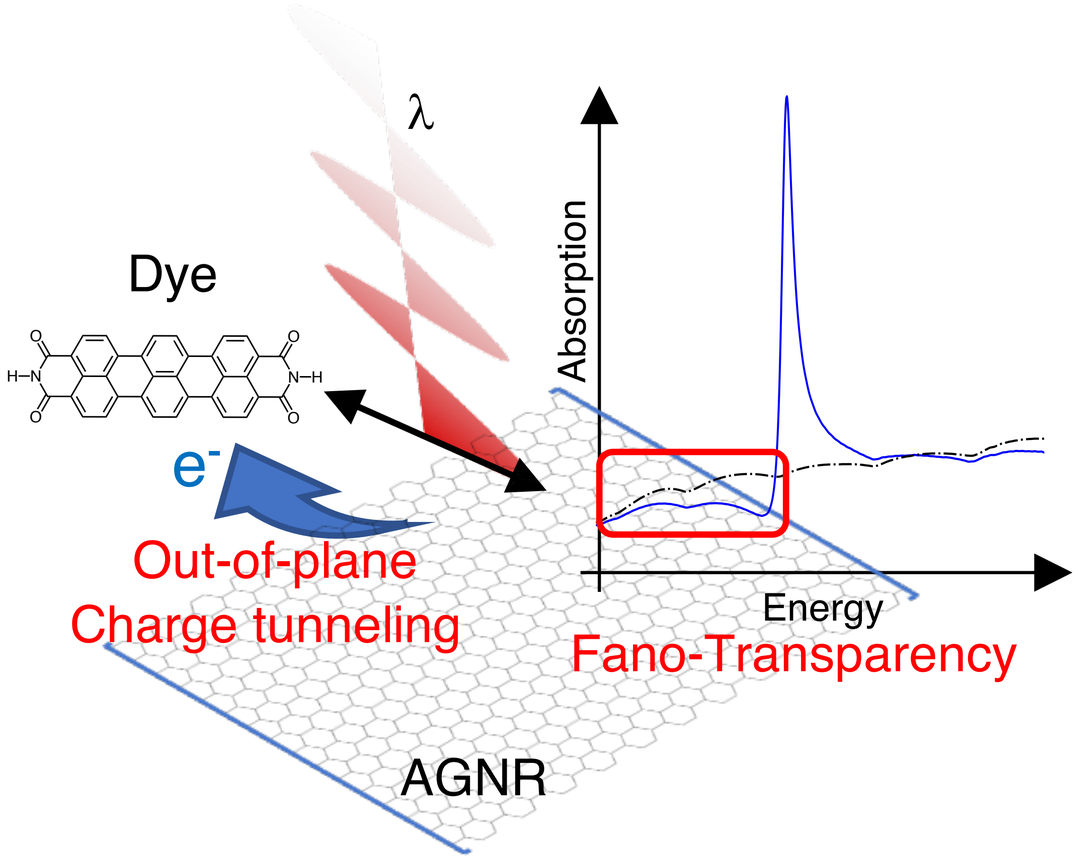
Real-time TD-DFTB simulations and modeling of Fano-induced transparency in molecular van der Waals Heterostructures



Universität Bremen

Bremen Center for BCCMS Computational Materials Science

DFTB

Carlos R. Lien-Medrano
February 2022

cmedrano@uni-bremen.de

VISTA

Virtual International Seminar on Theoretical Advancements

PhD

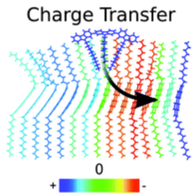
UNC Universidad Nacional de Córdoba

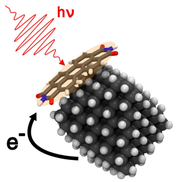
FCQ Facultad de Ciencias Químicas

Prof. Cristián Sánchez

PhD in Chemistry (2015 - 2019)

"Photodynamical simulations of materials for organic solar cells"

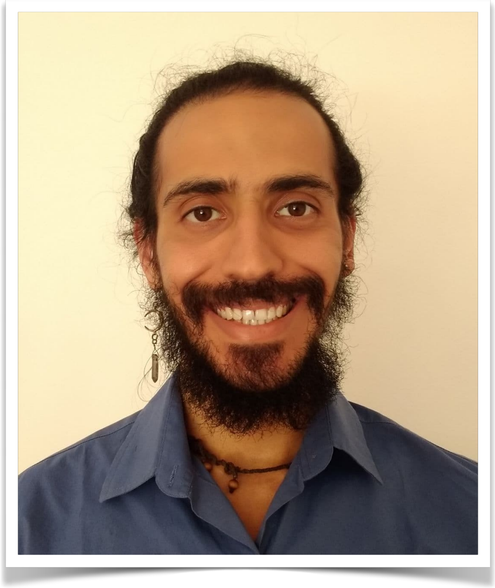




Argentina

Me

Carlos R. Lien-Medrano (Charly)



Postdoc

Universität Bremen

2020 - now

Bremen Center for BCCMS Computational Materials Science

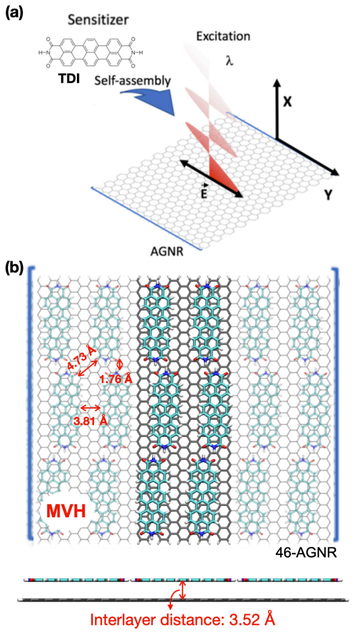
Prof. Thomas Frauenheim

Germany

DFTB+ package

My project

Molecular van der Waals Heterostructures (MVHs)



Fano Resonance and Incoherent interlayer excitons in molecular van der Waals heterostructures
arXiv:2108.07364v1 [cond-mat.mes-hall] 16 Aug 2021

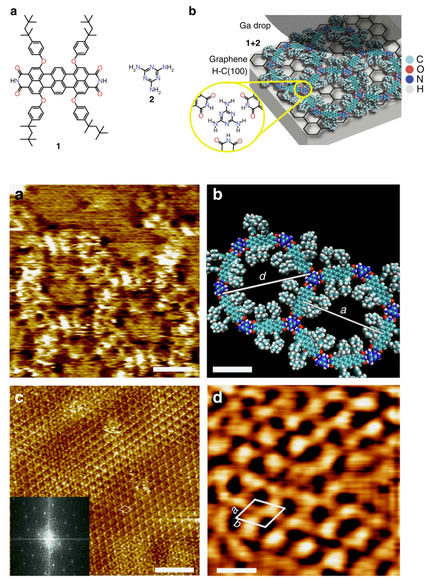


Figure 3 | STM images showing the assembly of 1 + 2 on graphite and graphene-passivated H-C(100) diamond substrates. (**a**) STM constant

Photoresponse of supramolecular self-assembled networks on graphene–diamond interfaces
Nat Commun **7,** 10700 (2016)

Theory

- Software development
- Simulations
- Explanations and predictions
- Optical and CT properties

