nanoGe Fall Meeting
Torremolinos-Spain
October 22-26, 2018

nanoGe

« Effect of electronically inert organic spacers on the optoelectronic properties of 2D hybrid perovskites »

Nadège Marchal

University of Mons
Laboratory for Chemistry of Novel Materials

Supervisor: Prof. David Beljonne,
Co-supervisor: Dr. Claudio Quarti

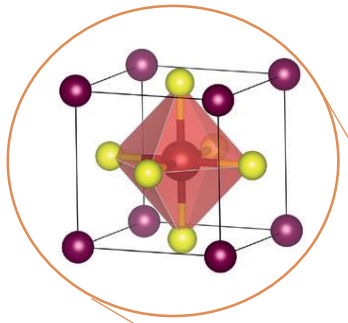
UMONS Université de Mons

Faculté des Sciences

CMN

materials
UMONS RESEARCH INSTITUTE FOR MATERIALS SCIENCE AND ENGINEERING

Table of contents



Introduction

Methodology:
(TD-)DFT

Results

Table of contents

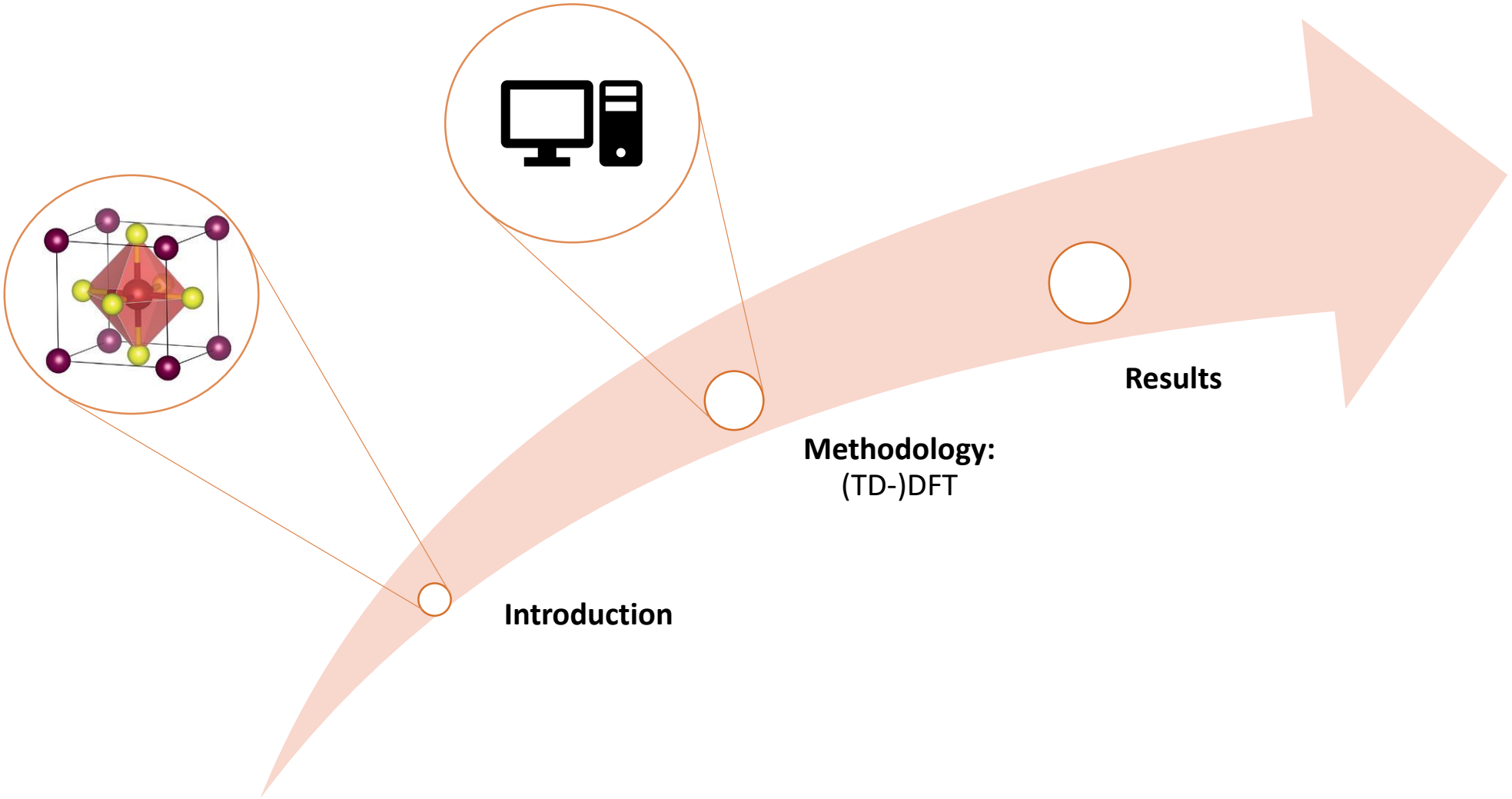
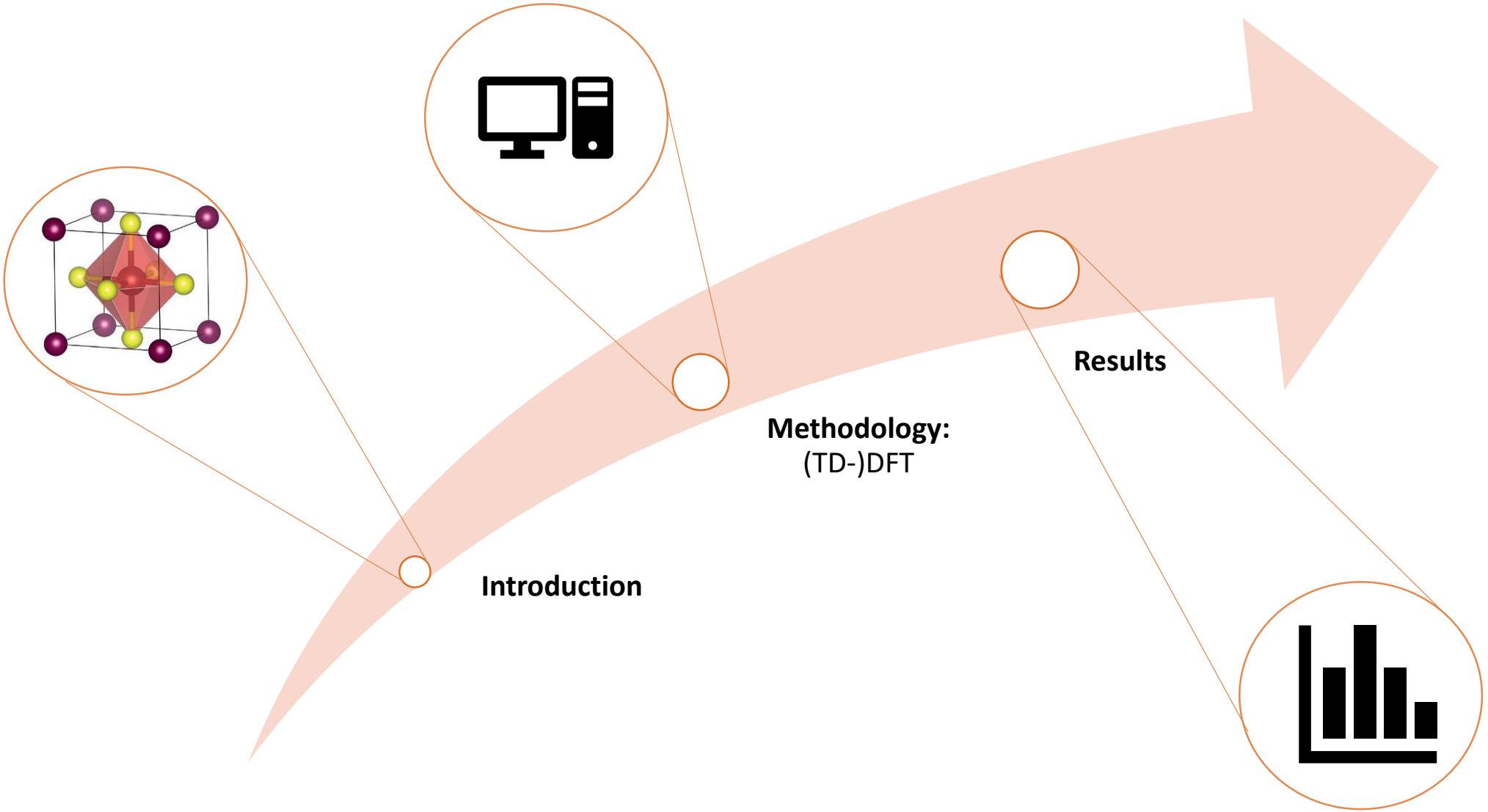


