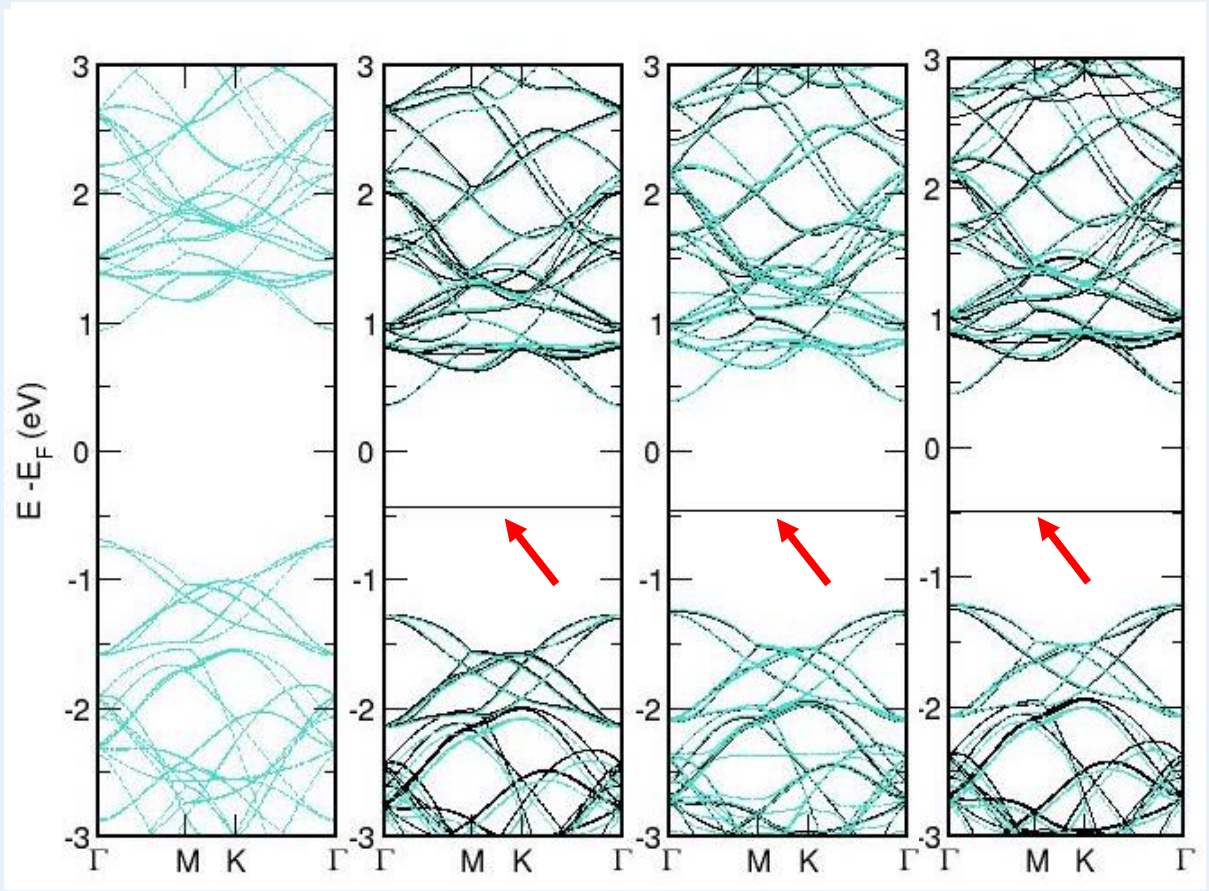
- **No molecule levels** in the system midgap!

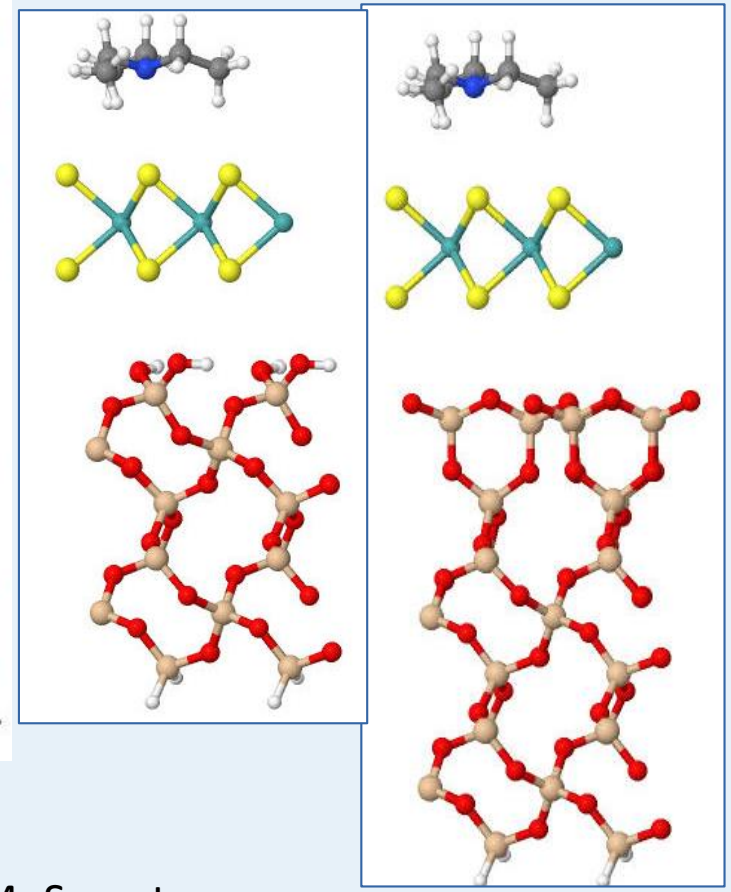
➔ No doping !

Possible origin of experimental molecular discrimination



# Substrate effects: $SiO_2$



$MoS_2$ $TEA/MoS_2$ on silanol on siloxane

- **Weak interaction** between oxide and $TEA/MoS_2$ system for both the silanol and siloxane $SiO_2$ reconstructions

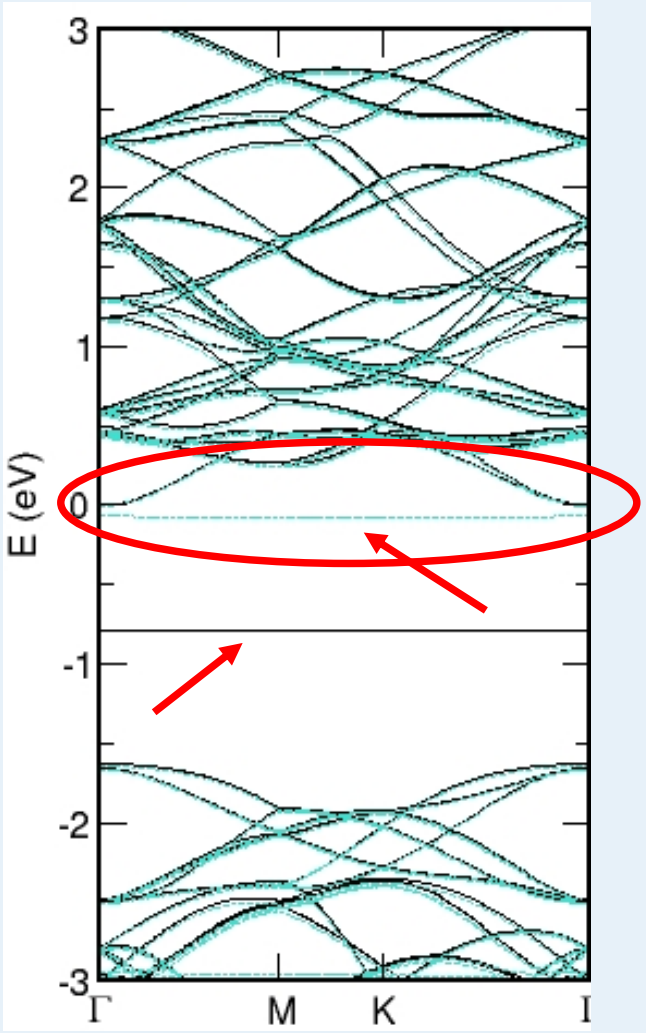
# Transverse electric field

- But still:
  - **Small charge transfer**

→ try to induce some extra charge transfer by **applying transverse electric field**

**➔Shift of molecule level towards CBM**
**➔Still filled level: doping**


(huge!)
But exploratory …




**Charge transfer from TEA to $MoS_2$ increases in 0.18 e**

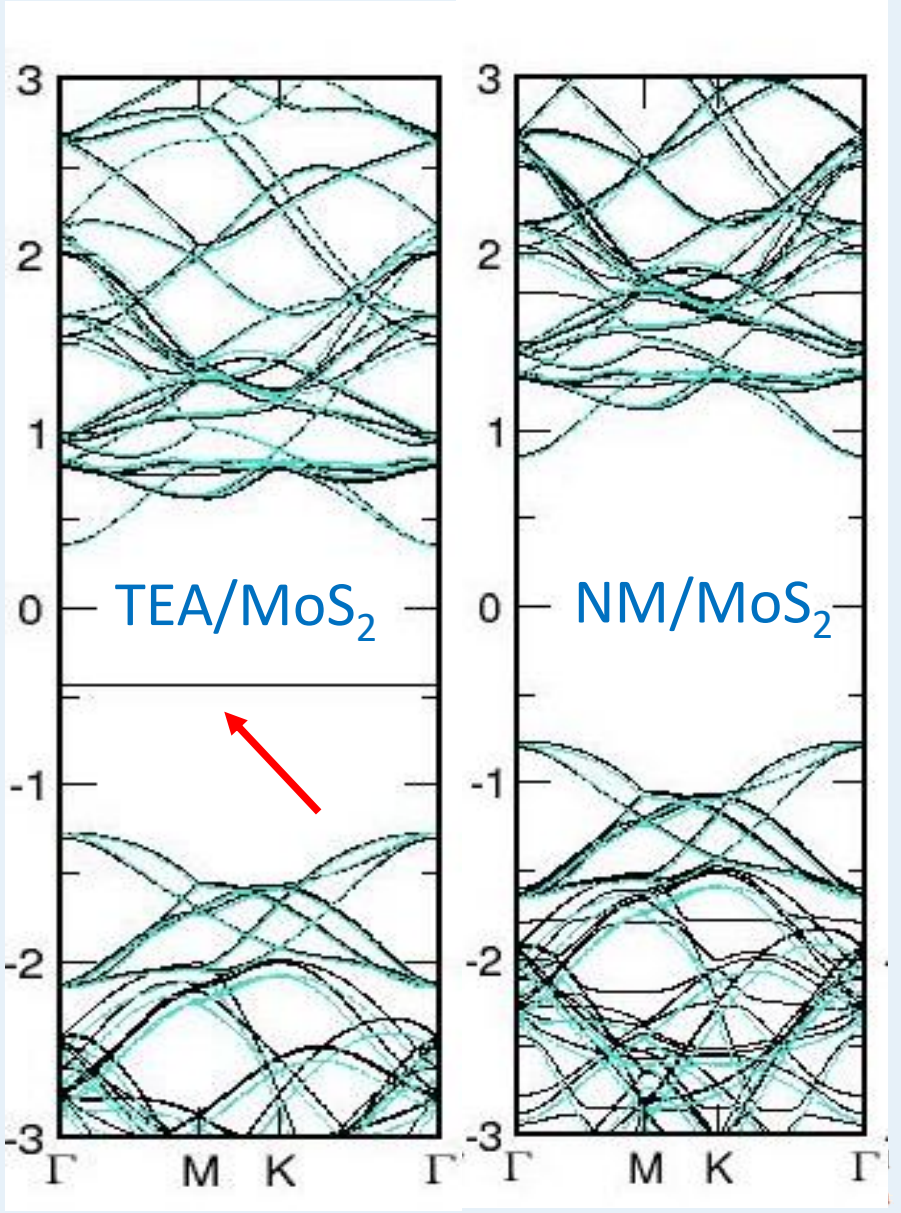
# Conclusions

- Plausible explanation to molecular discrimination:

➔**Doping by introduction of molecular (filled) states in the midgap**

- Very little charge transfer between molecule and $MoS_2$
- Large adsorption distances

**Compatible with physisorption process**



# Work in progress

Overestimation of adsorption energies → better basis !

- **Basis sets optimization** (*simplex* algorithm including diffusive orbitals)
- **Plane waves** calculations (VASP)
- **Transport** calculations → changes in conductance?
- **Other adsorbates**

B. Biel *et al*. -In preparation

# Structural, electronic and transport properties of distorted nanographenes


European Research Council

ugr | Universidad de Granada

NanographOUT

ugr | Universidad de Granada

# NANOGRAPHOUT

NanographOUT

- NANOGRAPHOUT: Design, synthesis, study and applications of  distorted nanographenes
- ERC Starting Grant awarded to Dr. Araceli G. Campaña, Dept. of Organic Chemistry, University of Granada

DEPARTAMENTO
QUIMICA ORGÁNICA
UNIVERSIDAD DE GRANADA

ugr Universidad de Granada

# Goals of NANOGRAPHOUT

To **embed seven- and higher membered rings** into an otherwise planar NANOGRAPHene lattice as a new tool for the preparation of unprecedented materials for organic electronics. It is proposed that **such defects would induce a saddle-type curvature** in the planar sheet pushing the structure OUT of the plane.

# Outcome

Understanding behind the influence of topological defects in nanographene properties

→ structure/property relationships

We aim for:

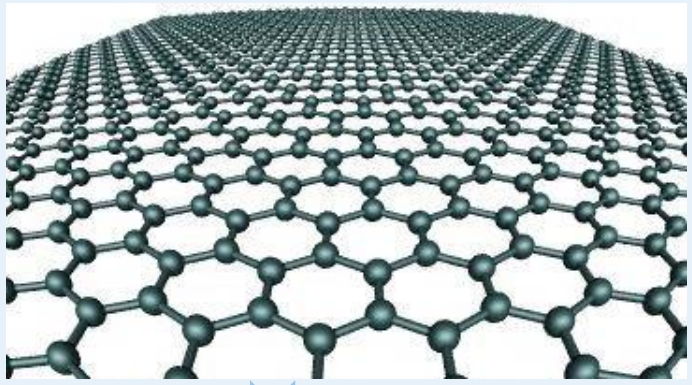
- Large structures, easy to synthesize
- Small optical and electronic bandgaps
- Long fluorescence times
- Soluble!