Experiment

- Synthesis
- Self-assembly
- Characterization

Quantum dynamic simulations

Nanomorphology control of next OSCs

Theory

Prof. Thomas Frauenheim

Experiment

Prof. Carlos-Andrés Palma

Theory

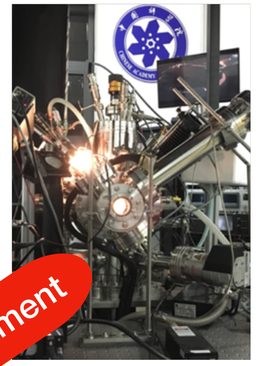
Prof. Cristián Sánchez

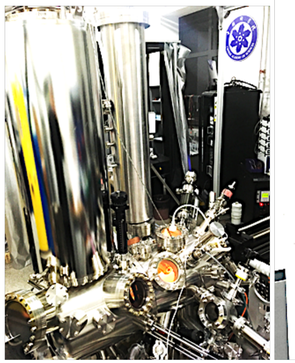
LT-AFM/STM-PEEM
H_2-plasma

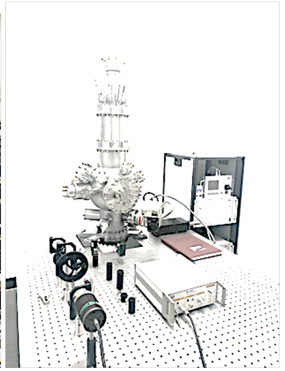
VT-AFM-Raman-
UV-Vis H_2-plasma

1K-AFM/STM
MS-TOF H-source

20 K Super-res.
PEEM-TOF



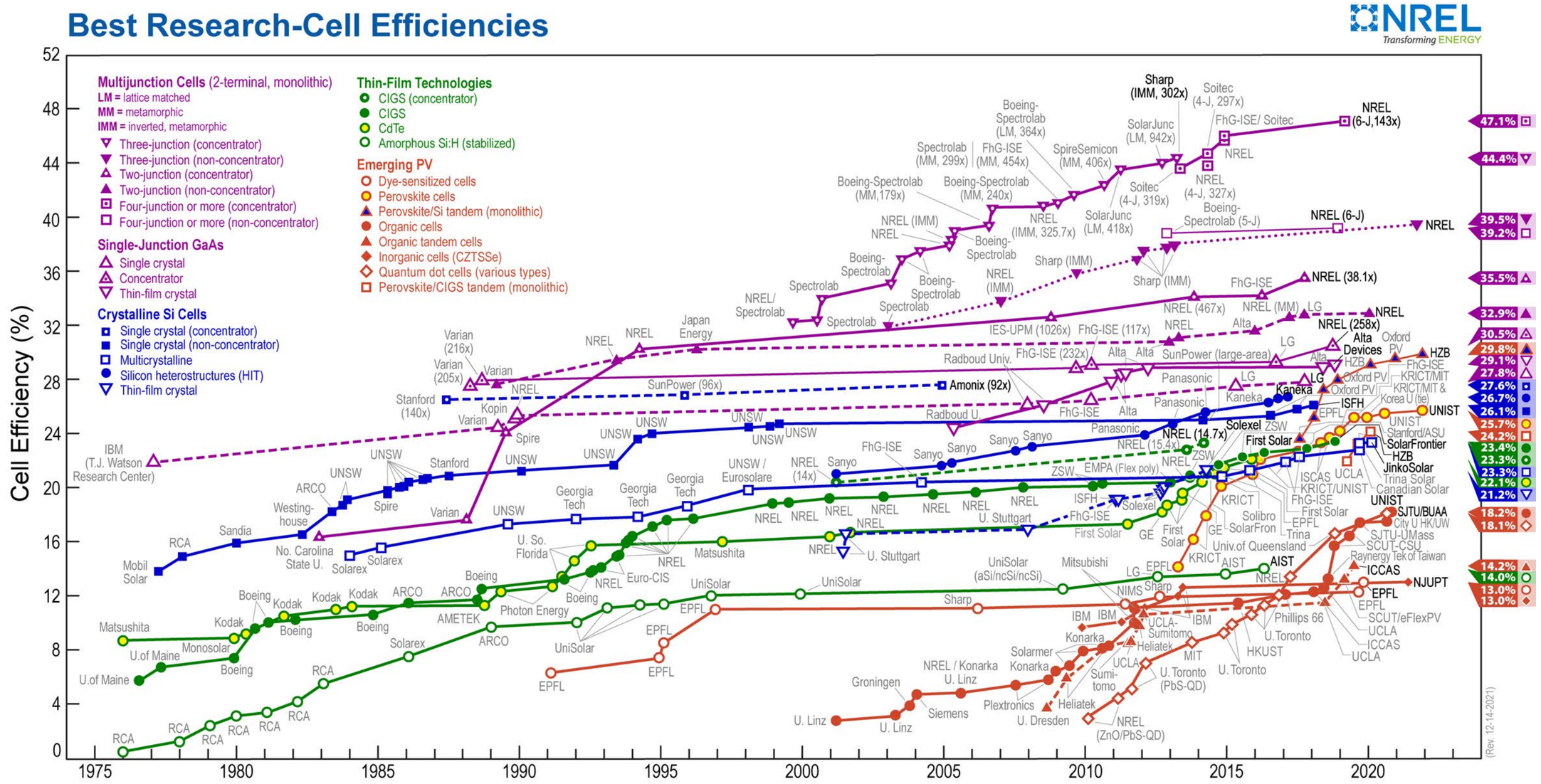




Equipment

1. Motivation

Organic Solar Cells (OSCs)



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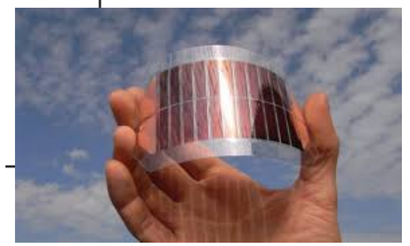
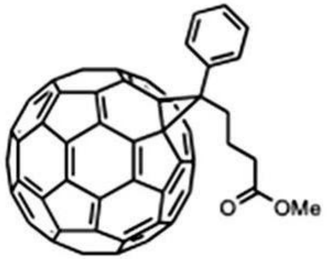


1. Motivation

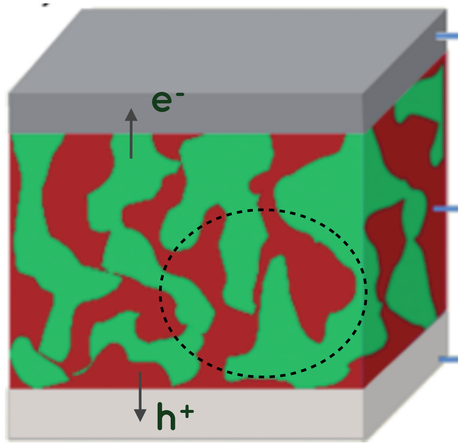
Organic Solar Cells (OSCs)

P3HT



PCBM

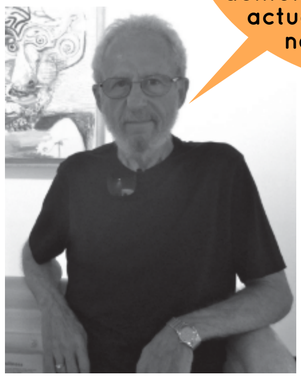
Bulk Heterojunction



Cathode

Donor-acceptor heterojunction

Anode (ITO)



"The fact that time after time with newly synthesized donors and fullerene acceptors, phase separation occurs on approximately the right length scale is fortunate, but remains a mystery..." "**...But no one has demonstrated a method to actually control the nanomorphology.**"[1]

Prof. Alan J. Heeger Nobel in Chemistry 2000 for his experimental development of conductive polymers.

1 Heeger, A. J., 25th anniversary article: Bulk heterojunction solar cells: Understanding the mechanism of operation. *Advanced Materials*, **2014**, *26*(1), 10–28.

1. Motivation

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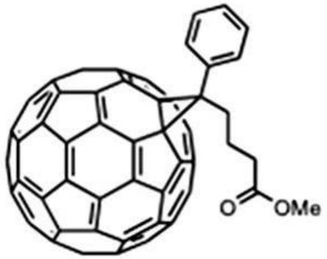
P3HT



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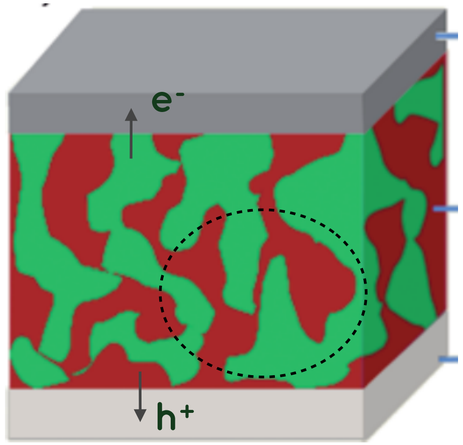

Cathode

Donor-acceptor heterojunction

Anode (ITO)

Spaghetti Bolognesa

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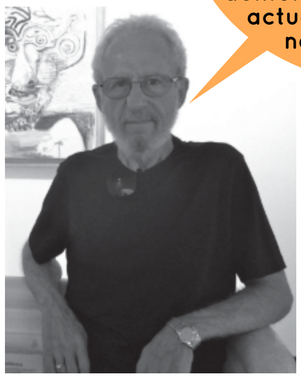

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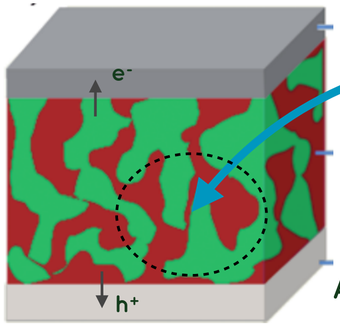
1. Motivation

New Paradigm for OSCs

Bulk Heterojunction



Cathode

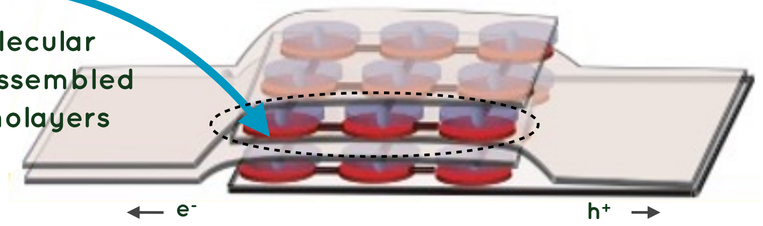
Active layer

Donor-acceptor heterojunction

Anode (ITO)

Molecular van der Waals Heterostructures (MVHs)

Molecular self-assembled monolayers



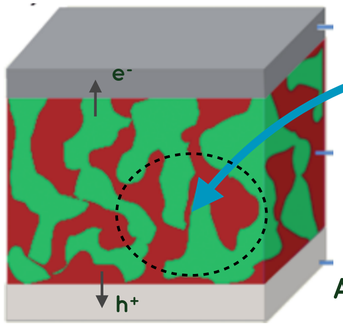
There is no method to control the nano morphology of the active layer

Spaghetti Bolognesa

1. Motivation

New Paradigm for OSCs

Bulk Heterojunction



Cathode

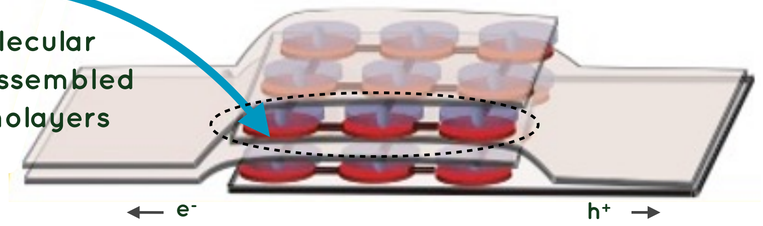
Active layer

Donor-acceptor heterojunction

Anode (ITO)