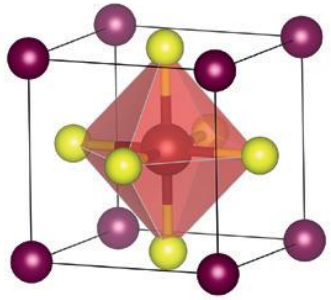
Table of contents

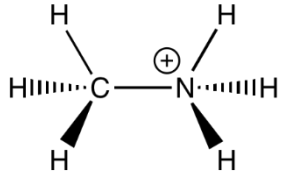


Hybrid perovskites ?

Methylammonium Lead iodide ($MAPbI_3$)

Perovskite structure → ABX_3





A

B Pb^{2+}

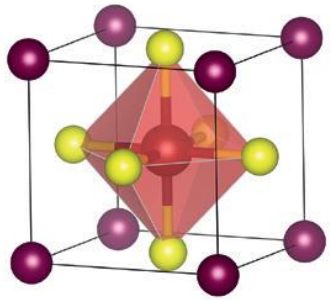
X I^-

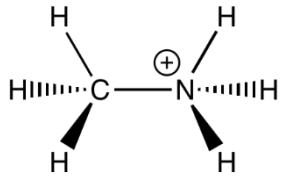
S. Stranks, H. Snaith, *Nature Publishing group* **10**, 391-402 (2015)

Hybrid perovskites ?

Methylammonium Lead iodide ($MAPbI_3$)