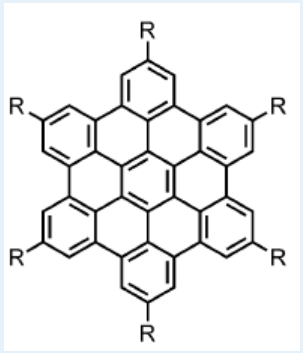
**Electronic and optical devices:**

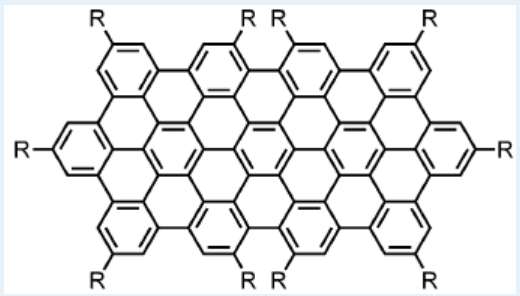
thin-film transistors , circularly polarized light detectors and/or emitters based on the first helically chiral distorted nanographenes

# Synthetic nanographenes and graphene nanoribbons

## Ideal GRAPHENE

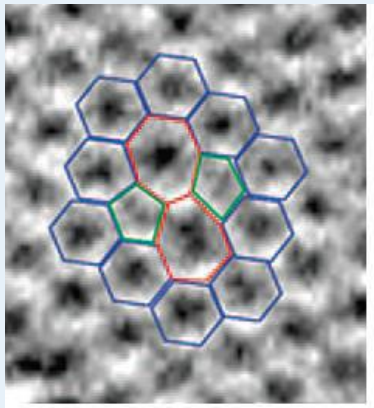


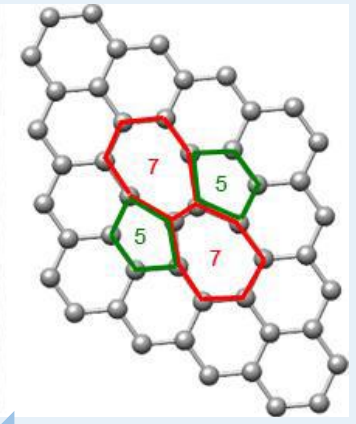


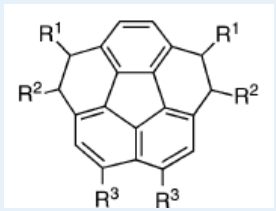

K. Müllen, *et al. Angew. Chem. Int. Ed.*, **2012**, *51*, 7640.

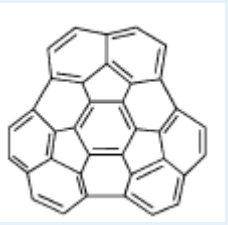
## Real GRAPHENE

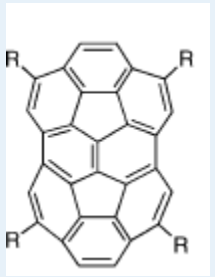





- Pentagons, heptagons
- Pentagon/heptagon pairs





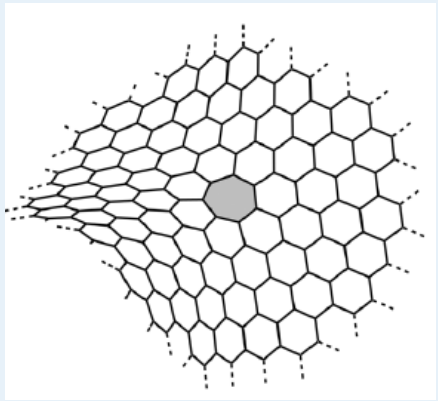

**Limited to pentagons!**

J. S. Siegel, *et al. Chem. Rev.*, **2006**, *106*, 4843

Courtesy of Dr. A.G. Campaña

F. Banhart, J. Kotakoski, A. C. Krasheninnikov, *ACS Nano* **2011**, 5, 26

# Topological defects *vs*. graphene properties

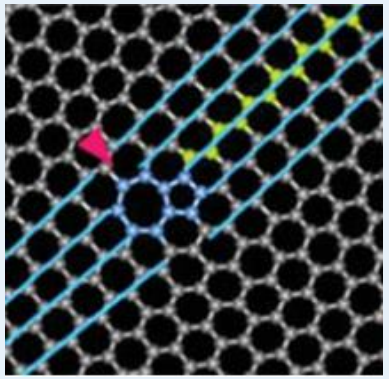


*"We suggest that the defect in the hexagonal network responsible for **negative curvature** may be a single **heptagonal** ring."*

S. Iijima, *et al. Nature,* **1992**, *356*, 776.

*"We can envisage more **diversified applications** in nanocarbon materials by taking advantage of these defects."*

S. Iijima, *et al. Nature,* **2004**, *430*, 870.



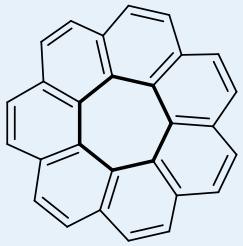
*"**Effective methods for the synthesis** of **heptagon**-containing nonplanar PAHs **are highly needed** to explore these exotic nanocarbons."*

L. T. Scott, K. Itami, *et al. Chem. Asian J.,* **2015**, *10*, 1635.

Courtesy of Dr. A.G. Campaña

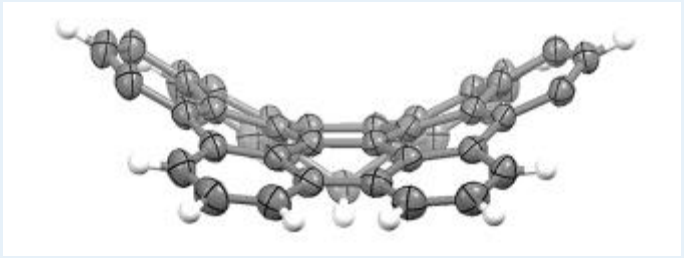
# Previous Works: heptagon-containing graphene molecules

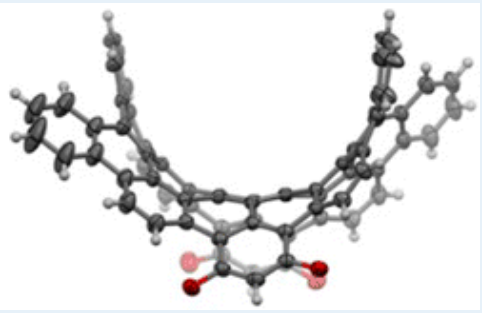
## [7]Circulene



K. **Yamamoto**, *et al.*,
*J. Am. Chem. Soc.* **1983**, *105*, 7171;
*Angew. Chem. Int. Ed.* **1996**, *35*, 69.

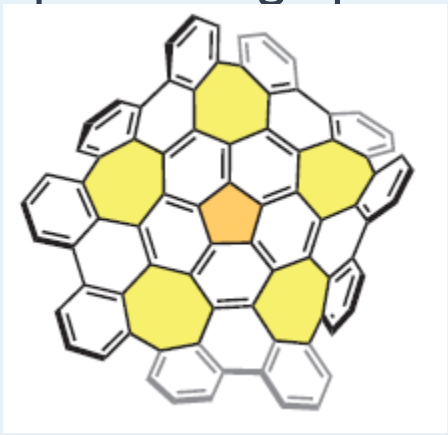
## Aromatic Saldles





Q. **Miao**, *et al.*,
*J. Am. Chem. Soc.* **2012**, *134*, 13796;
*J. Am. Chem. Soc.* **2015**, *137*, 3910.

## Warped Nanographene



L. T. **Scott**, K. **Itami**, *et al.*,
*Nat. Chem.* **2013**, *5*, 739;
*Chem. Asian J.*, **2015**, *10*, 1635.

## Heptagons:

- larger bandgap
- better solubility
- higher fluorescence
- easier oxidation/reduction

**Systematic synthesis route**

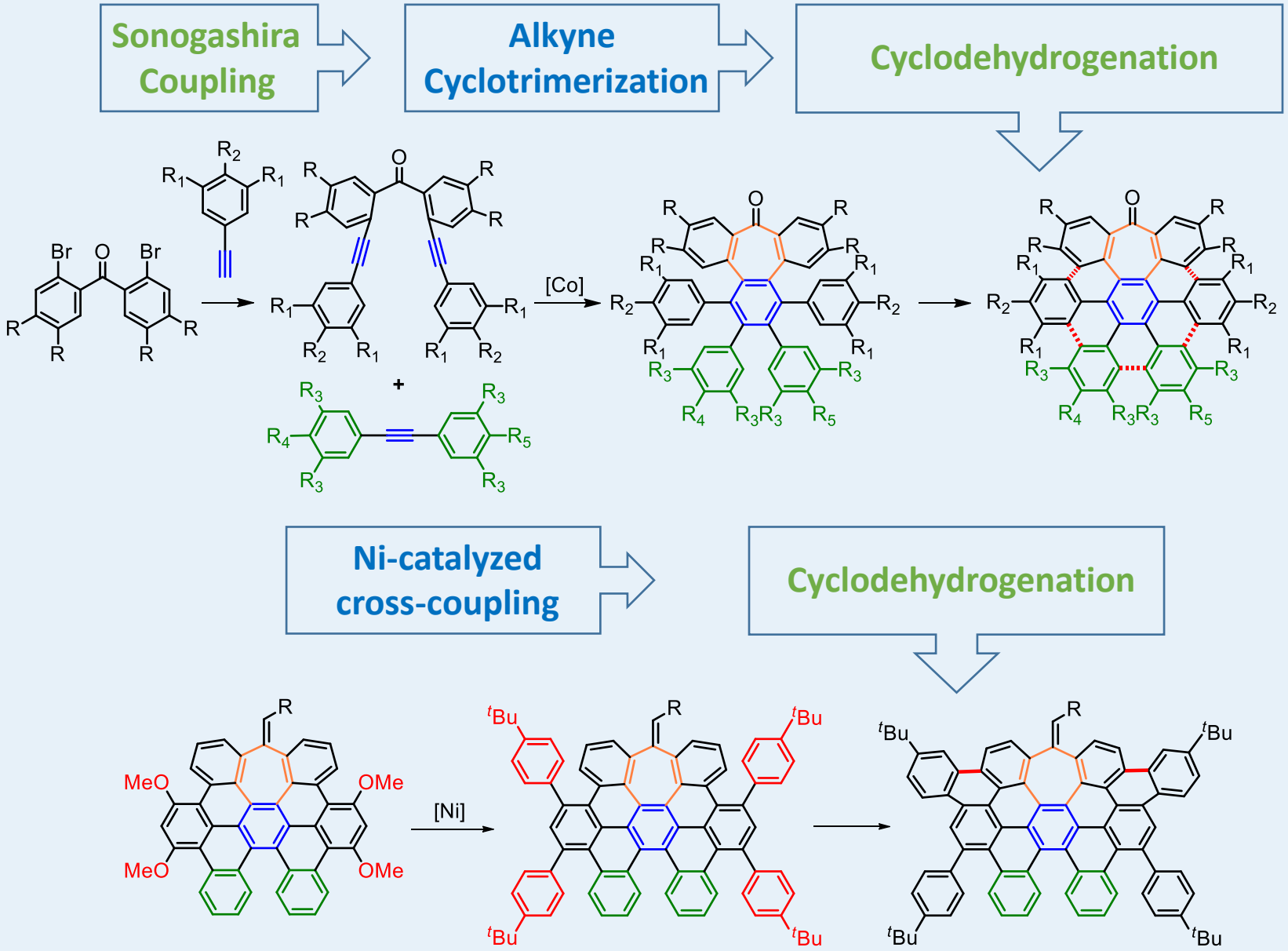
Courtesy of Dr. A.G. Campaña

ugr Universidad de Granada

# Experimental strategy

- Bottom-up approach
- Based on well-established organic reactions→ controlling size and number of defects
- Comparison of their morphology and optical and electronic properties with purely hexagonal compounds

# Versatile and flexible synthesis



# Simulations

## Strategy:

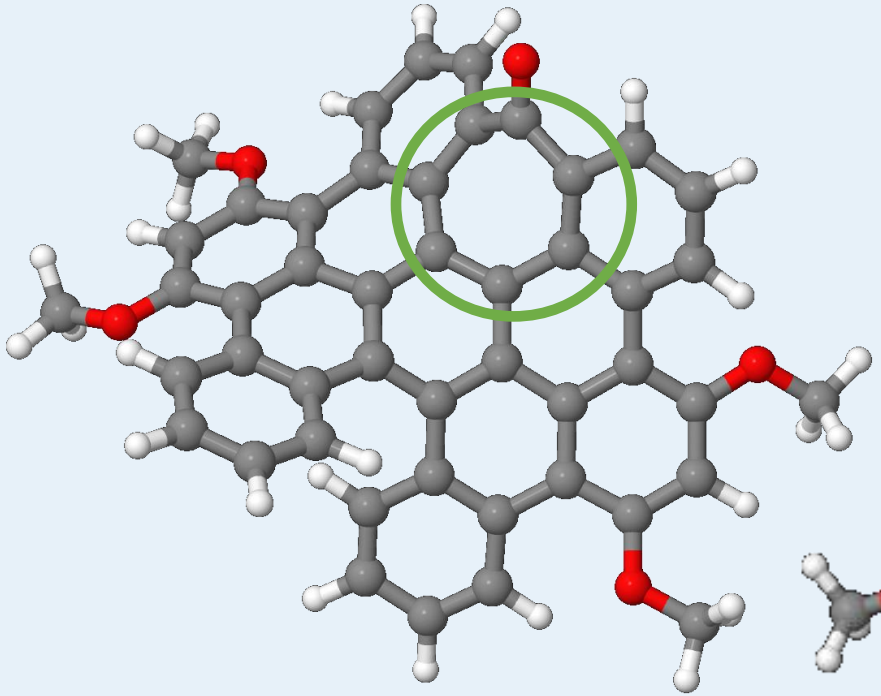
- Start from X-ray coordinates → optimization
- Characterization of electronic properties → trends (in bandgaps, …)
- Stacking → different possibilities (information not always accesible)
- Transport properties of selected compounds

## Methodology:

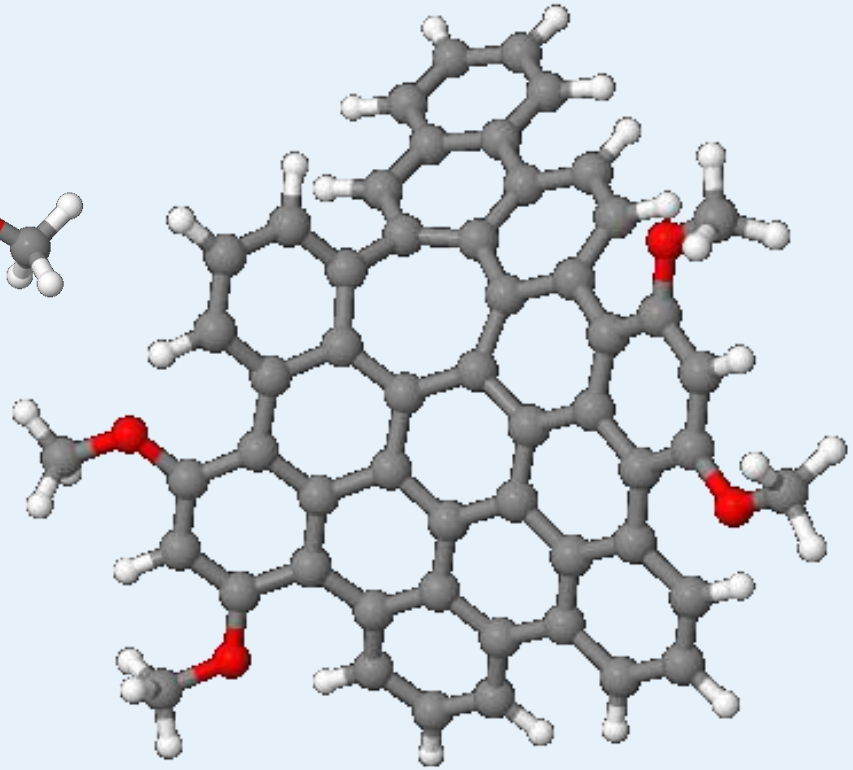
- SIESTA → strictly localized pseudoatomic orbitals
- DZP basis set
- PBE-KBM (van der Waals)
- EnergyShift = 50 meV (> 5 Å cutoff)
- MeshCutoff = 350 Ry
- Force Tolerance < 0.02 eV/Å

# Firstly synthesized heptagon-containing nanographenes

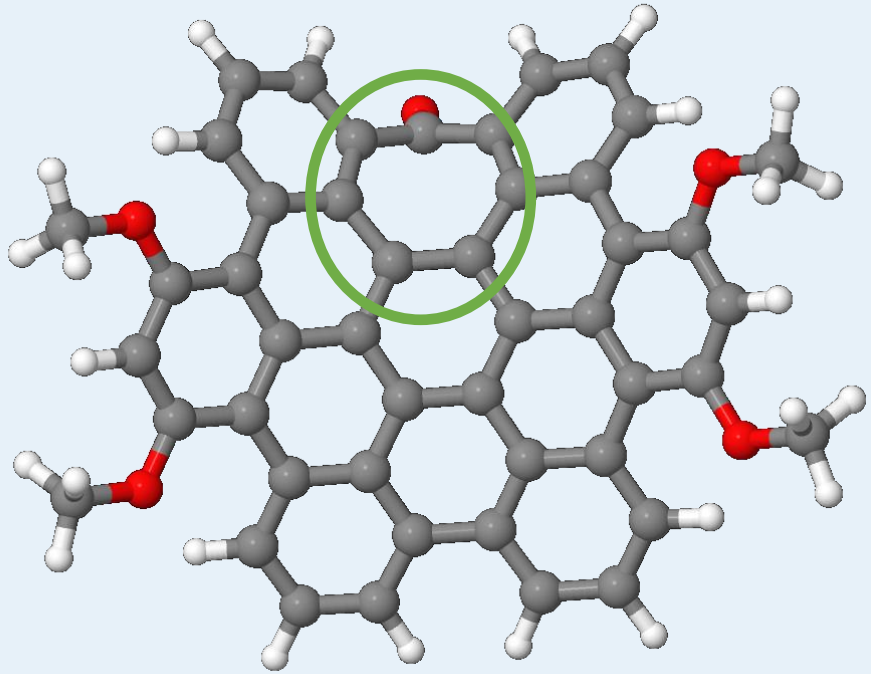
**6a - $C_{47}H_{28}O_5$**



**6* - $C_{54}H_{30}O_4$**



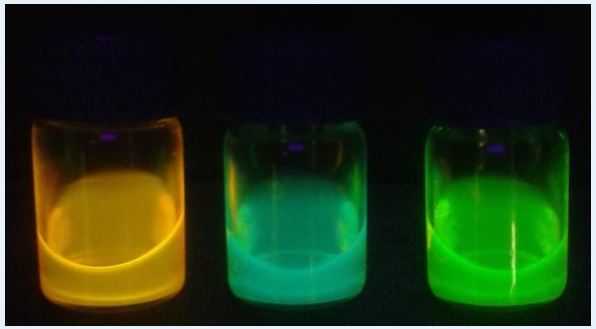
**6h - $C_{47}H_{26}O_5$**



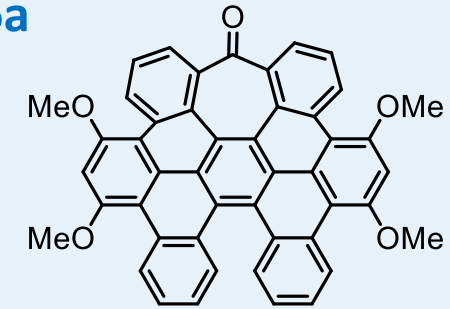
X-Ray Crystal Structures

Highly distorted !