Molecular van der Waals Heterostructures (MVHs)

Molecular self-assembled monolayers



There is no method to control the nano morphology of the active layer

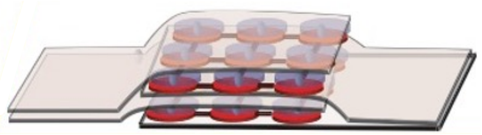
The nano morphology could be controlled with atomistic precision through the monolayers

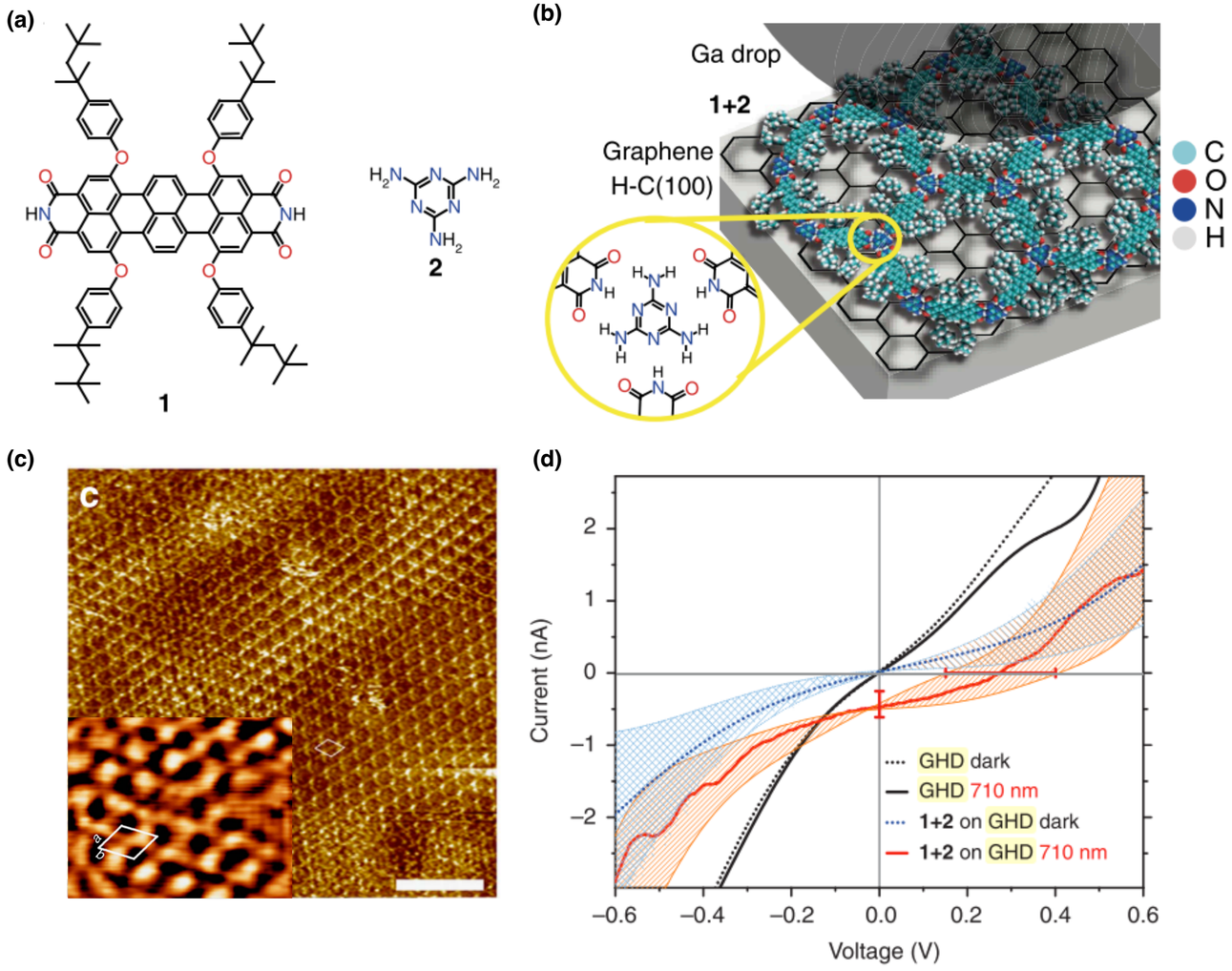
Spaghetti Bolognesa

Nano-Lasagna

1. Motivation How we simulate it? Computational Methods

First experimental demonstration MVHs in 2016





2 Wieghold, et al., Photoresponse of supramolecular self-assembled networks on graphene-diamond interfaces. *Nature Communications*, **2016**, 7, 1–8.

2. How we simulate it? Computational Methods

Real-Time Time-Dependent Density Functional Tight-Binding (RT-TD-DFTB)

- Self consisted tight binding Hamiltonian based on 2nd order expansion of the Kohn-Sham energy functional with respect to a reference electron density for the neutral atoms. We use the DFTB+ package.[1]

Excited-state description
Real time TD-DFTB[2]

Dirac delta perturbation

$$H(t) = H^0 + E_0\delta(t - t_0) \cdot \boldsymbol{\mu}(t)$$

Time propagation

$$\frac{\partial}{\partial t}\rho = -\frac{i}{\hbar}(S^{-1}H\rho - \rho H S^{-1})$$

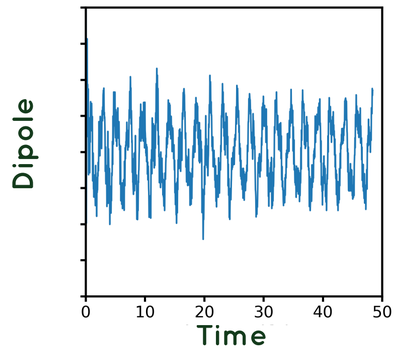
Dipole moment

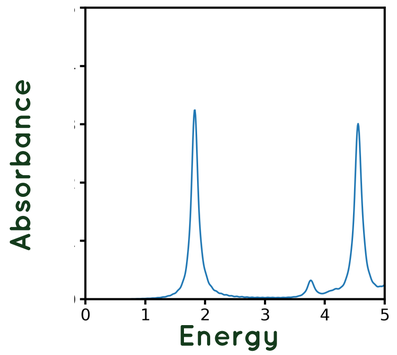
$$\boldsymbol{\mu}(t) = \mu_0 + \int_{-\infty}^{\infty} \boldsymbol{\alpha}(\tau)E(t - \tau)d\tau$$

FT

Polarizability tensor

$$\boldsymbol{\alpha}(\omega) = \frac{\boldsymbol{\mu}(\omega) - \mu_0}{E_0}$$





Explicit excitation during dynamics

3 Hourahine, B., et al., DFTB+, a software package for efficient approximate density functional theory based atomistic simulations. *The Journal of Chemical Physics* ***2020***, *152*(12), 124101.

4 F. P. Bonafé, et al., A Real-Time Time-Dependent Density Functional Tight-Binding Implementation for Semiclassical Excited State Electron-Nuclear Dynamics and Pump–Probe Spectroscopy Simulations, *Journal of Chemical Theory and Computation* **2020**,16, 4454.

3. Simulation of a model MVH

Structure based on 1D Graphene Nanorribon

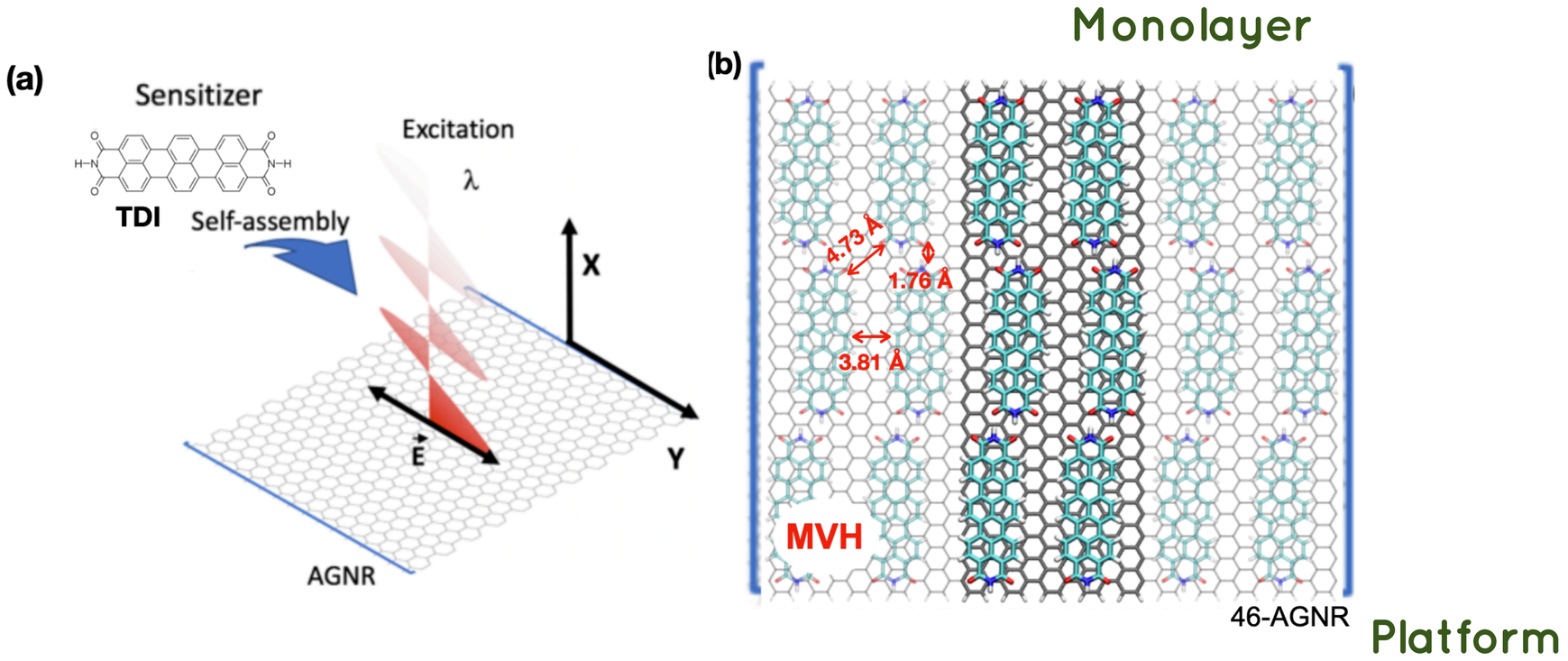


Fig 3: Structure of the simulated MVH and simulated absorption spectra

- We model the MVH as a monolayer of TDI on the top of a 46 atom-wide armchair graphene nano ribbon (46-AGNR, platform).