Perovskite structure → ABX_3



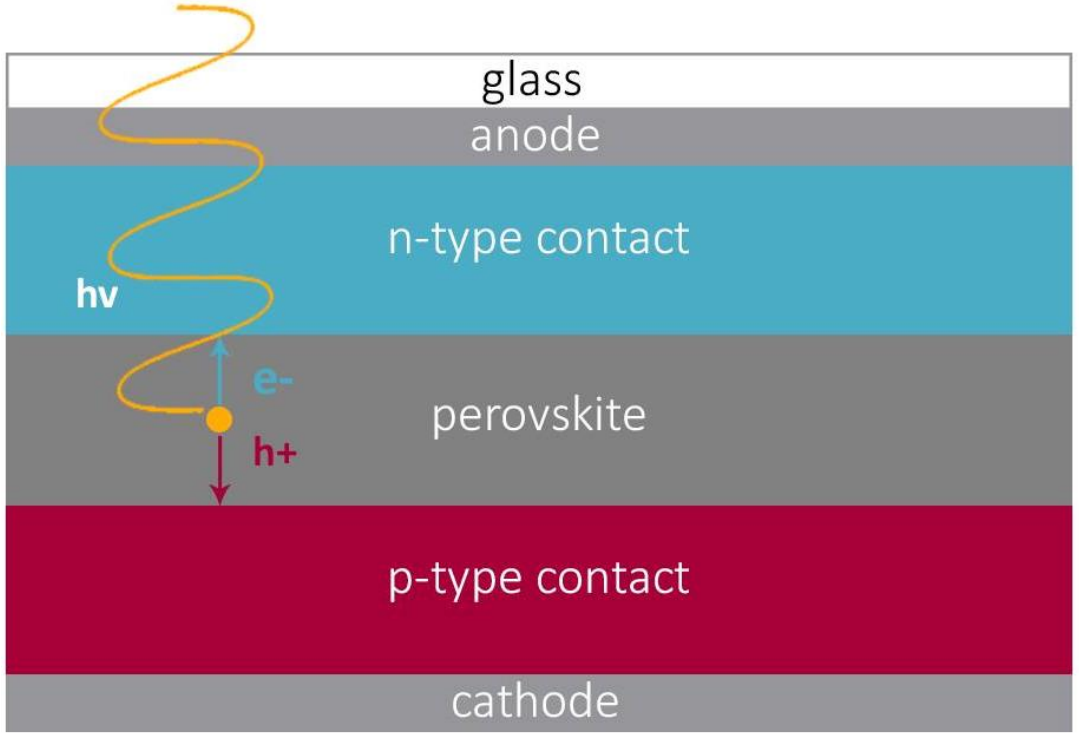


A

B **Pb^{2+}**

X **I^-**

Applications : **Photovoltaics**

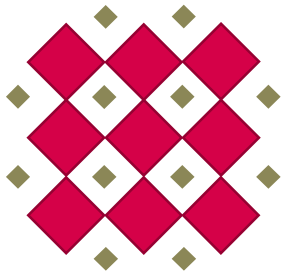


S. Stranks, H. Snaith, *Nature Publishing group* **10**, 391-402 (2015)

Dimensionality

3D Perovskite

- Low temperature solution synthesis
- PV quantum efficiency (23,3%)
- Instability due to ionic diffusion in the inorganic network



M. Yuan, L. N. Quan et al., *Nat. Nanotechnol.* **2016**

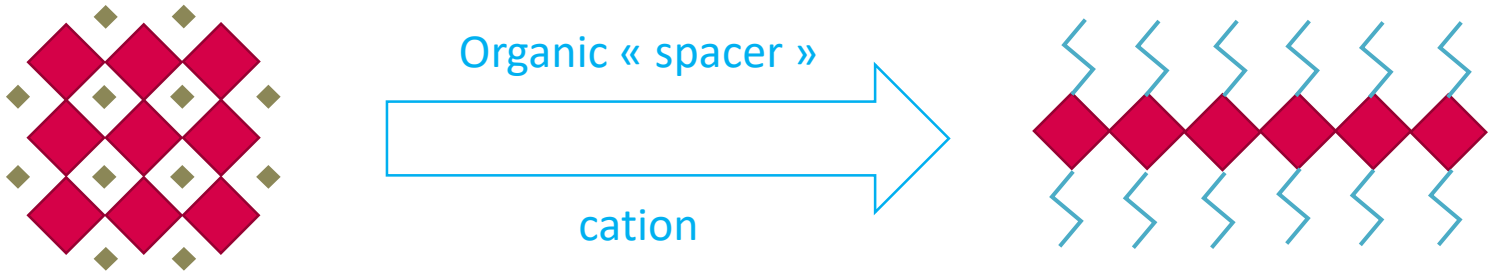
Dimensionality

3D Perovskite

- Low temperature solution synthesis
- PV quantum efficiency (23,3%)
- Instability due to ionic diffusion in the inorganic network

2D Perovskite

- Low temperature solution synthesis
- PV quantum efficiency (12% 2D - Mixed 3D/2D)
- Higher stability



G. Grancini, et al., *Nat. Comm. 8* **2017**

M. Yuan, L. N. Quan et al., *Nat. Nanotechnol.* **2016**

Dimensionality

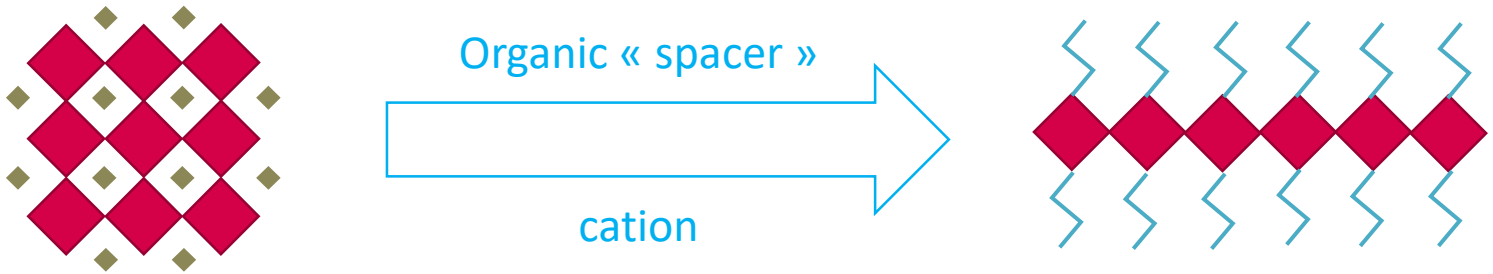
3D Perovskite

- Low temperature solution synthesis
- PV quantum efficiency (23,3%)
- Instability due to ionic diffusion in the inorganic network
- Goldsmicht tolerance factor