# Firstly synthesized heptagon-containing nanographenes

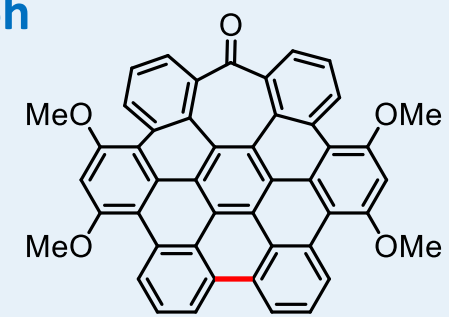


6a



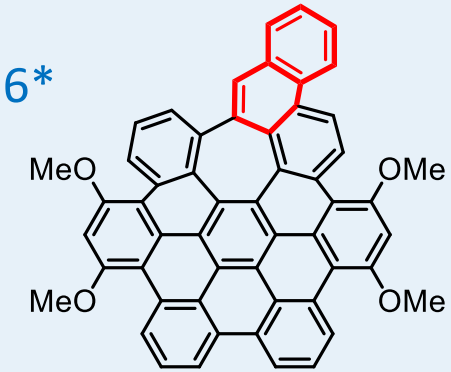

2

6h




3

6*




4

| | | | |
|---|---|---|---|
| **Experimental HOMO/LUMO gap** | **2.35 eV** | **2.72 eV** | **2.59 eV** |
| **DFT-PBE HOMO/LUMO gap** | **1.71 eV** | **2.11 eV** | **1.94 eV** |

Confirmation of experimental trend

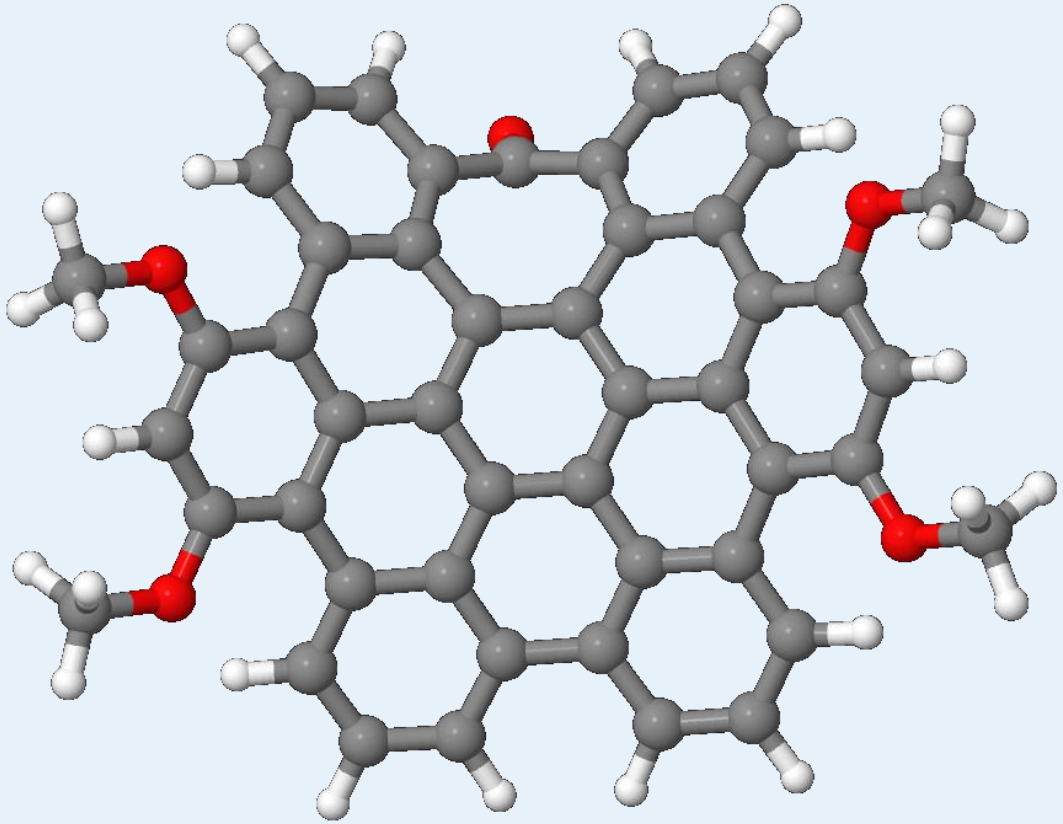
## Electronic Properties: Redox Behaviour

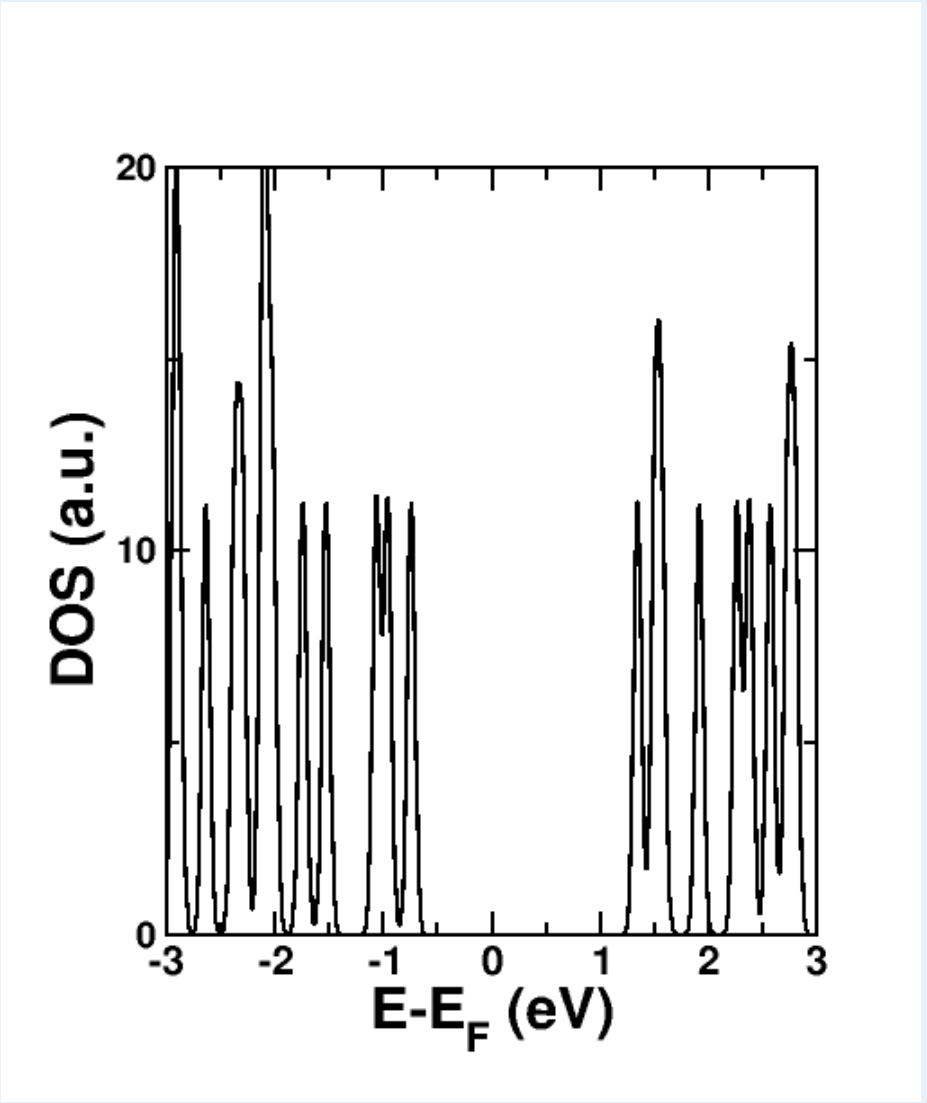
| | | | |
|---|---|---|---|
| **Quantum Yields:** | **$\Phi$ = 0.29** | **$\Phi$ = 0.11** | **$\Phi$ = 0.22** |
| **Fluorescence Lifetimes:** | **$\tau_1$ = 5.36 ns** | **$\tau_1$ = 5.64 ns; $\tau_2$ = 2.65 ns** | **$\tau_1$ = 5.15 ns; $\tau_2$ = 3.68 ns** |

**UV-Vis absorption and fluorescence measurements**

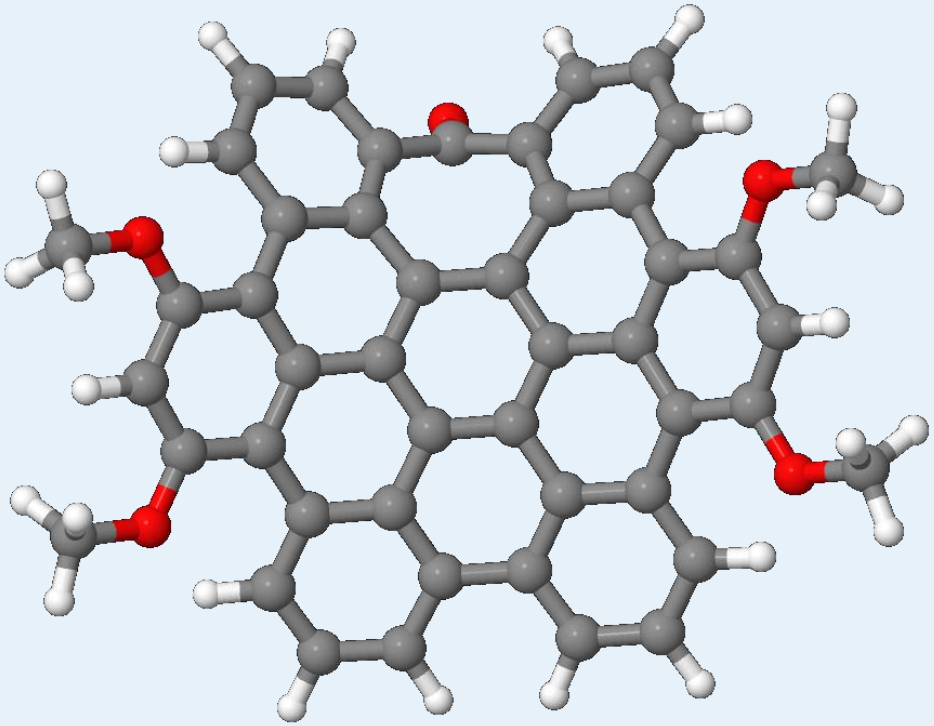
# Firstly synthesized heptagon-containing nanographenes – 6h

Single molecule

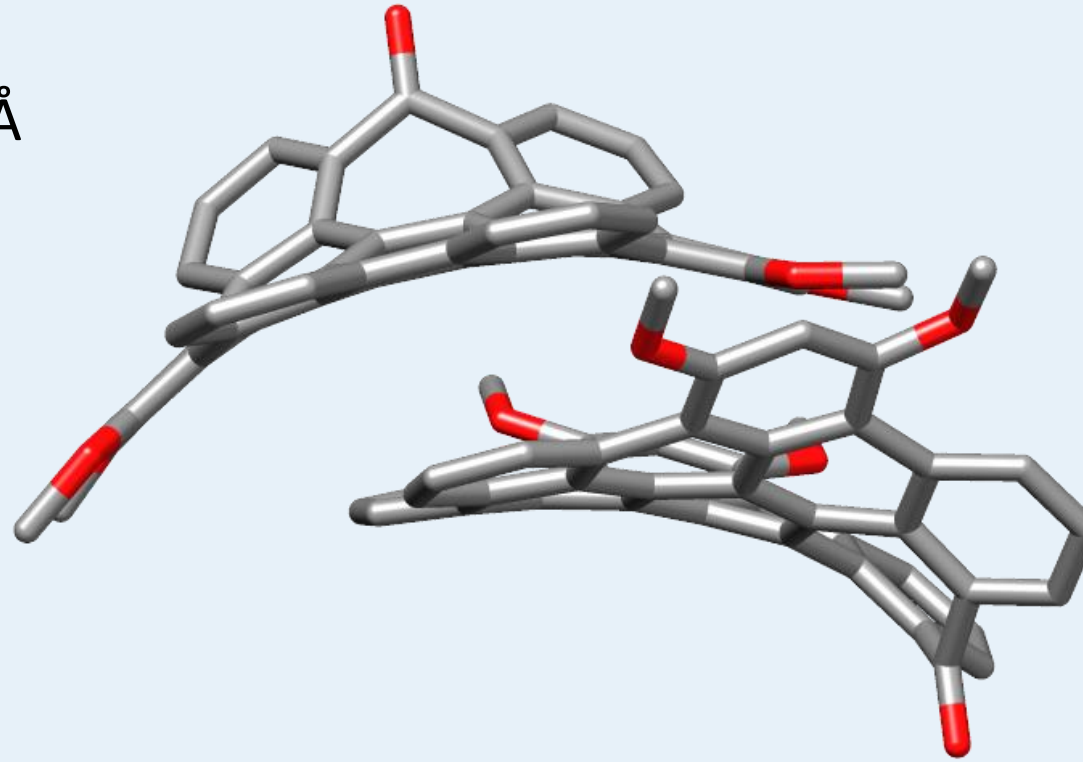




# Firstly synthesized heptagon-containing nanographenes – 6h



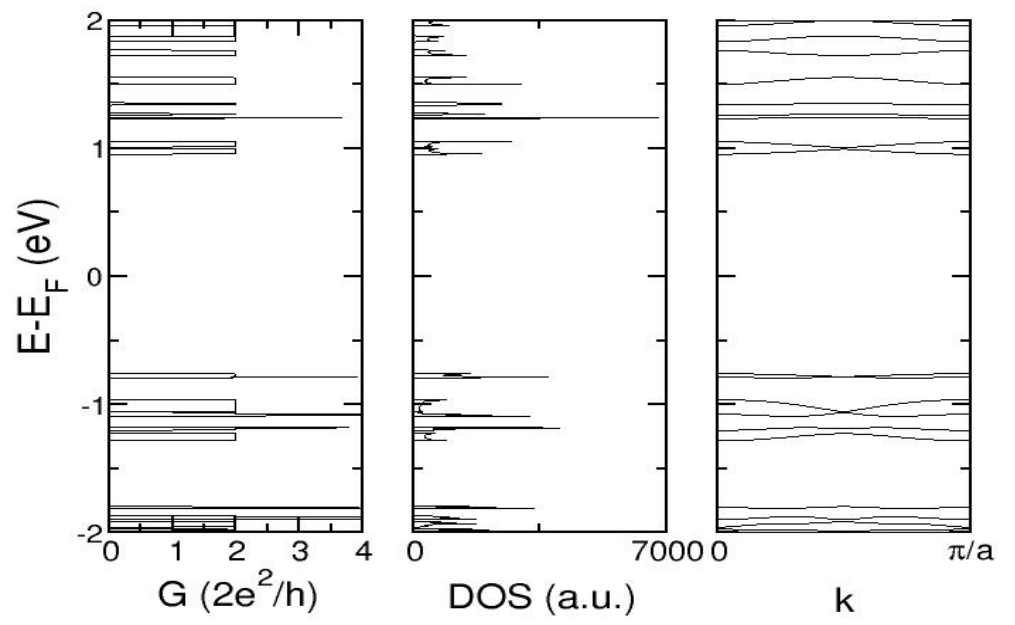
π-π interaction: 3.8 Å
(KBM ~ 4 Å)

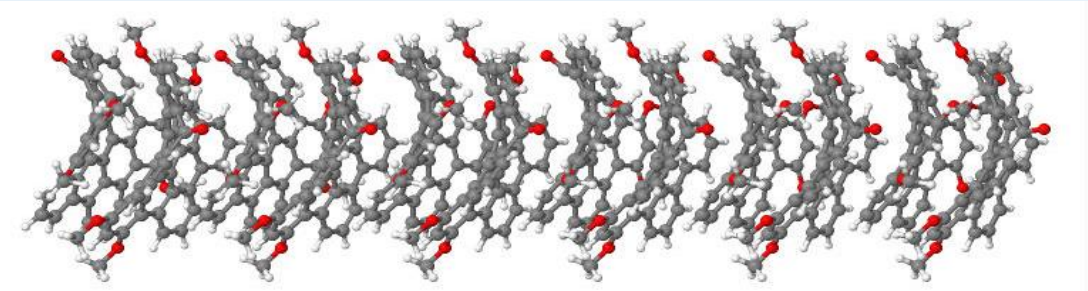


π-π Interactions → semiconductor properties !