3. Simulation of a model MVH

Absorption Spectrum

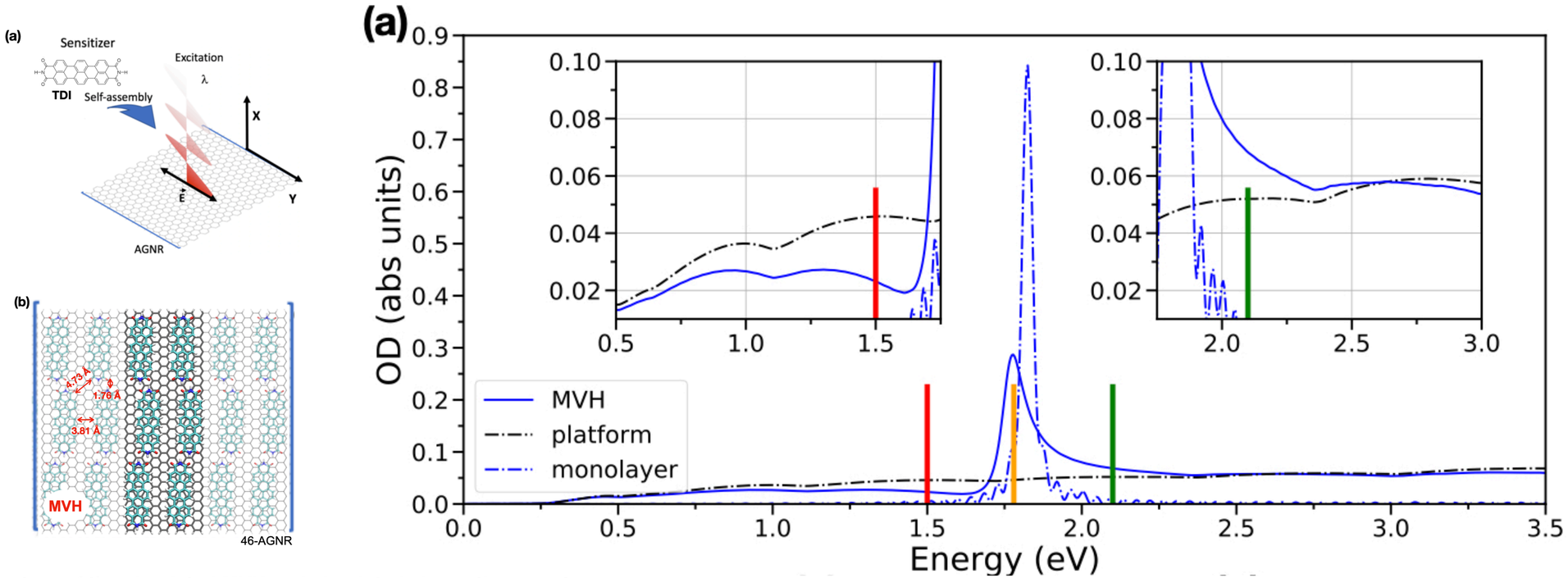
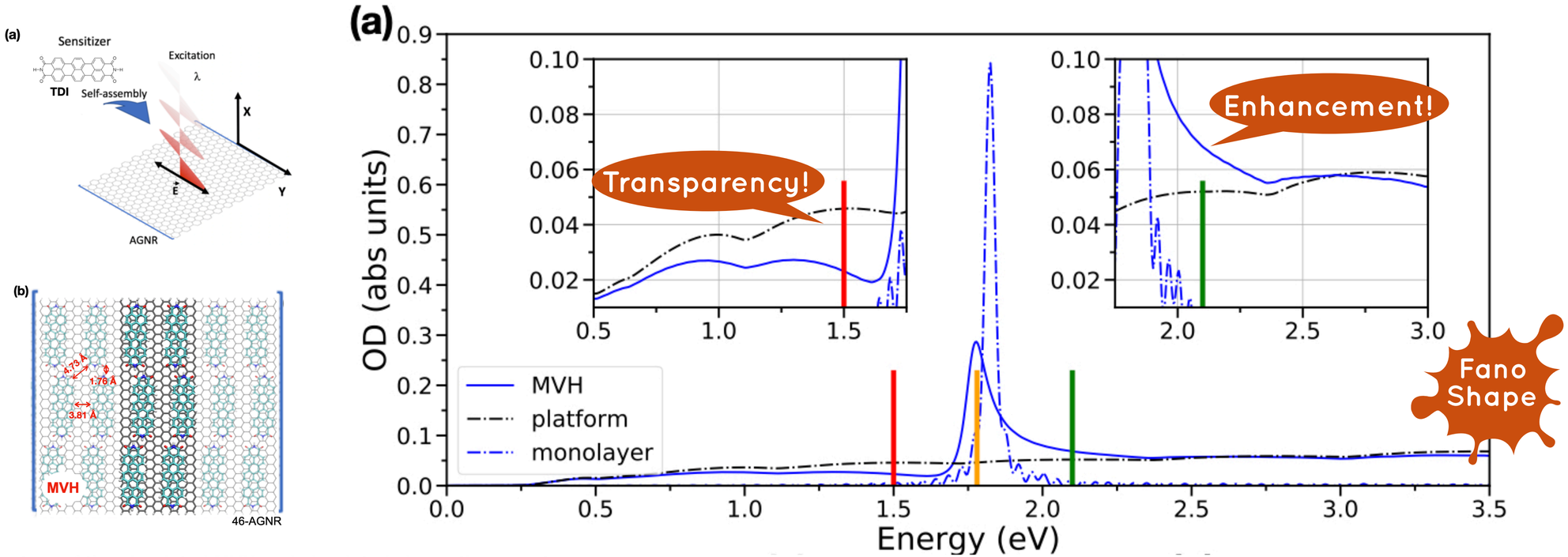


Fig 3: Structure of the simulated MVH and simulated absorption spectra

- The calculated spectra in Fig. **reveal absorption suppression or enhancement upon adsorption of the sensitizers** around the dye energy excitation with a characteristic Fano shape, when compared to the sum of the absorption of the separate components, i.e. the platform (ribbon) and the dye monolayer.[4]

3. Simulation of a model MVH

Absorption Spectrum



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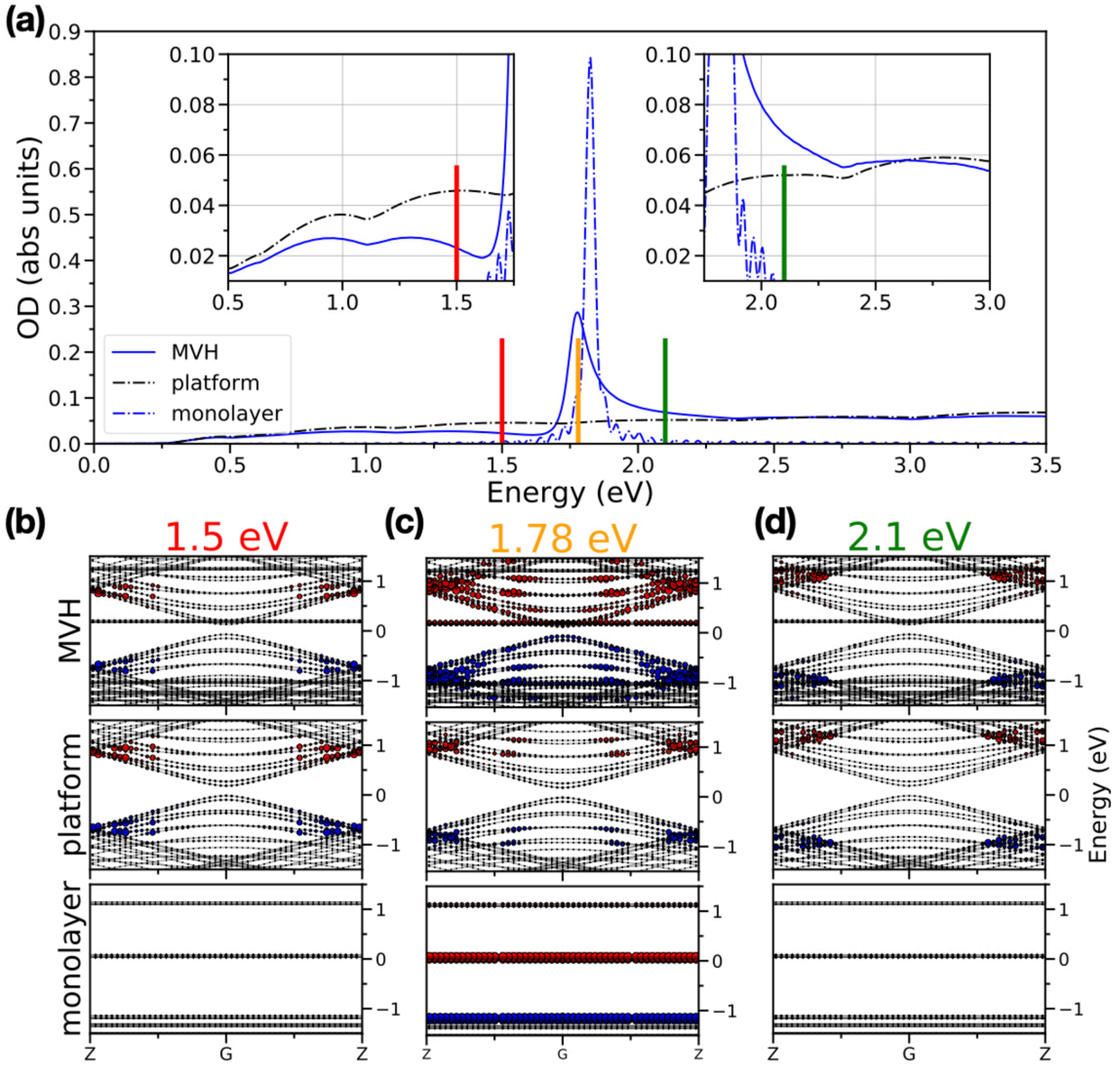
3. Simulation of a model MVH