# Firstly synthesized heptagon-containing nanographenes – 6h

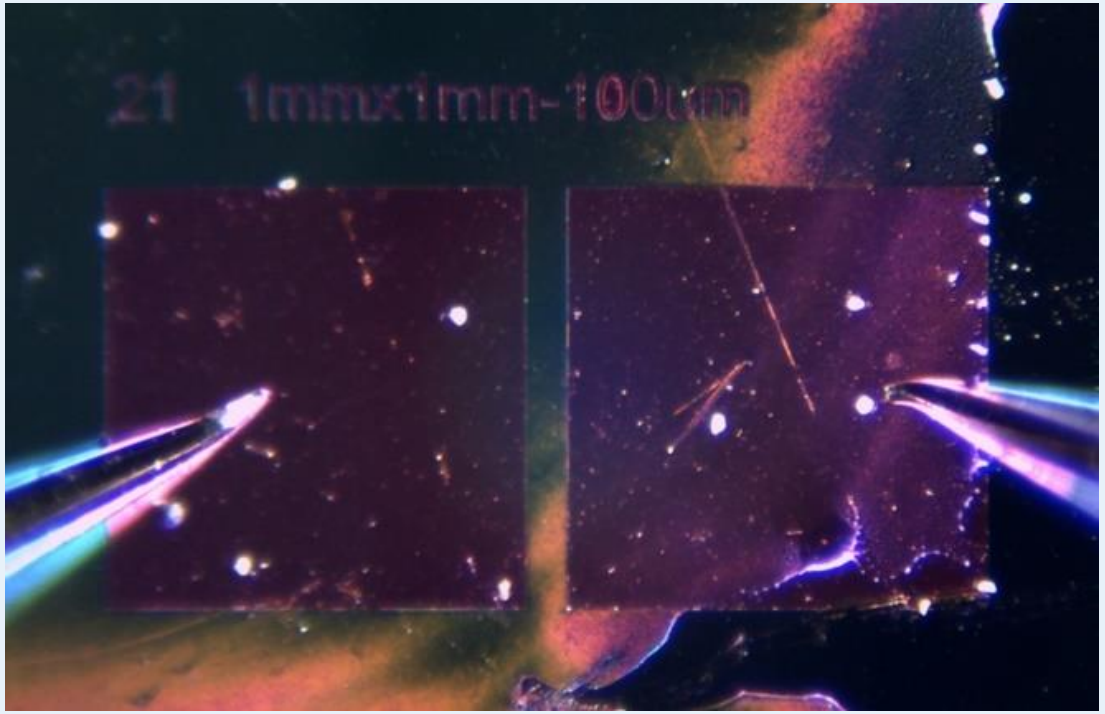
## Preliminary attempts to build OTFTs:



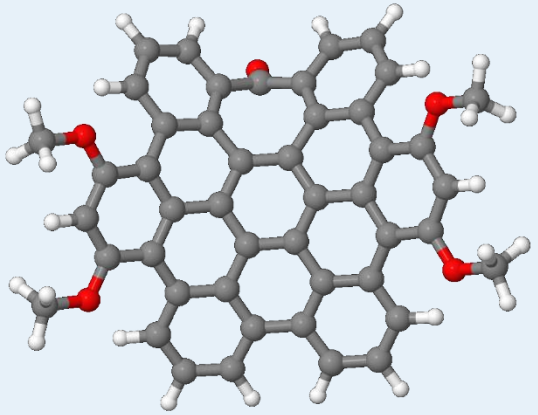



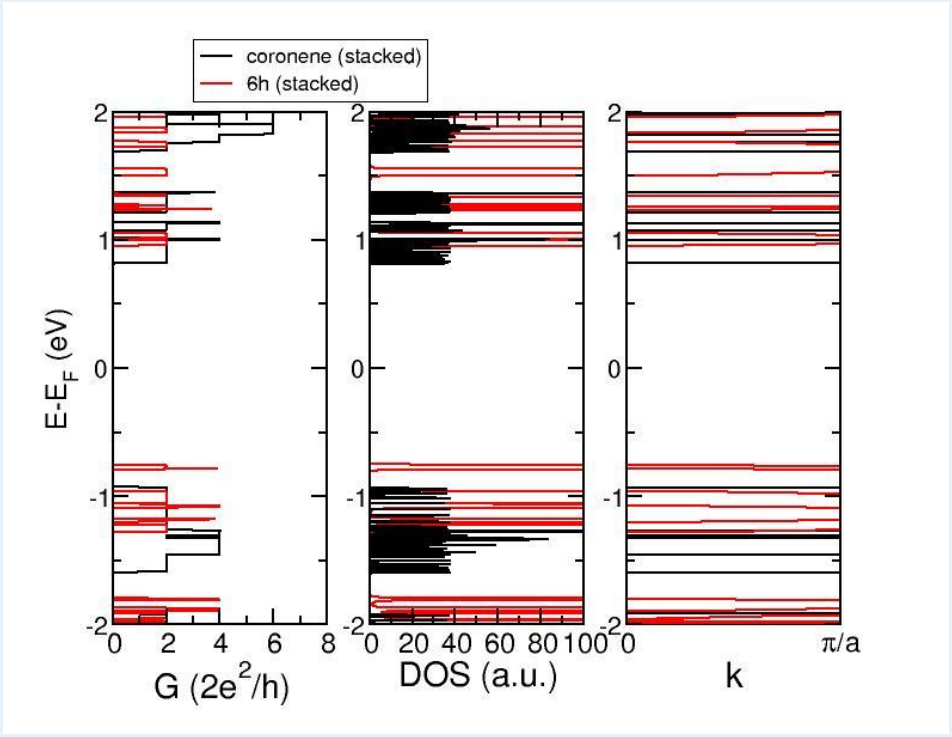
Bottom-contact configuration
(film prepared by dip casting technique)

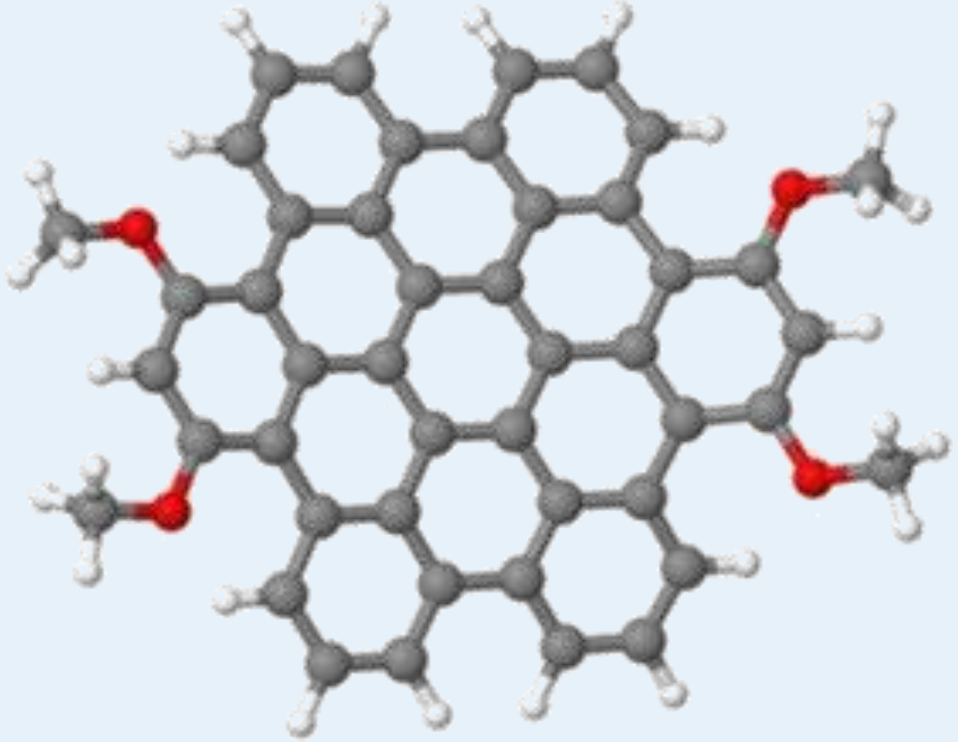
(Dr. Teresa González - IMDEA Nanociencia)



# 6h – comparison with defect-free





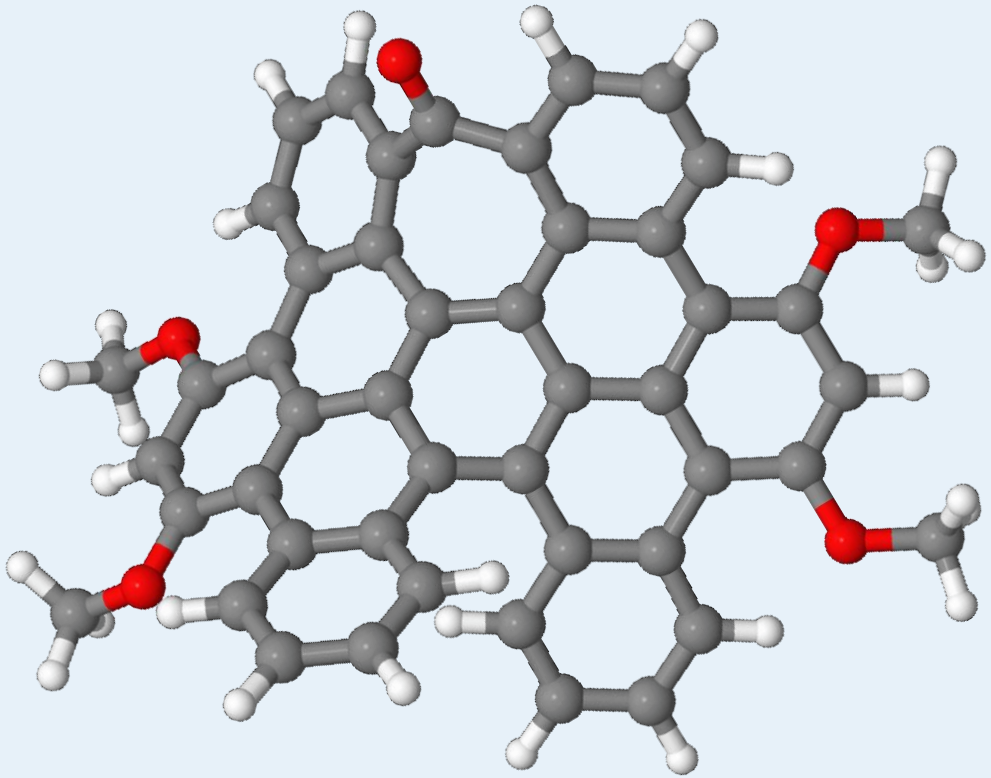



- Gap - no defect → 2.10 eV (chain 1.75 eV)
- Gap – defect → 2.11 eV (chain 1.71 eV)

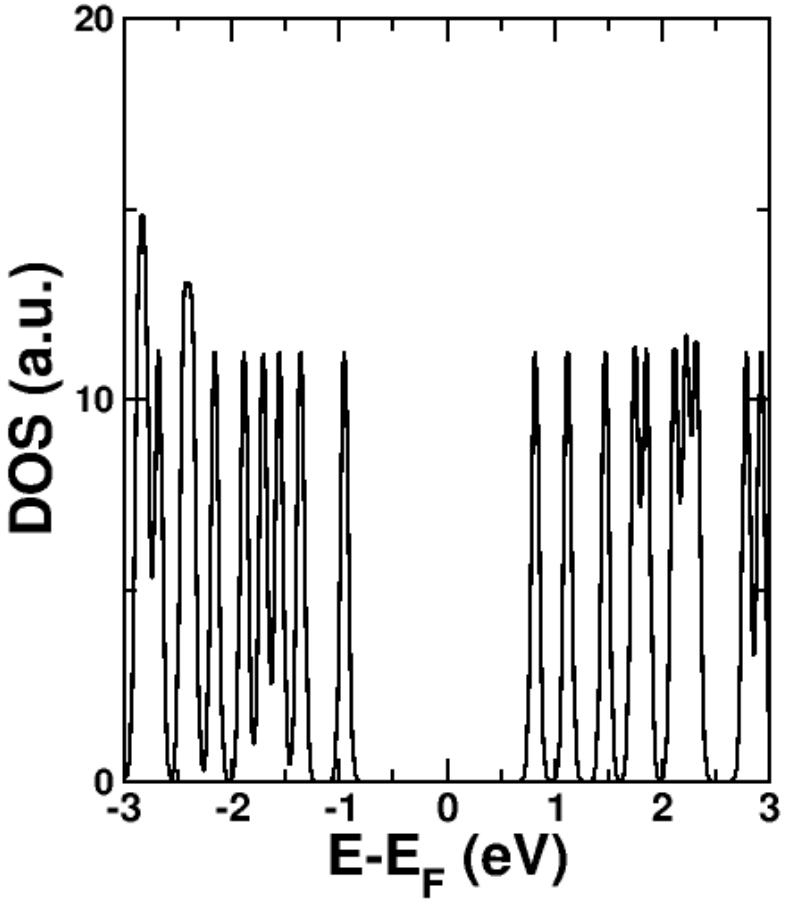
In progress → w/o ketone group

# Firstly synthesized heptagon-containing nanographenes - 6a

## 6a - $C_{47}H_{28}O_5$

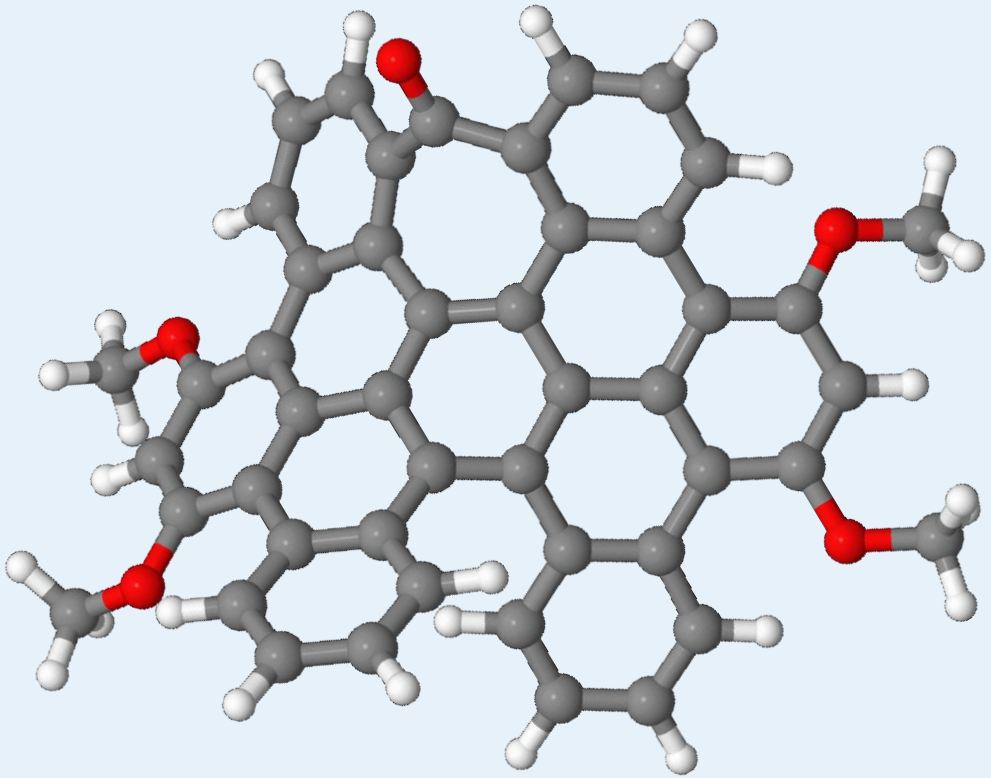


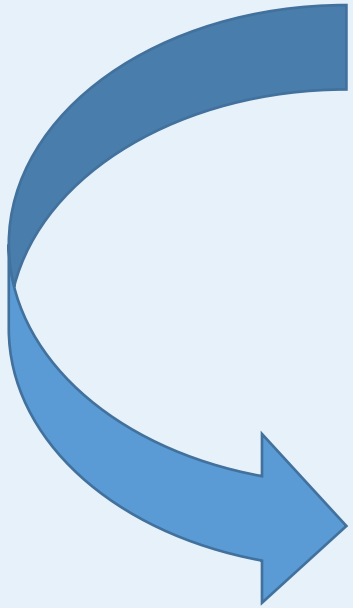
HOMO-LUMO gap (PBE) = 1.71 eV
(exp.) = 2.35 eV

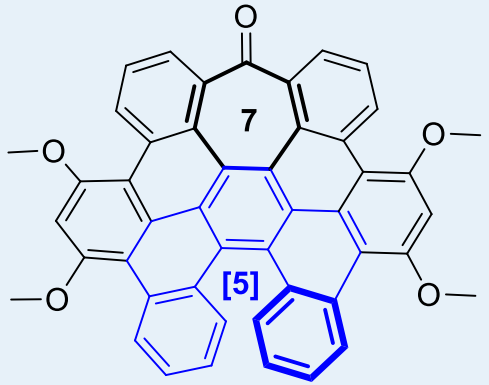


# Firstly synthesized heptagon-containing nanographenes - 6a

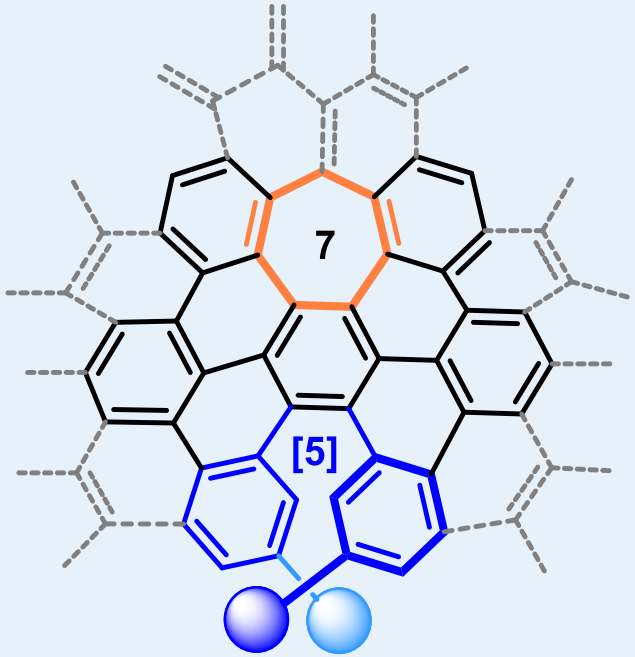
**6a - $C_{47}H_{28}O_5$**







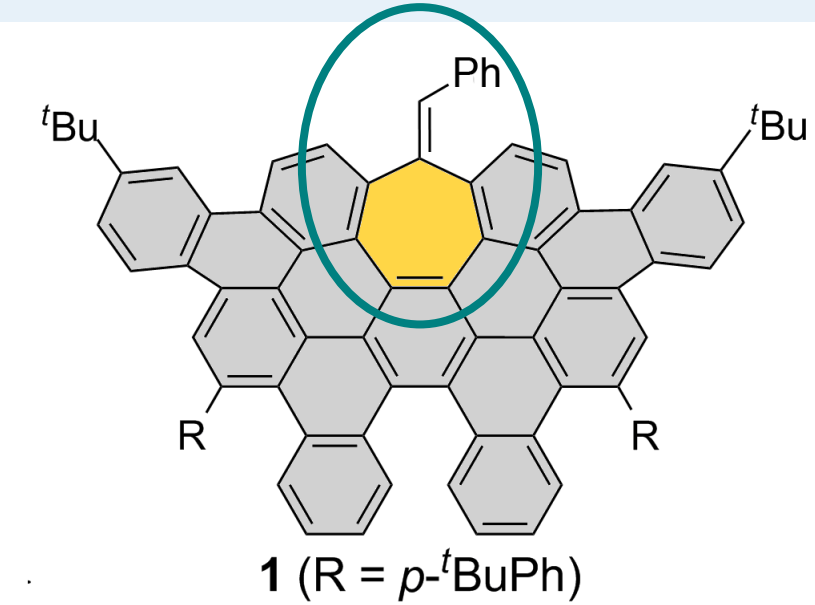

[5]helicene




**Goal → high and efficient chiral luminescence**

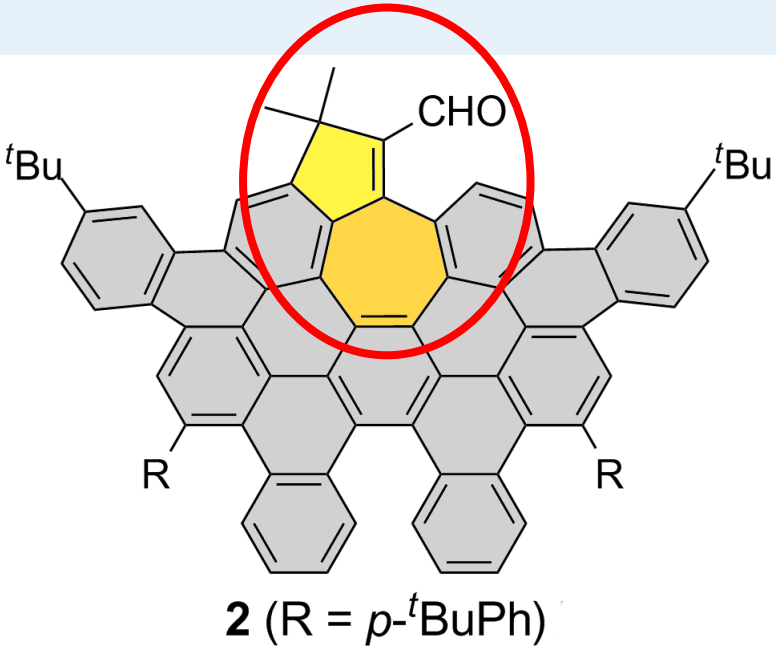
Bulky / Enantiopure groups

# Expanded distorted nanographenes: properties




**1** (R = *p*-$^t$BuPh)

Experimental gap = 2.66 eV




**2** (R = *p*-$^t$BuPh)

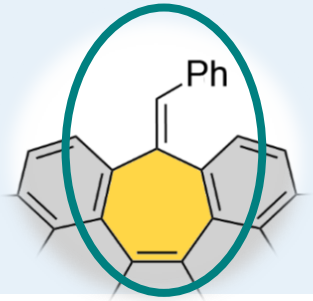
Experimental gap = 2.27 eV

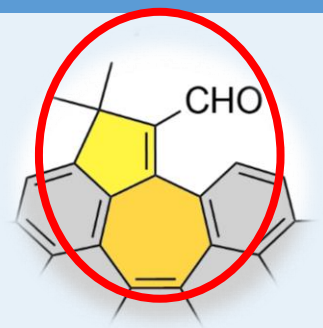
organic field effect transistors and solar cells

A. G. Campaña, *et al.* *Chem. Sci.*, **2016**, In press. **DOI: 10.1039/C6SC02895K**

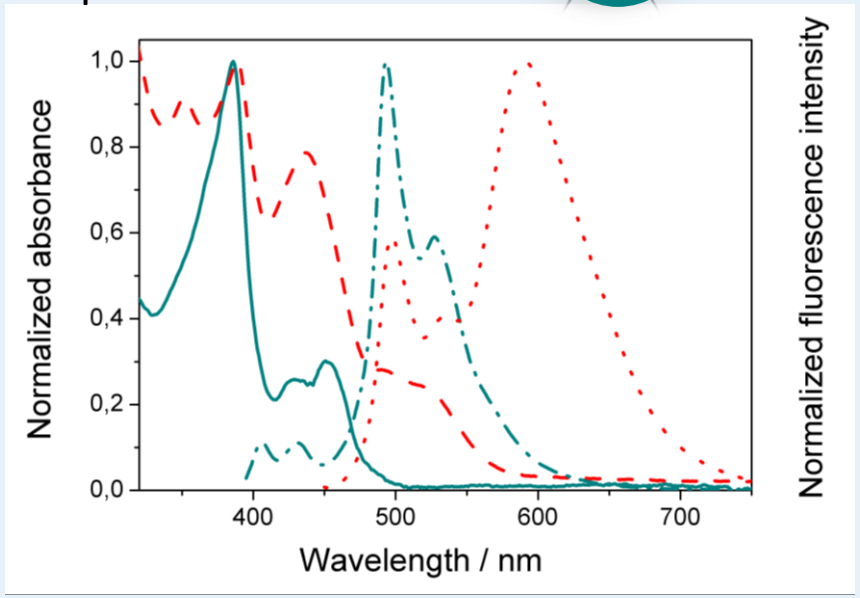
# Expanded distorted nanographenes: properties

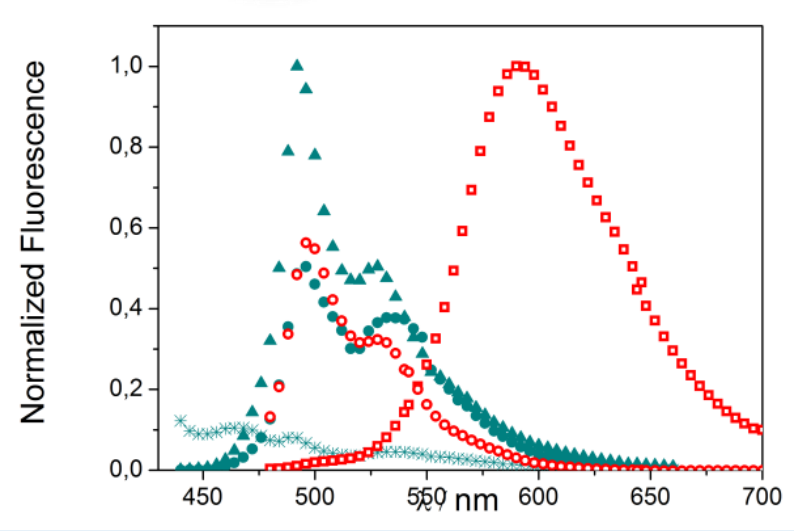
UV-Vis/Emission Spectra




Time-Resolved Emission Spectra

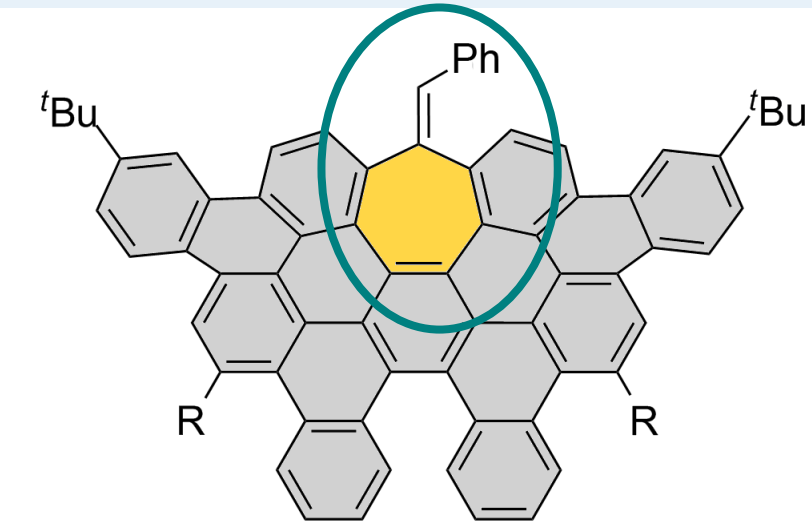


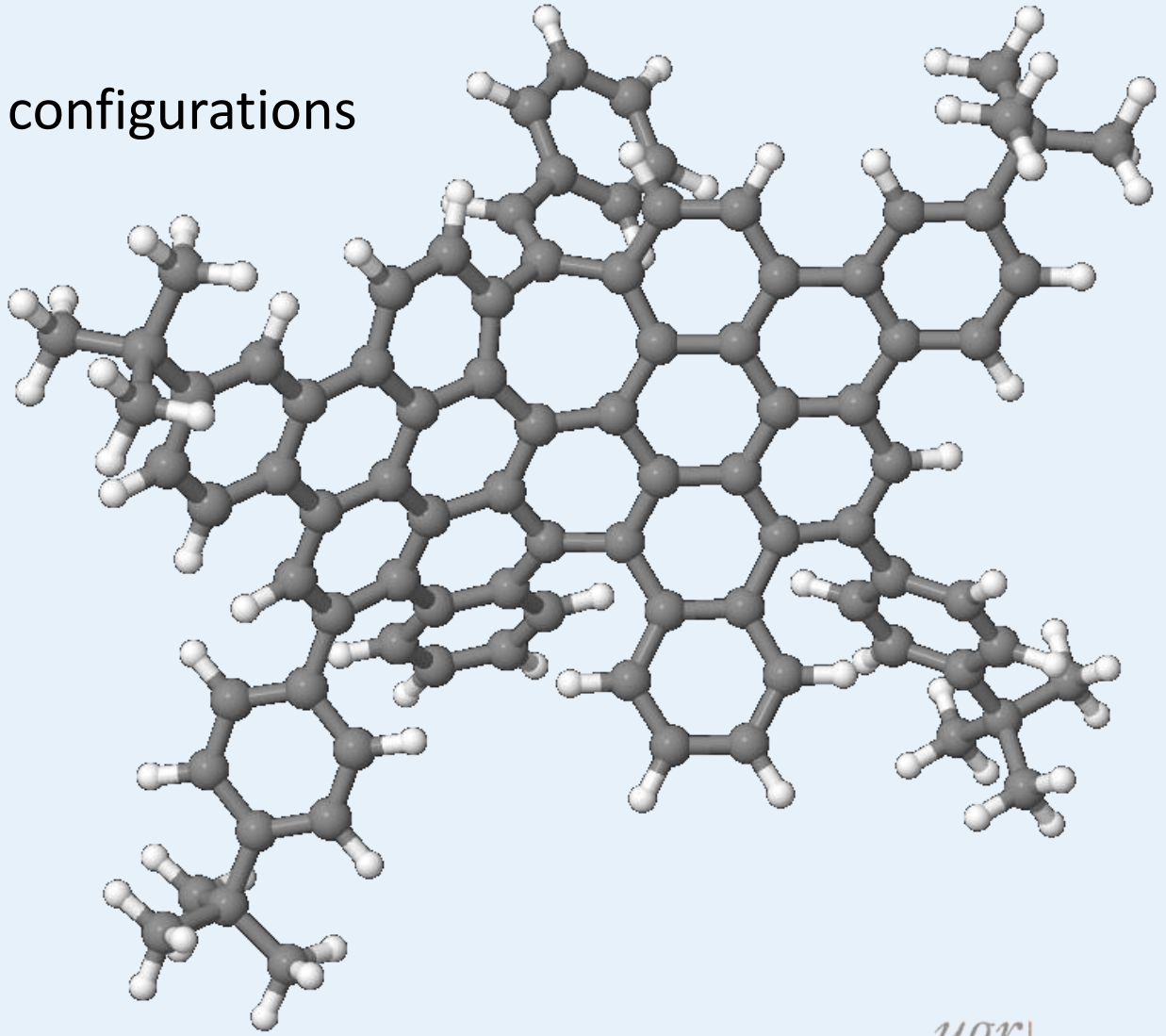

| Compound | Absorbance $\lambda_{max}$ /nm | Fluorescence $\lambda_{max}$ /nm | Quantum Yields (Φ) | Fluorescence Lifetimes (τ) / ns ▲ ● | |
|---|---|---|---|---|---|
| | | | | $\tau_1$ ○ | $\tau_2$ □ |
| **1** | 386 | 493 | 0.072 | 14.51 | 4.14 |
| **2** | 389 | 590 | 0.075 | 12.92 | 3.7 |