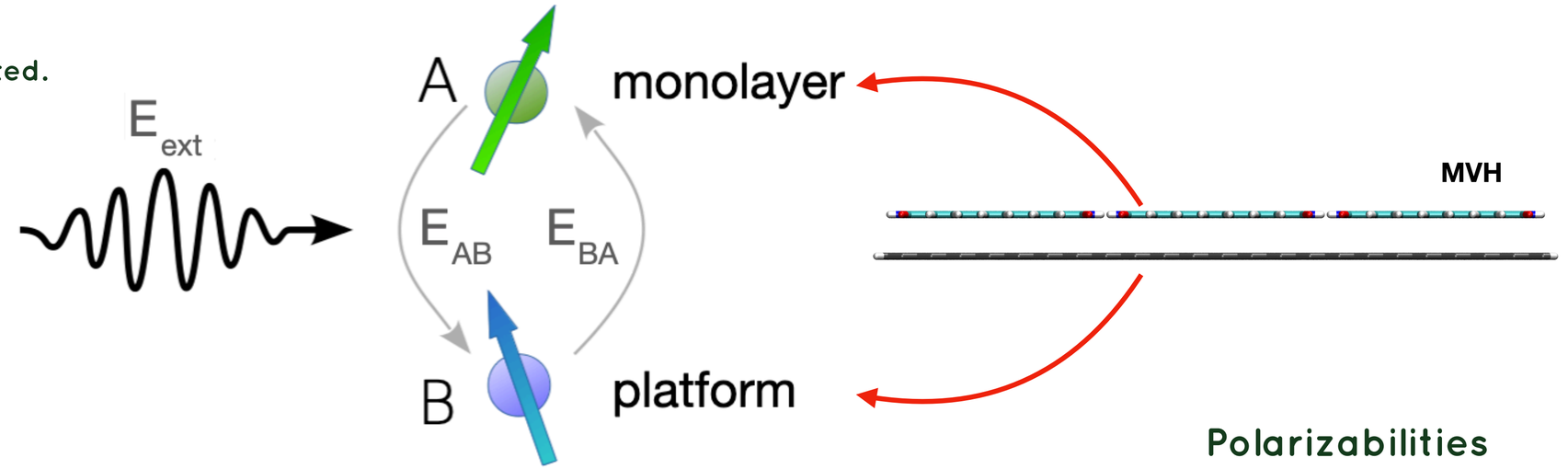
Absorption Spectrum and band population analysis



4. Which is the origin of the Fano Resonance?

Adapted Gersten-Nitzan model

- Adapted Gersten-Nitzan (aGN) model to calculate the polarizability.
- Two point dipoles, coupled to the external field.
- Image field effects are neglected.



Polarizabilities

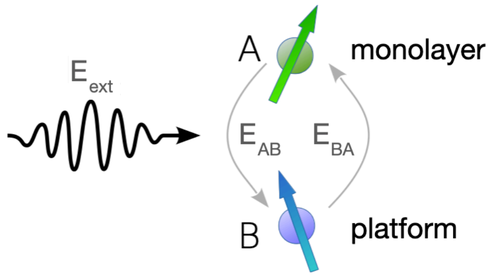
$$\alpha^{\mathrm{eff},A} = \alpha^{A}(\omega) + \alpha^{A}(\omega) D \alpha^{B}(\omega)$$

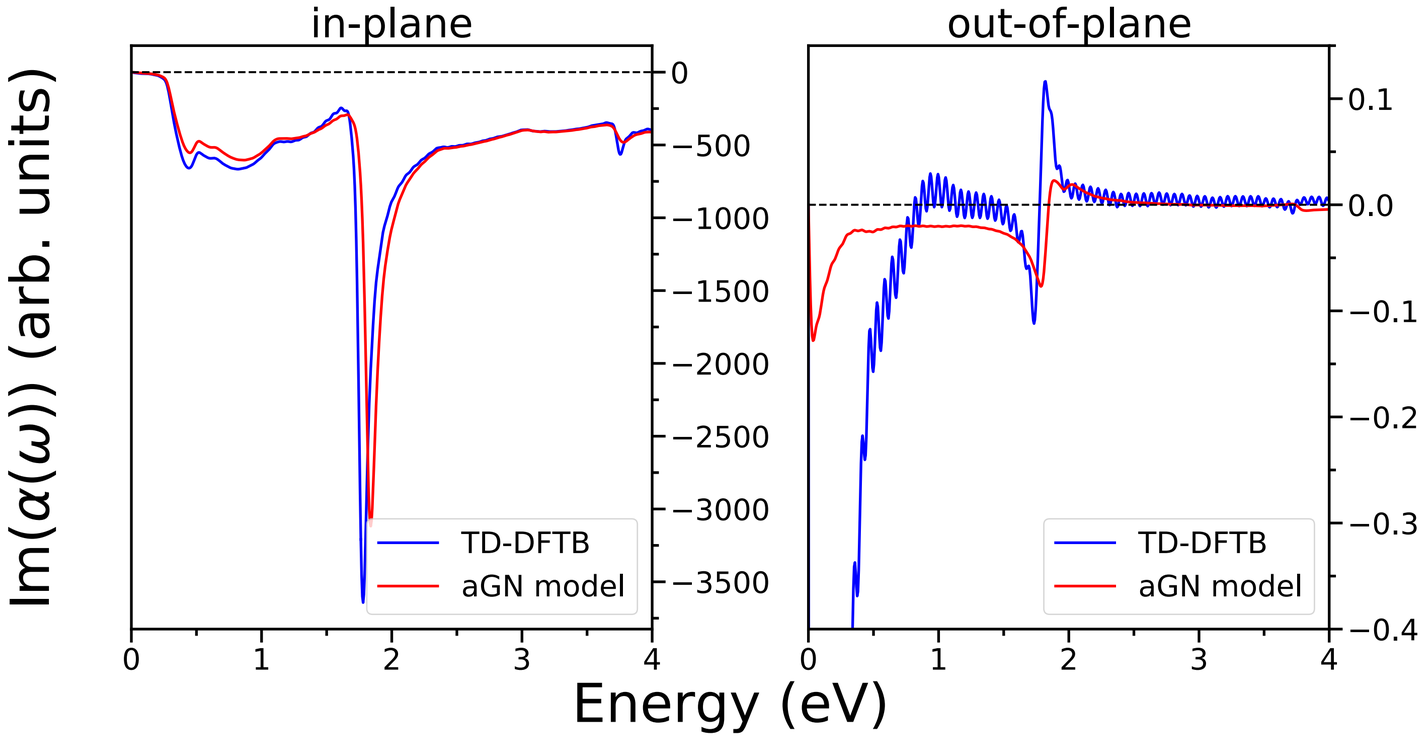
$$\alpha^{\mathrm{eff},B} = \alpha^{B}(\omega) + \alpha^{B}(\omega) D \alpha^{A}(\omega)$$

$$\alpha_{T}^{eff} = \alpha^{\mathrm{eff},A} + \alpha^{\mathrm{eff},B}, \; D = \frac{1}{4\pi\epsilon_0 R_{AB}^{3}} \begin{bmatrix} 2 & 0 \\ 0 & 1 \end{bmatrix}$$