# Expanded distorted nanographenes: properties

- Soluble
- No X-ray information → tentative stacking configurations

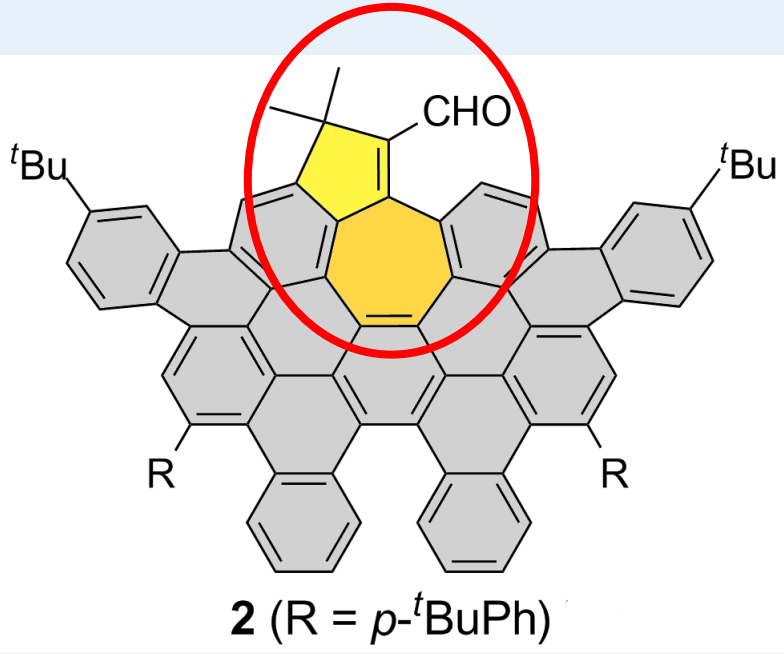



**1** (R = *p*-$^t$BuPh)

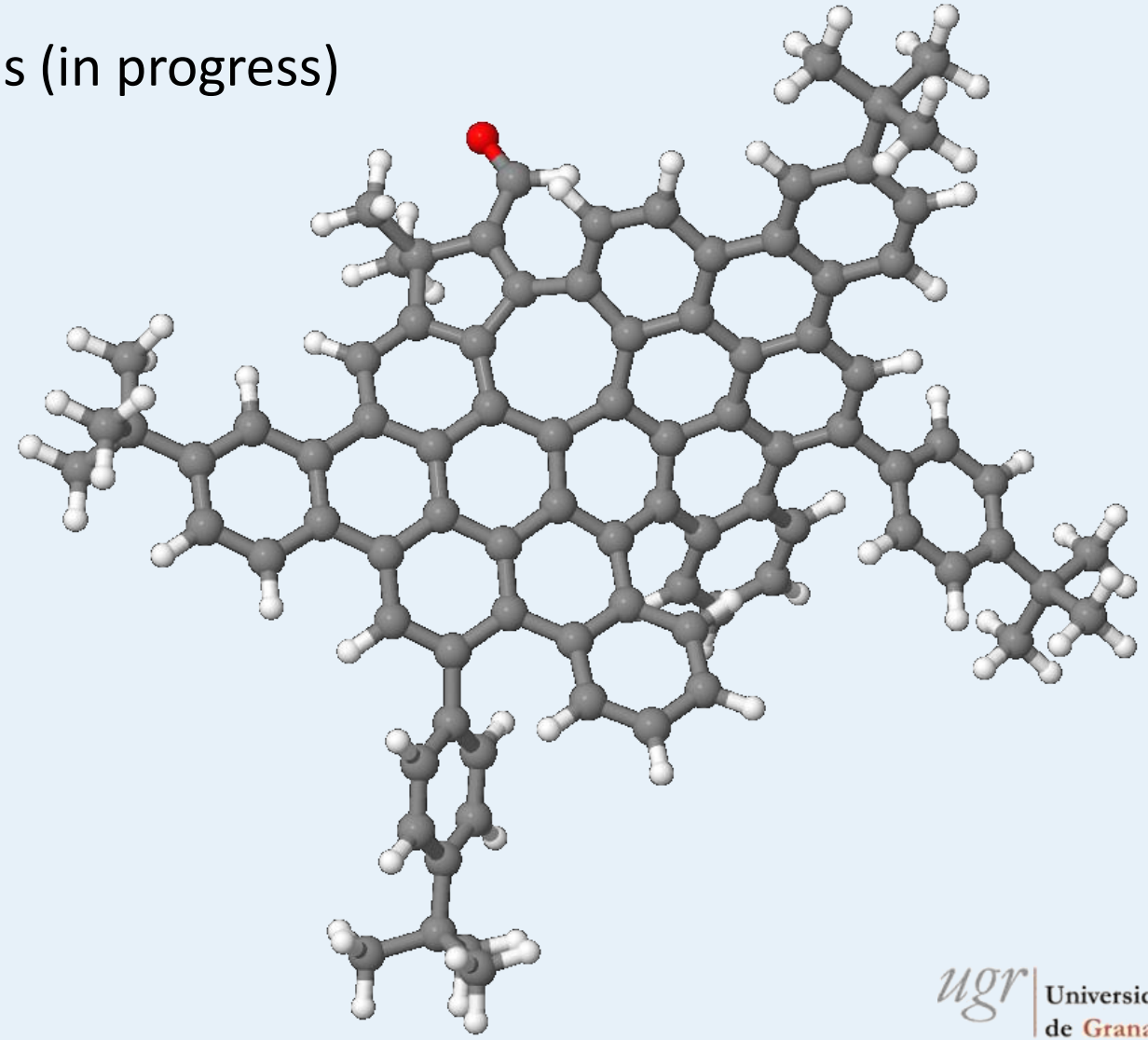


# Expanded distorted nanographenes: properties

- Soluble
- X-ray information → transport calculations (in progress)




**2** (R = *p*-$^t$BuPh)



# Our first publication

Chemical Science

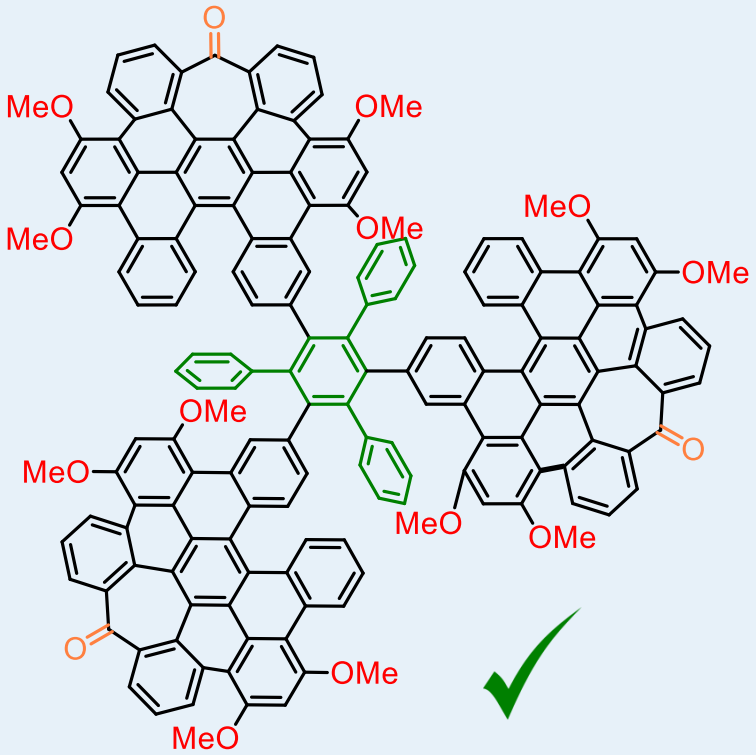
Accepted Manuscript

## Versatile Synthesis and Enlargement of Functionalized Distorted Heptagon-Containing Nanographenes

Irene R. Márquez,[a] Noelia Fuentes,[a] Carlos M. Cruz,[a] Virginia Puente-Muñoz,[b] Lia Sotorrios,[c] M. Luisa Marcos,[d] Duane Choquesillo-Lazarte,[e] Blanca Biel,[f] Luis Crovetto,[b] Enrique Gómez-Bengoa,[c] M. Teresa González,[g] Ruben Martin,[h] Juan M. Cuerva,[a] and Araceli G. Campaña*[a]

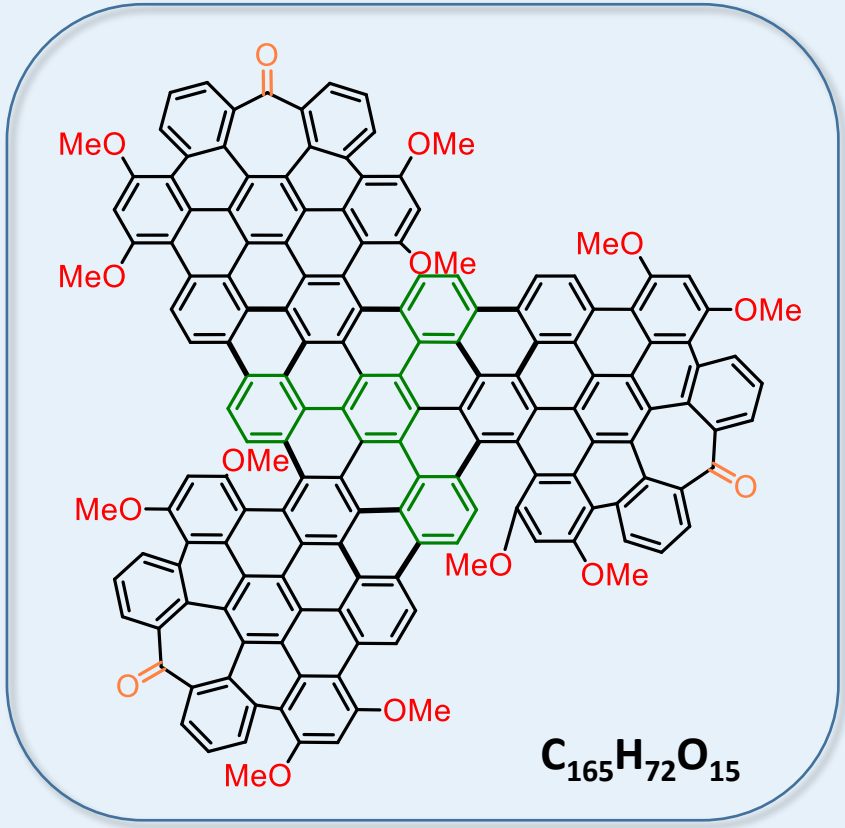
This article can be cited before page numbers have been issued, to do this please use: I. R. Marquez, N. Fuentes, C. M. Cruz, V. Puente-Muñoz, L. Sotorrios, M. L. Marcos, D. Choquesillo-Lazarte, B. Biel, L. Crovetto, E. Gomez-Bengoa, M. T. Gonzalez , R. Martin, J. M. Cuerva and A. G. Campaña, *Chem. Sci.*, 2016, DOI: 10.1039/C6SC02895K.