4. Which is the origin of the Fano Resonance?

Polarizabilities analysis





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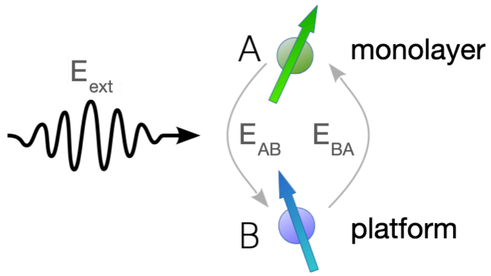
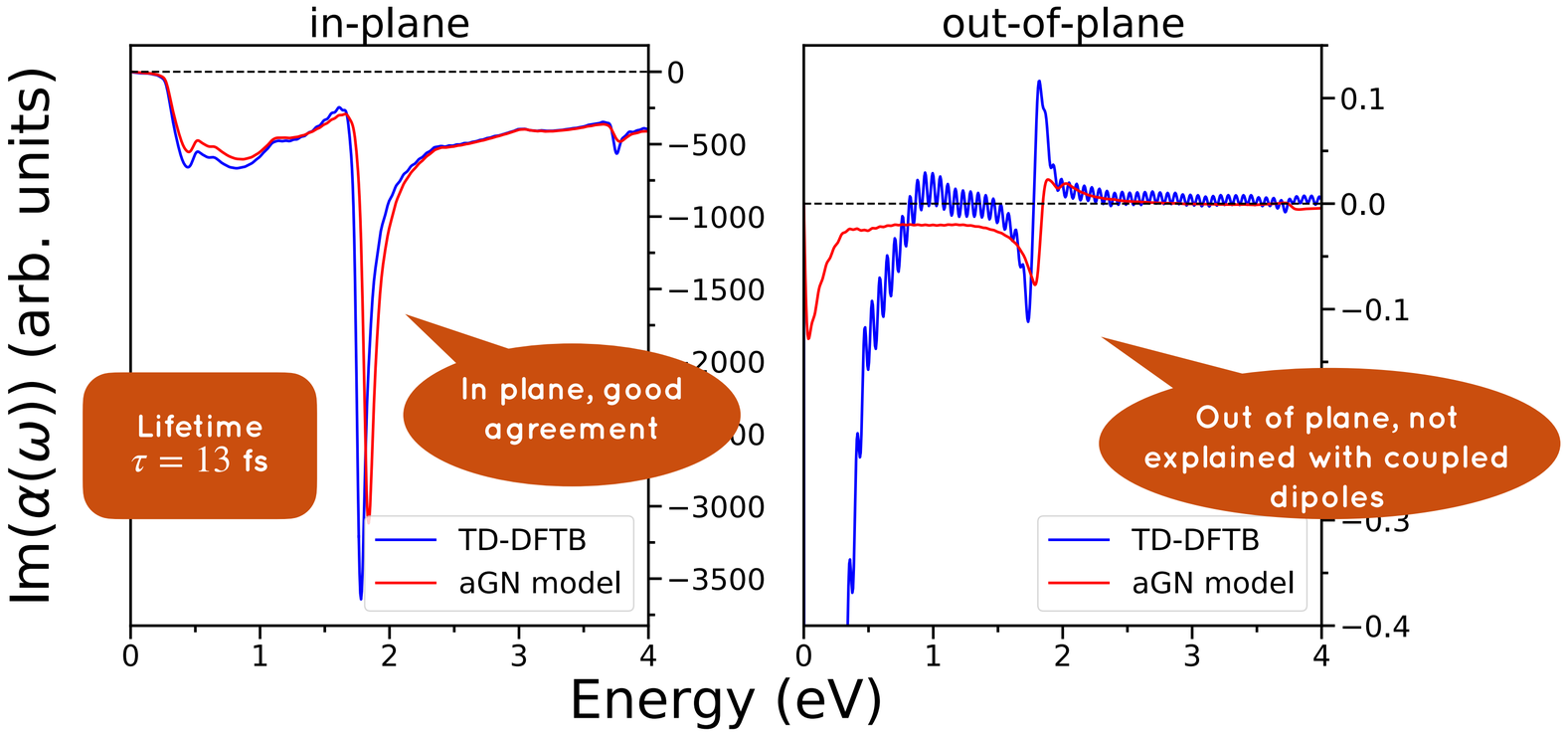


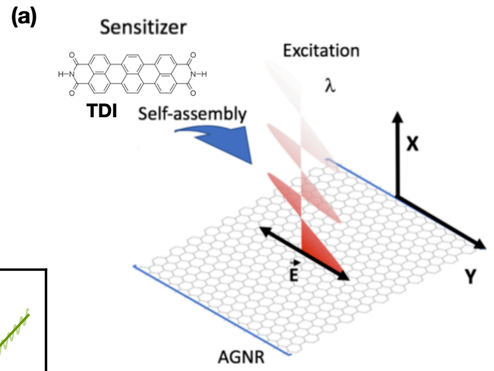


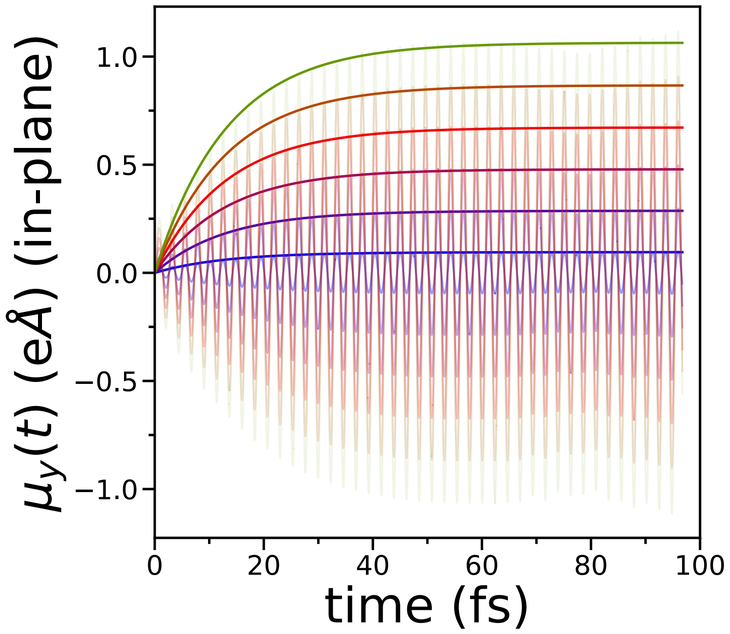
- in-plane polarizability agrees quantitatively with the TD-DFTB one

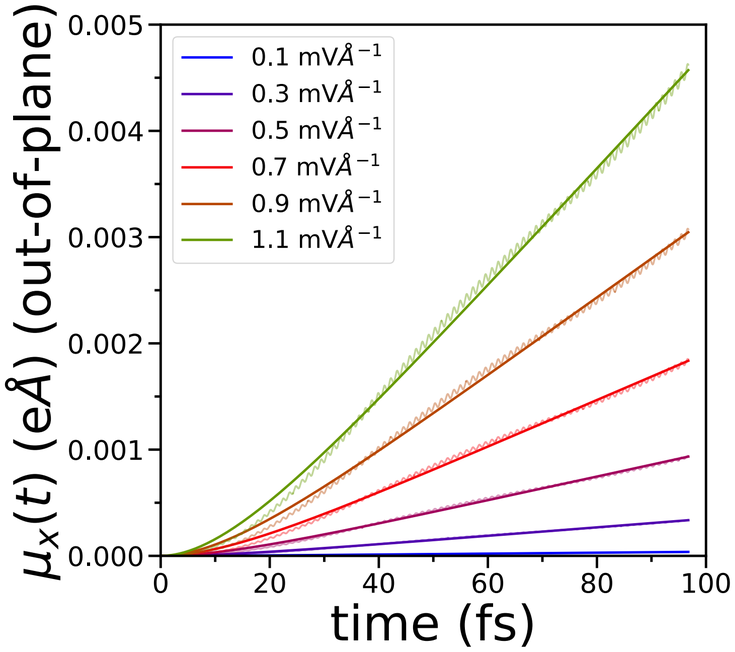
- **The transparency (or enhancement) arises fundamentally from a dipolar coupling between the systems.**
- The out-of-plane polarizability calculated from the aGN model grees only qualitatively with the TD-DFTB one. **This is an indication of a new relaxation channel.**[4]

5. What is happening out-of-plane?

Dynamic analysis of dipole moments







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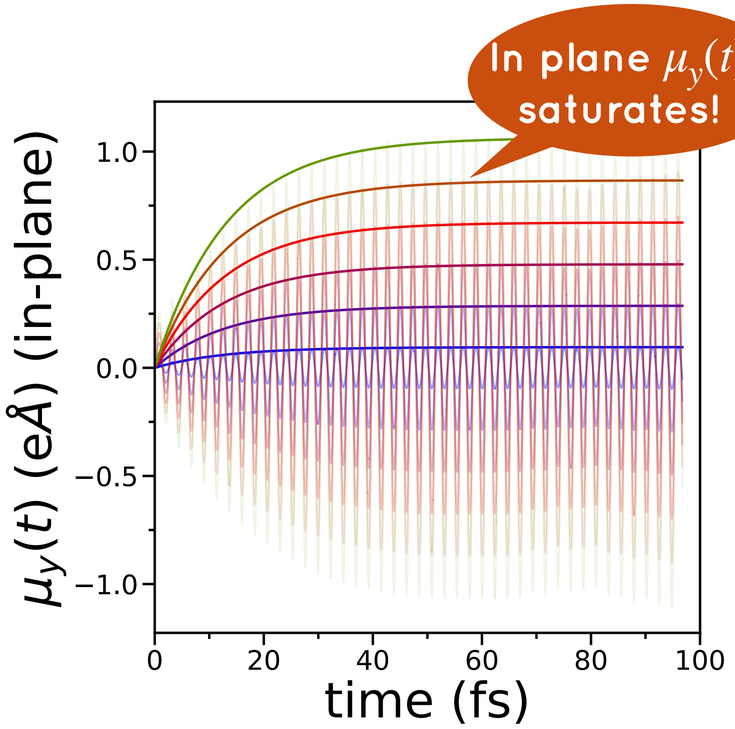

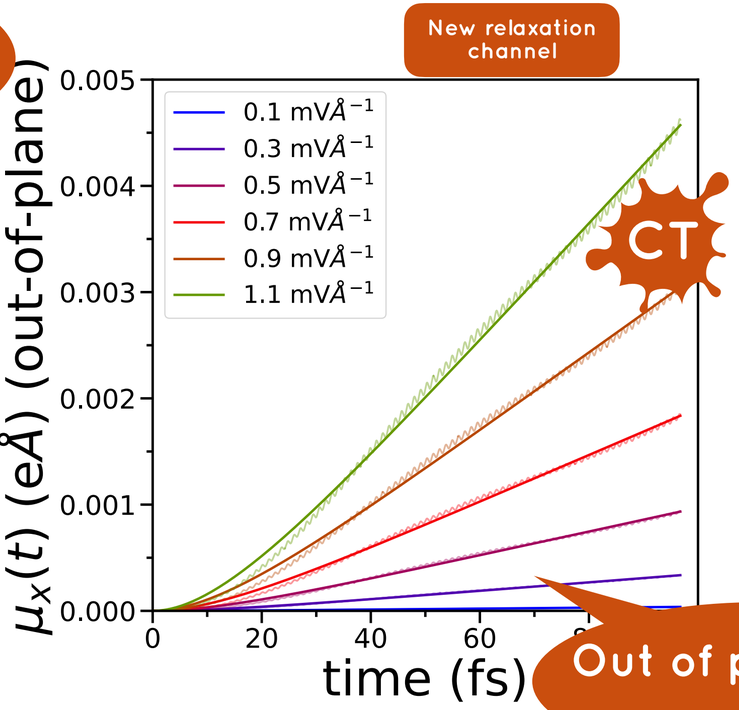

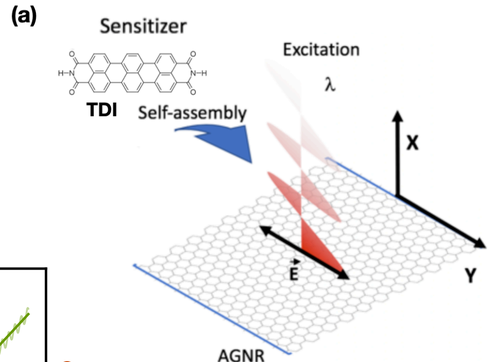

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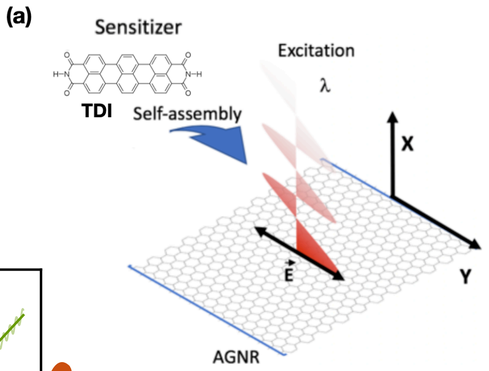
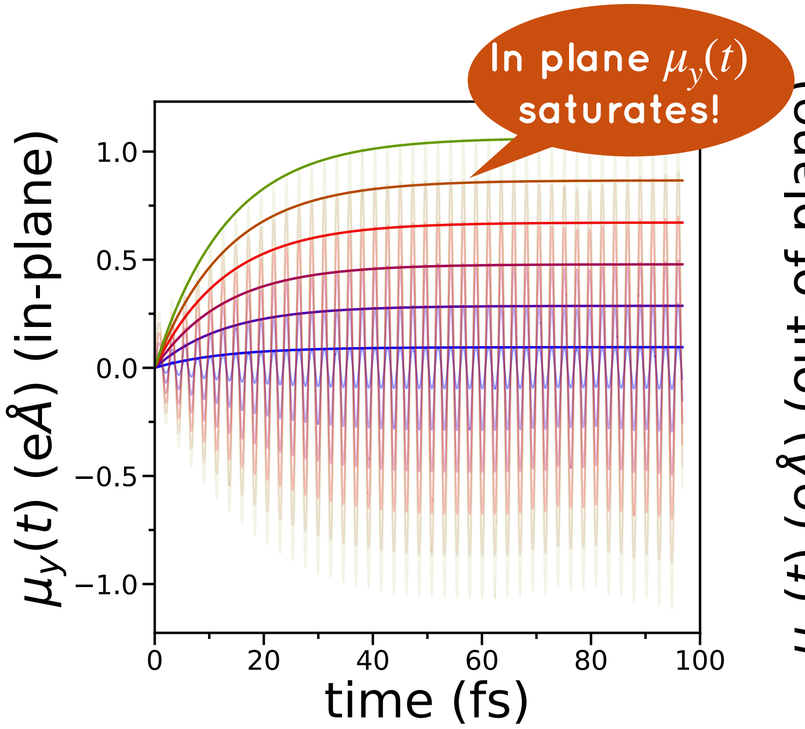
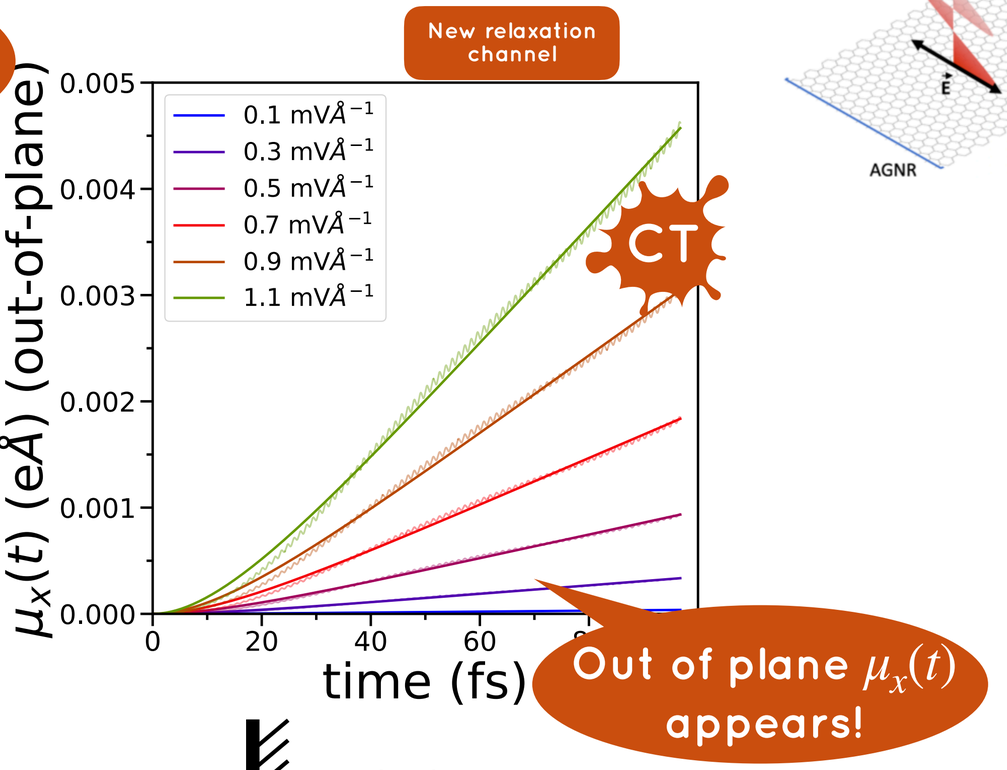
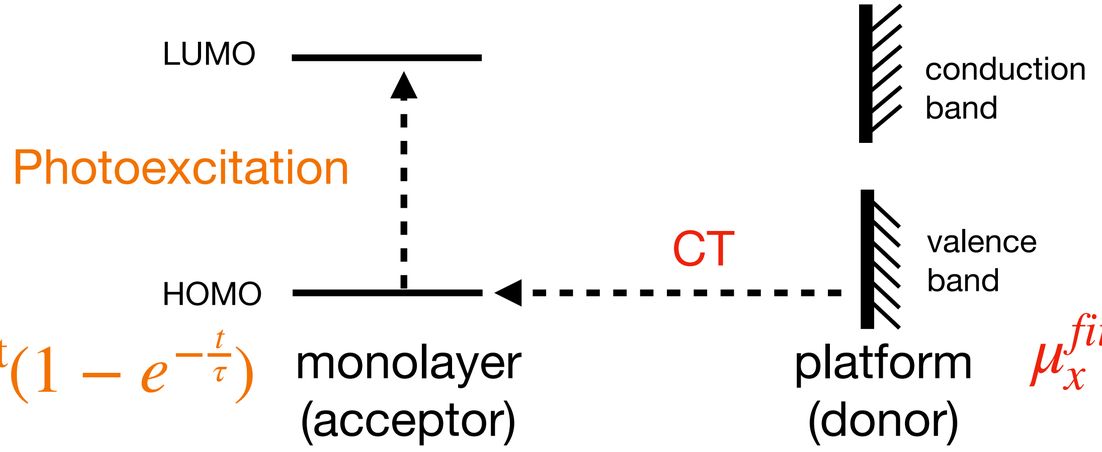