# Work in progress




**Soluble in hexane!**

**One step**



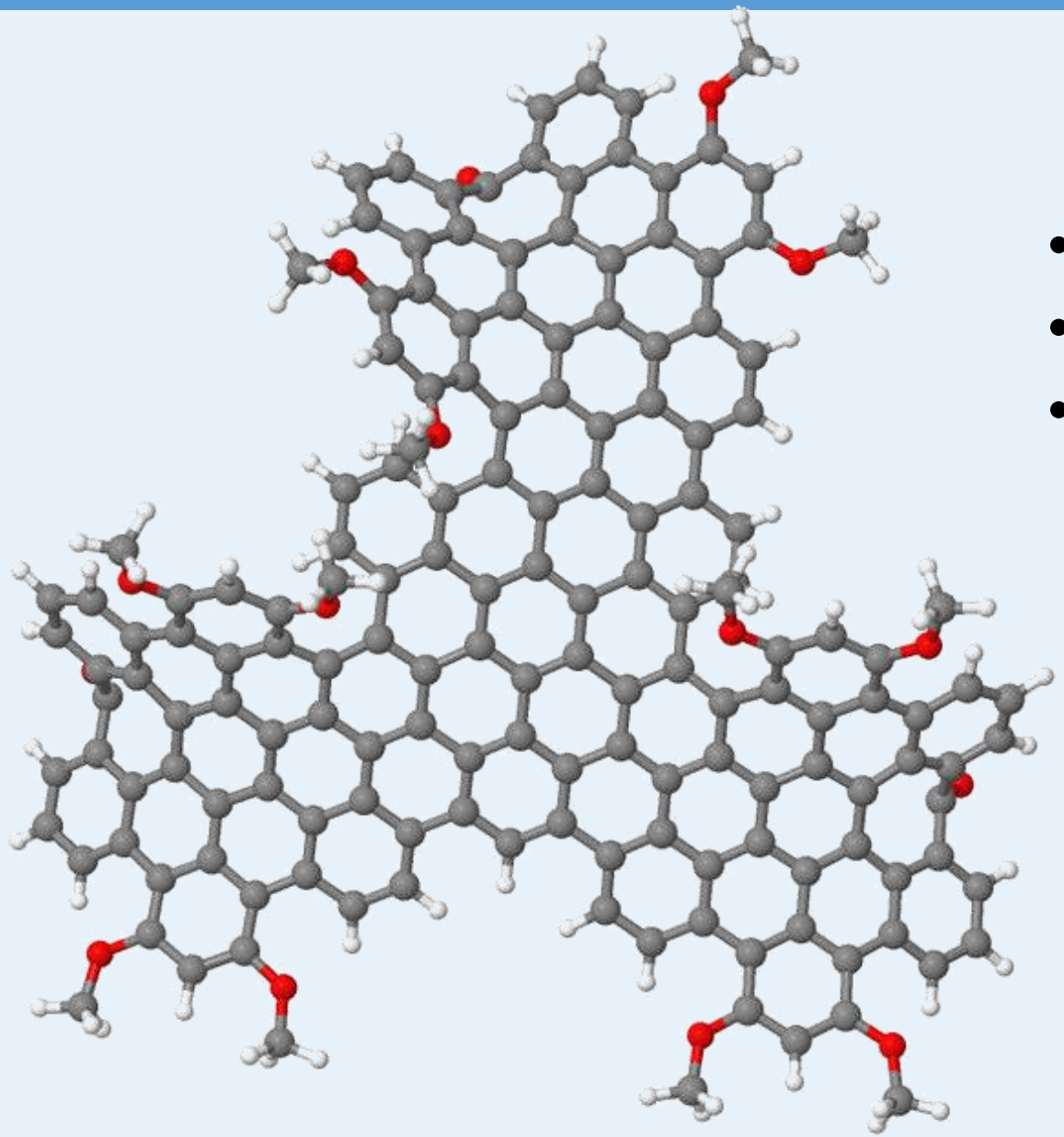

**Further extension is possible:**

**Ketone moieties**

**Methoxide groups**

Distorted PAH containing 3 heptagons

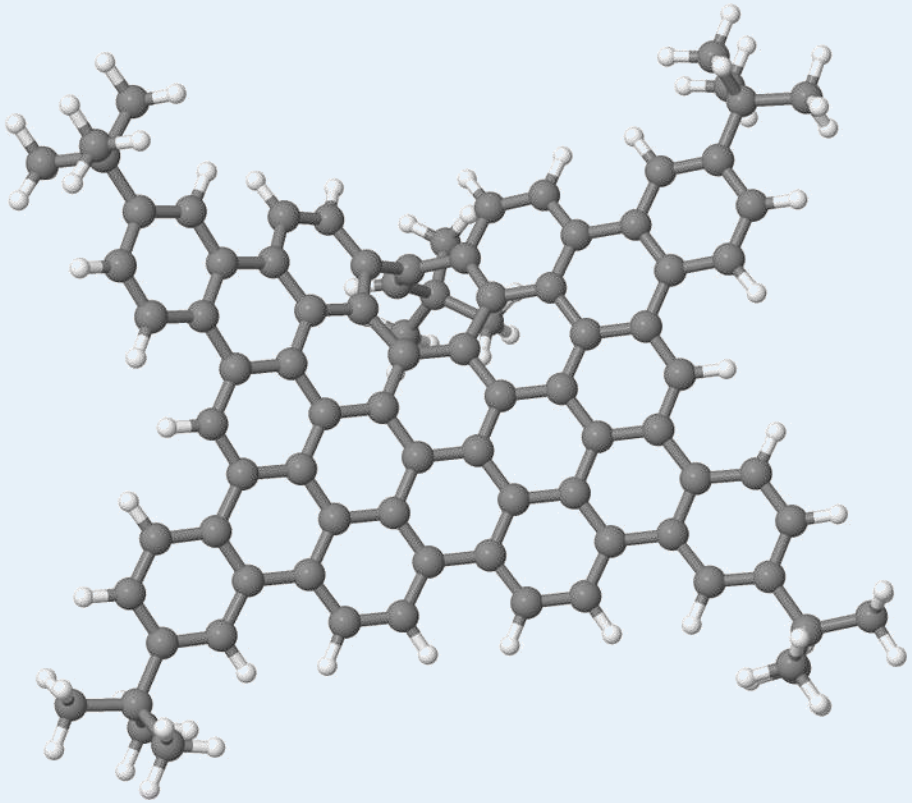
# Work in progress



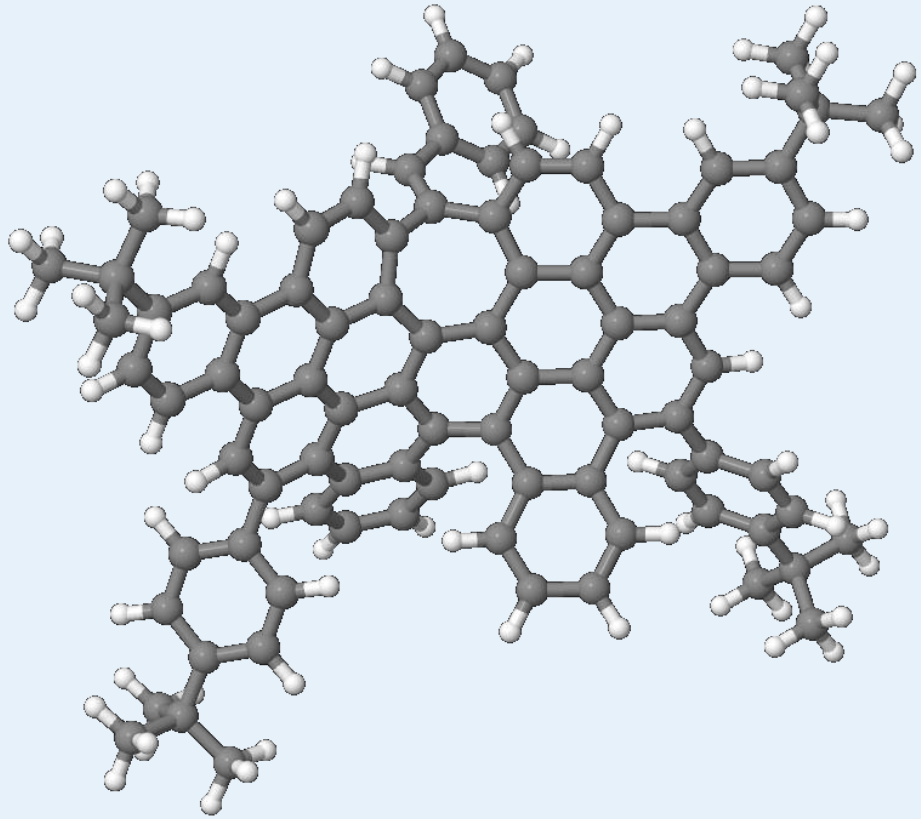

- Estructural optimization
- Isolated molecules and chain
- Transport

# What didn’t work

Goal

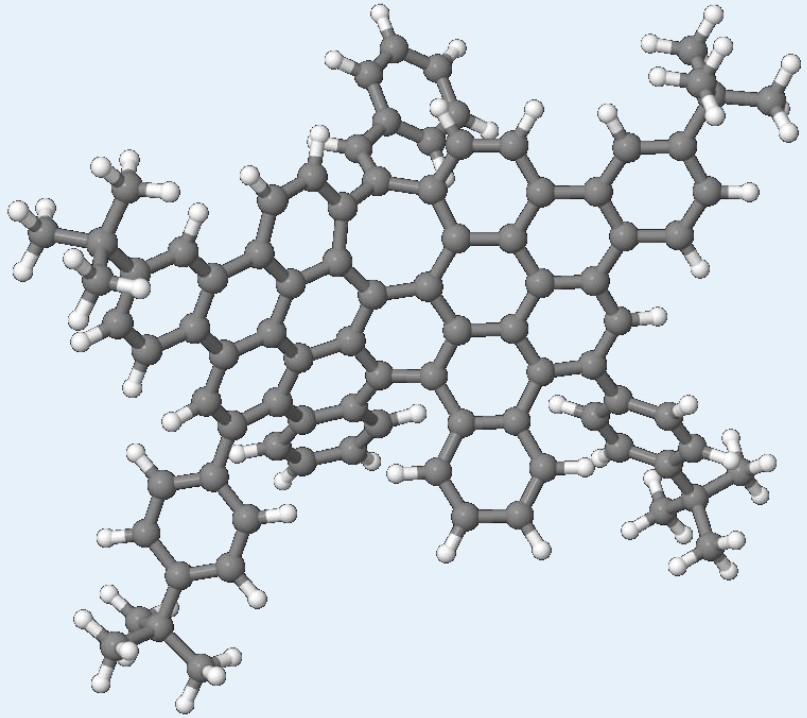


Final compound

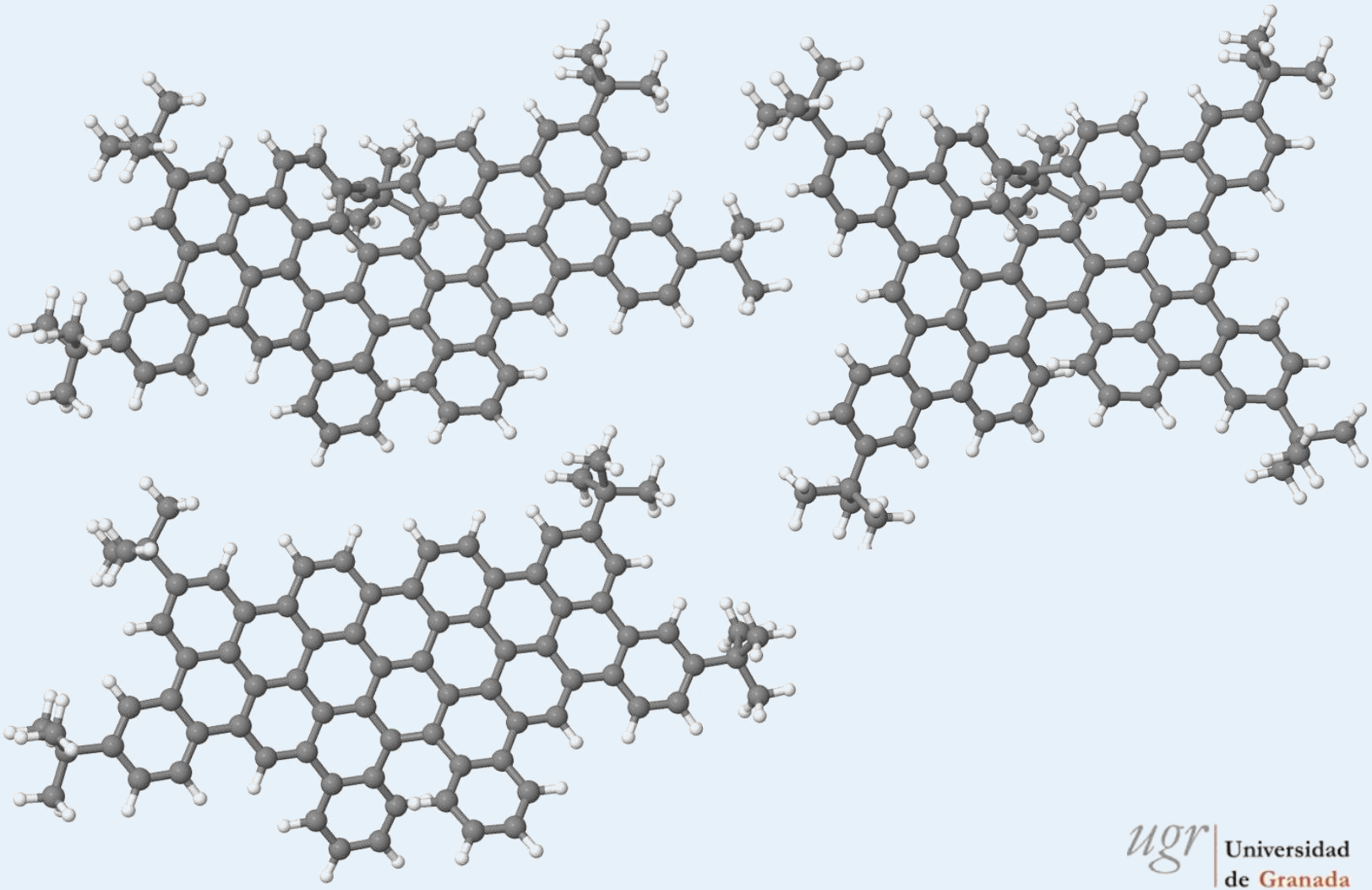


# What didn’t work

## Final compound



## Intermediate steps



# In preparation

- Theoretical/Experimental paper →systematic comparison with purely hexagonal compounds, different stacking sequencies, etc.

- Conductance with realistic contacts (Au, Pt)

# Acknowledgements


## Financial support:


**Ramón y Cajal Fellowship Program**

## Computational resources:



ugr | Universidad de Granada

# Thank you for your attention!

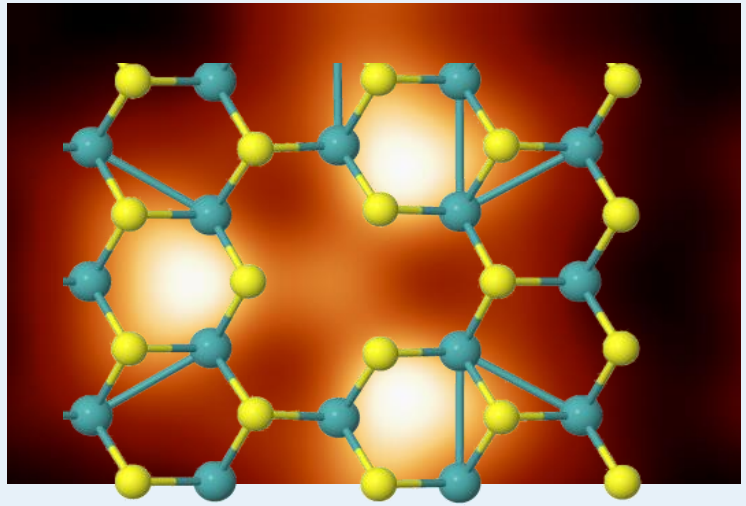
# Questions?

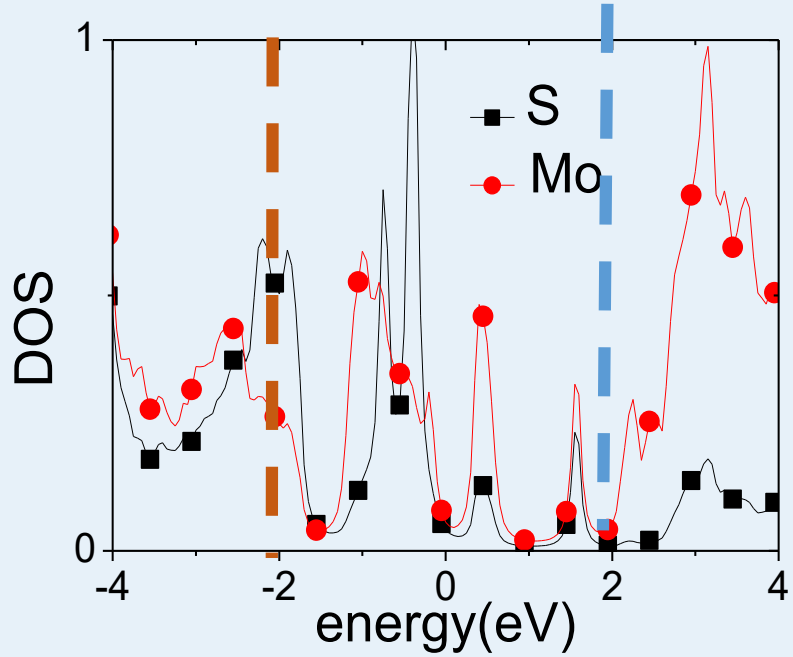
**Biel@ugr.es**

ugr | Universidad de Granada

# STM simulation of atomic defects in $MoS_2$

## Mo monovacancy:






- **Images @ +1.9 V** (empty states) → 3 protrusions in neighboring S atoms, not directly over the S atoms

  → *p*-character of the S dangling bond → opposite direction to the original bond

- **Images @ −1.9 V** (filled states) → dangling bond effect reduced

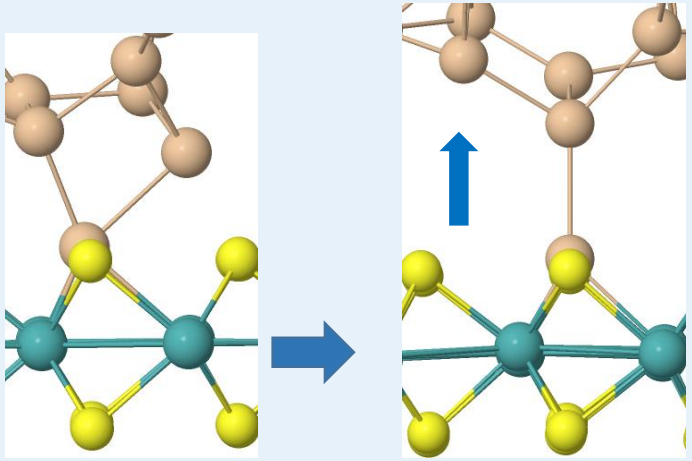
  → three spots relocated over the S atoms → **contrast change**