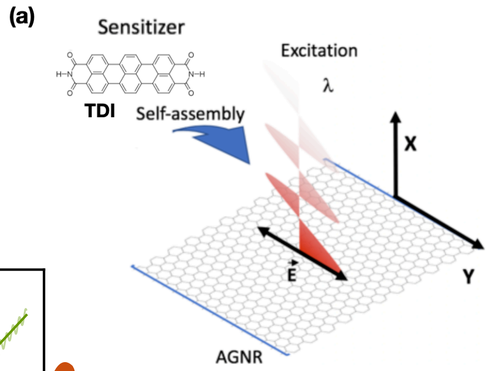


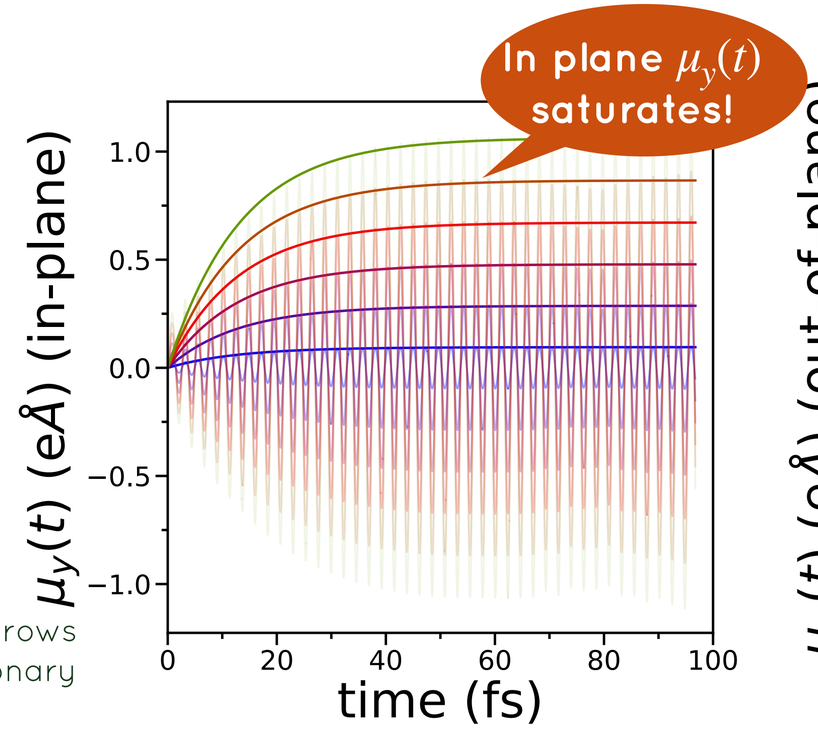
$$\mu_y^{fit} = \mu_y^{\mathrm{sat}}(1 - e^{-\frac{t}{\tau}})$$

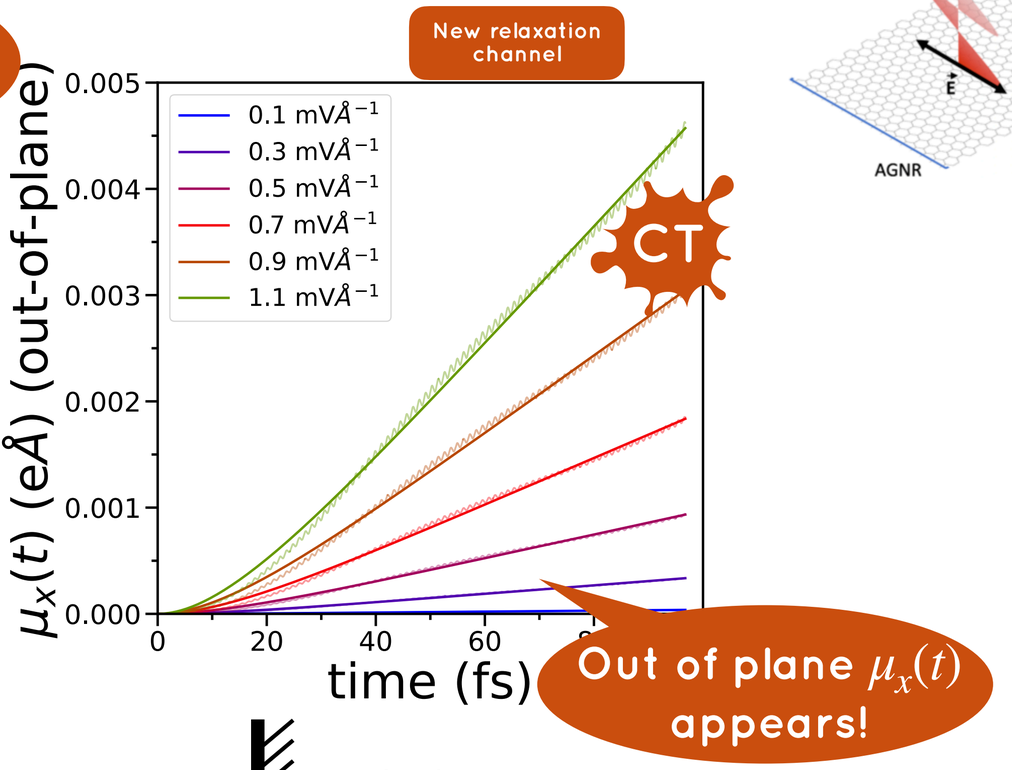
$$\mu_x^{fit} = \gamma\mu_y^{\mathrm{sat}}(t - \tau(1 - e^{-\frac{t}{\tau}}))$$

5. What is happening out-of-plane?

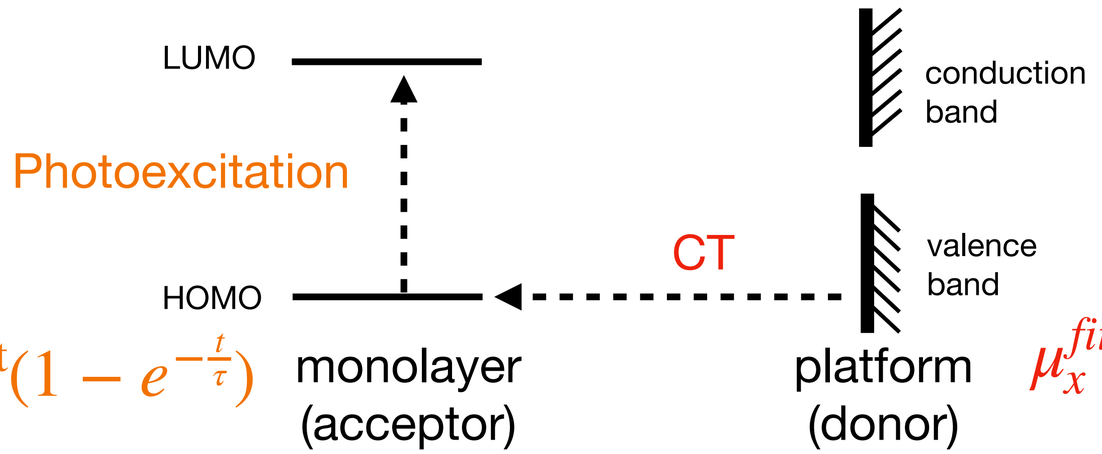
Dynamic analysis of dipole moments







- The in-plane dipole moment grows linearly and then reaches a stationary state (saturation μ_y^{sat}).
- The saturation is an evidence of a **secondary process after the photoexcitation of dye molecules**.
- The cause decay of the excitation is **interlayer charge transfer (CT)** from the platform to the monolayer.



$$\mu_y^{fit} = \mu_y^{\mathrm{sat}}(1 - e^{-\frac{t}{\tau}})$$

$$\mu_x^{fit} = \gamma\mu_y^{\mathrm{sat}}(t - \tau(1 - e^{-\frac{t}{\tau}}))$$

6. Conclusions

- We have found evidence of **induced transparency and opacity** of the substrate arising from a **Fano spectral shape** upon formation of the MVH architecture.
- This is a **general feature of these types of systems**, and can already be captured by a simple module of electrostatically interacting dipoles.
- The model can not reproduce the out-of-plane polarisability. **New decay channel**.
- Our time-resolved carrier dynamics simulations suggest that such a process could be **understood as the formation of an incoherent interlayer exciton**.
- The **Fano profile contains information** about the **polarizability**, **molecular geometry** at interfaces and **distance** between molecules and substrate, so that optical studies could complement XPS and diffraction methods for interfacial structure elucidation.
- These results open a path for improved design of on-demand, wide-band-absorbing modular multilayer organic PV devices and for engineering new atomic-scale metamaterials with highly tunable optical properties.

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Fano Resonance and Incoherent Interlayer Excitons in Molecular van der Waals Heterostructures

Carlos R. Lien-Medrano, Franco P. Bonafé, Chi Yung Yam, Carlos-Andres Palma,* Cristián G. Sánchez,* and Thomas Frauenheim

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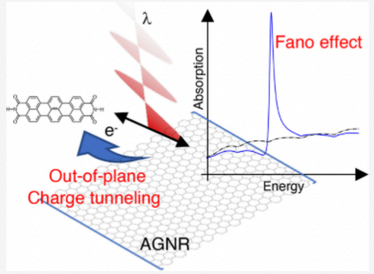
ABSTRACT: Complex van der Waals heterostructures from layered molecular stacks are promising optoelectronic materials offering the means to efficient, modular charge separation and collection layers. The effect of stacking in the electrodynamics of such hybrid organic−inorganic two-dimensional materials remains largely unexplored, whereby molecular scale engineering could lead to advanced optical phenomena. For instance, tunable Fano engineering could make possible on-demand transparent conducting layers or photoactive elements, and passive cooling. We employ an adapted Gersten−Nitzan model and real time time-dependent density functional tight-binding to study the optoelectronics of self-assembled monolayers on graphene nanoribbons. We find Fano resonances that cause electromagnetic induced opacity and transparency and reveal an additional incoherent process leading to interlayer exciton formation with a characteristic charge transfer rate. These results showcase hybrid van der Waals heterostructures as paradigmatic 2D optoelectronic stacks, featuring tunable Fano optics and unconventional charge transfer channels.



KEYWORDS: *Interlayer excitons, molecular vdW heterostructures, time-dependent density functional tight-binding, Fano resonance, 2D materials*

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