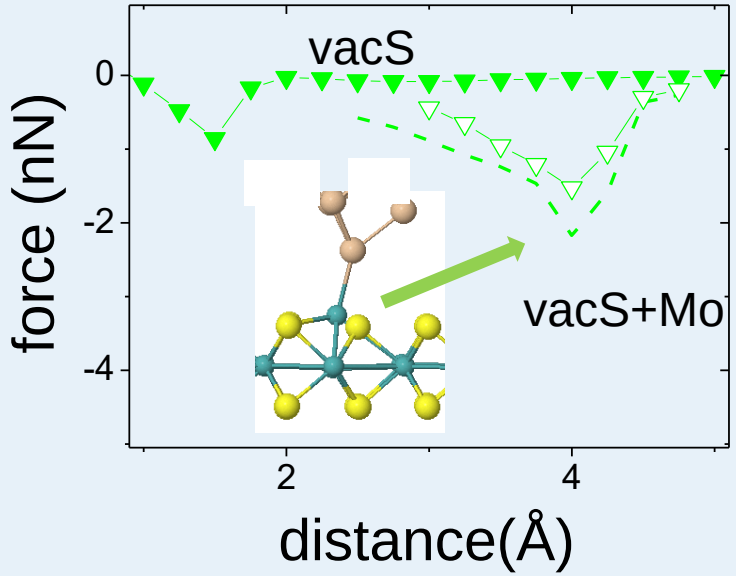
# AFM simulations of atomic defects in $MoS_2$

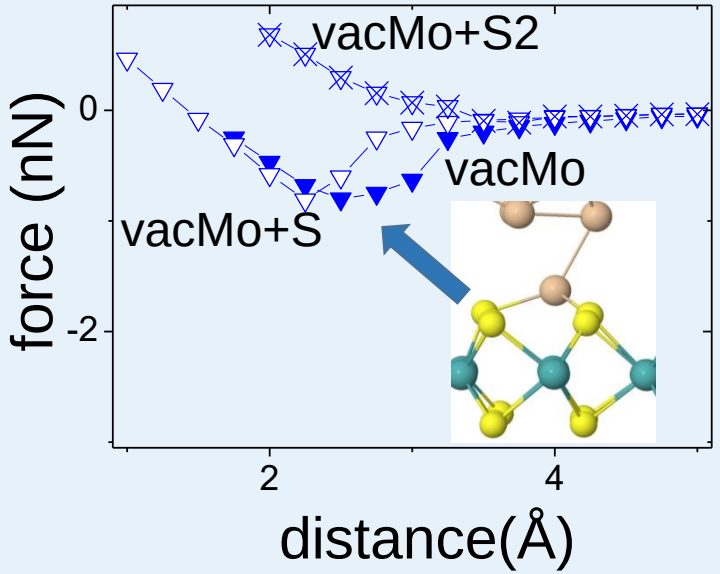
## Si tip:

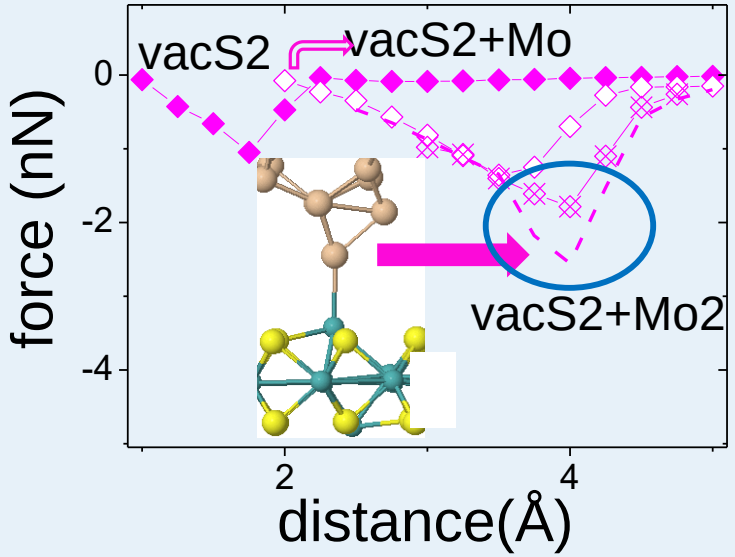
- Most attractive force
→ over a **2S+2Mo vacancy**

- **Capture of a S atom** in the S2-subs case

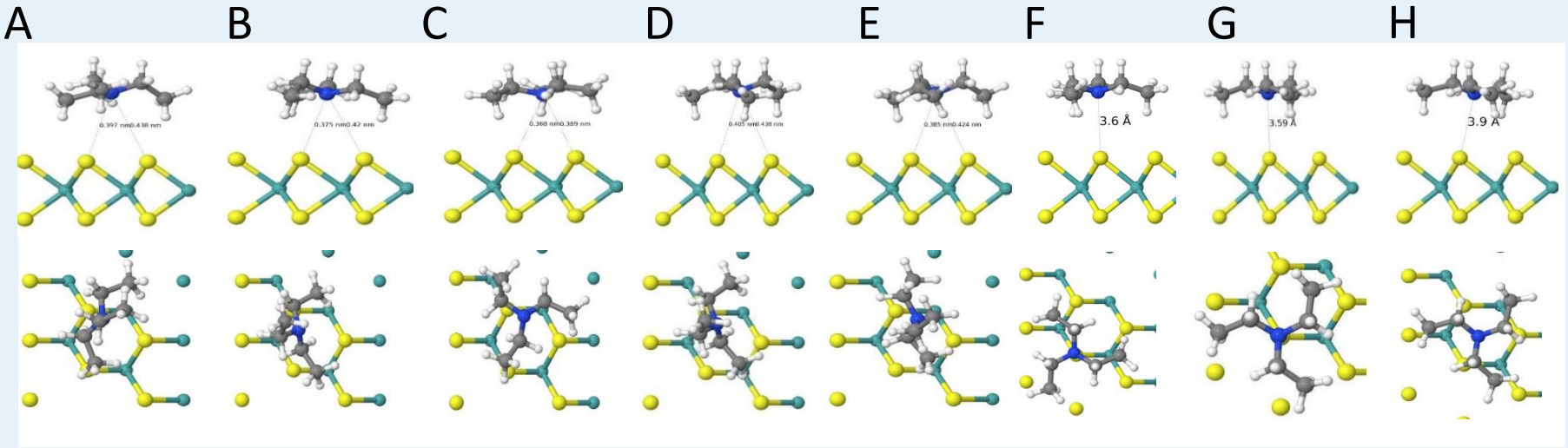




# Triethylamine



# Adsorption energies: TEA

**Adsorption energy (eV):** $E_{adsorption} = E_{moleculeMoS2} - E_{molecule} - E_{MoS2}$

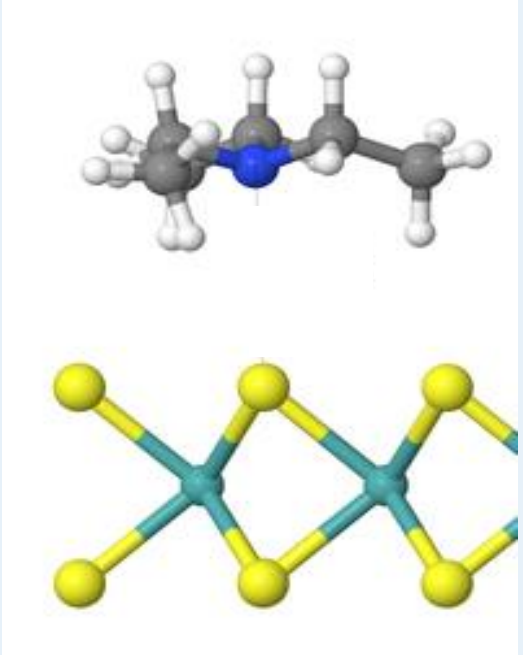
- Adsorptions energies for GGA:
  - Differences in total energy up to 0.16 eV

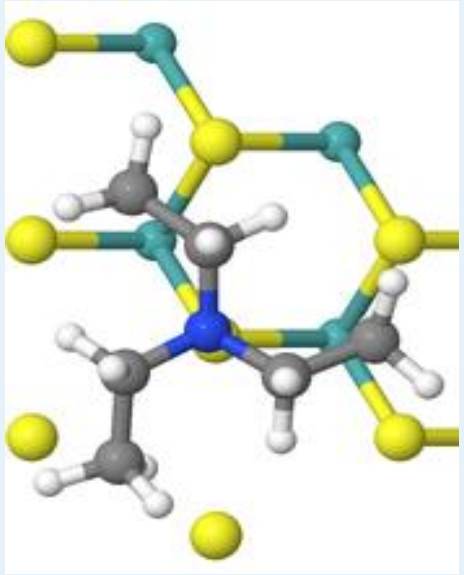
| position | F | G | D | H | B | K | A |
|---|---|---|---|---|---|---|---|
| $E_{ads}$ | 0.429 | 0.419 | 0.408 | 0.404 | 0.402 | 0.402 | 0.399 |

| position | C | J | E | L | M | I |
|---|---|---|---|---|---|---|
| $E_{ads}$ | 0.391 | 0.385 | 0.382 | 0.375 | 0.313 | 0.269 |

# Triethylamine

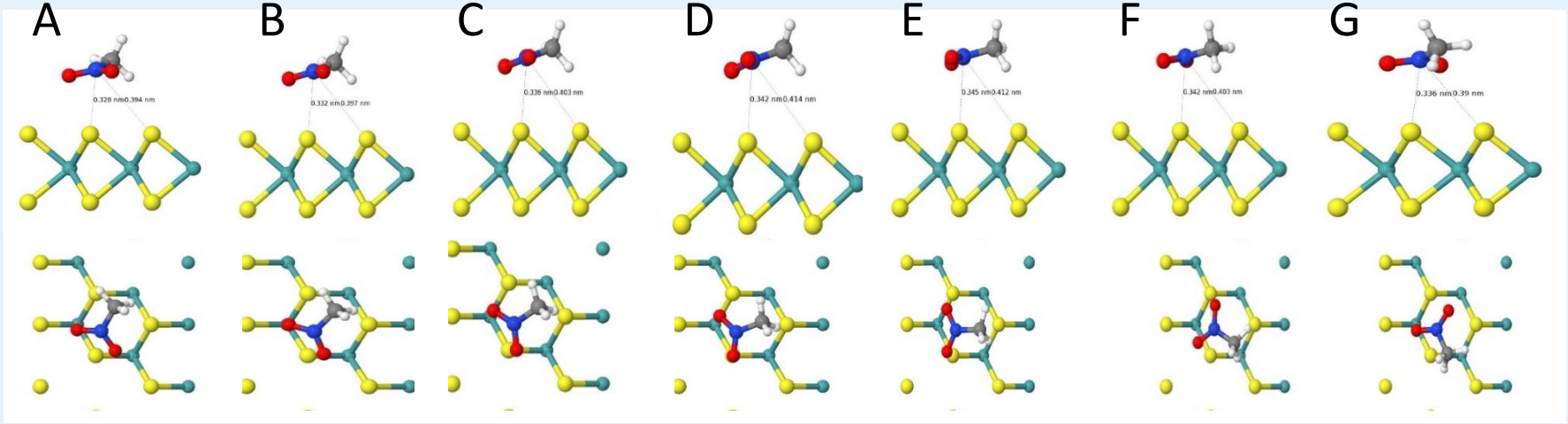
Most strongly absorbed:

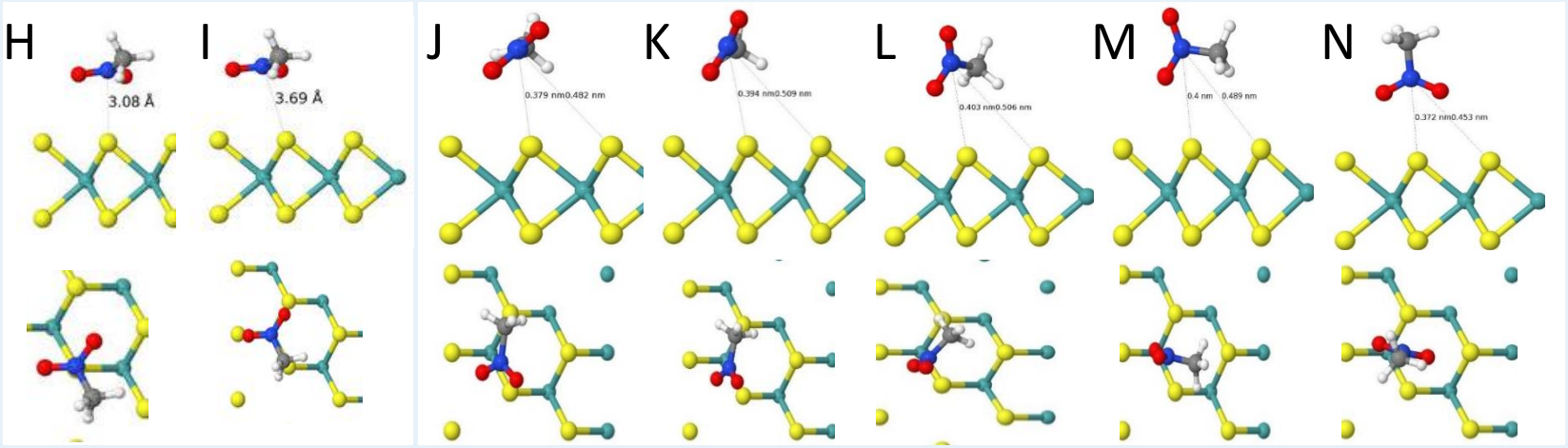




- vdW-KBM functional
  - Equilibrium distance: 3.17 Å, adsorption energy: 1.126 eV **?**

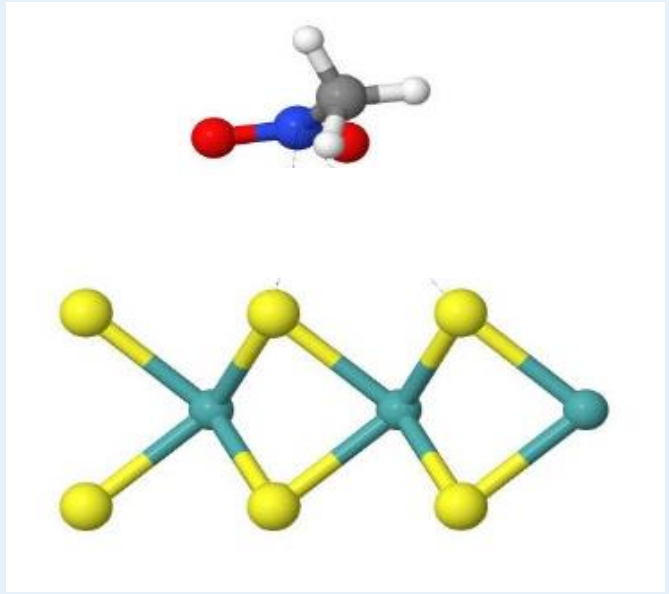
# Nitromethane

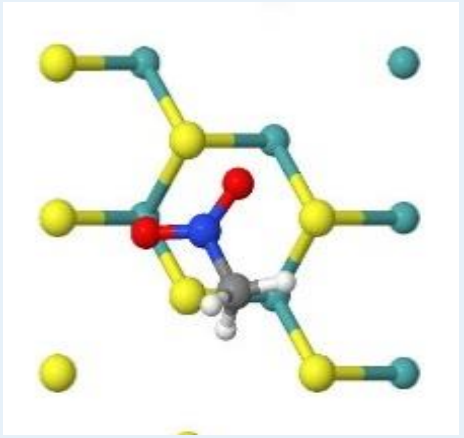


# Nitromethane

Most strongly absorbed:





- vdW-KBM functional
  - Equilibrium distance: 2.85 Å, adsorption energy: 0.79 eV ?

➔ **Basis too short/incomplete ?!**

# Adsorption energies: NM

**Adsorption energy (eV):** $E_{adsorption} = E_{moleculeMoS2} - E_{molecule} - E_{MoS2}$

- Adsorptions energies for GGA:
  - Differences in total energy up to 0.09 eV

| position | G | A | H | B | C | D | F |
|---|---|---|---|---|---|---|---|
| $E_{ads}$ | 0.392 | 0.384 | 0.380 | 0.375 | 0.37 | 0.357 | 0.351 |

| position | E | M | I | L | K | J | N |
|---|---|---|---|---|---|---|---|
| $E_{ads}$ | 0.329 | 0.324 | 0.322 | 0.311 | 0.31 | 0.308 | 0.302 |