$$t = \frac{r_A + r_X}{\sqrt{2(r_B + r_X)}} \qquad 0.7 > t > 1$$

2D Perovskite

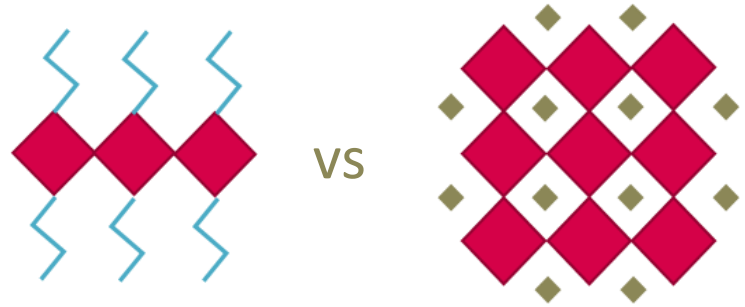
- Low temperature solution synthesis
- PV quantum efficiency (12% 2D - Mixed 3D/2D)
- Higher stability
- Chemical flexibility



G. Grancini, et al., *Nat. Comm. 8* **2017**

M. Yuan, L. N. Quan et al., *Nat. Nanotechnol.* **2016**

Dimensionality : 3D → 2D



1. Anisotropy

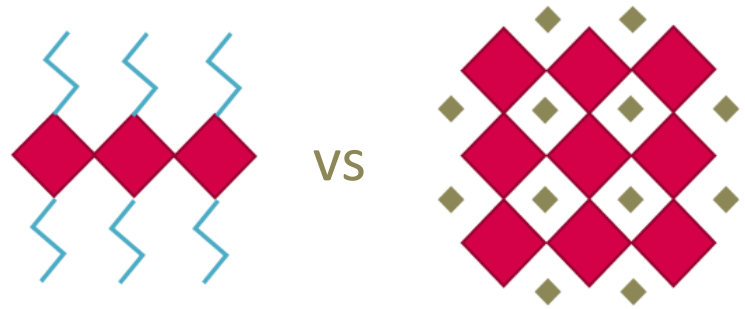
⇨ **Limited ionic diffusion, but also limited electron transport**

2. Chemical flexibility

⇨ **Reduced chemical space for 3D components (some cations, Pb, halide)**

↳ Larger number of possibilities for 2D, including the use of functional organic cations

Dimensionality : 3D → 2D



1. Anisotropy

⇨ **Limited ionic diffusion, but also limited electron transport**

2. Chemical flexibility

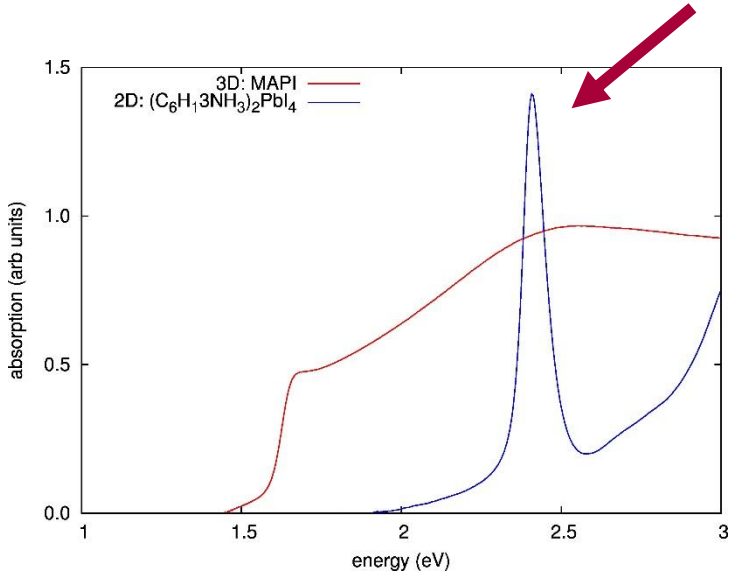
⇨ **Reduced chemical space for 3D components (some cations, Pb, halide)**

↳ Larger number of possibilities for 2D, including the use of functional organic cations

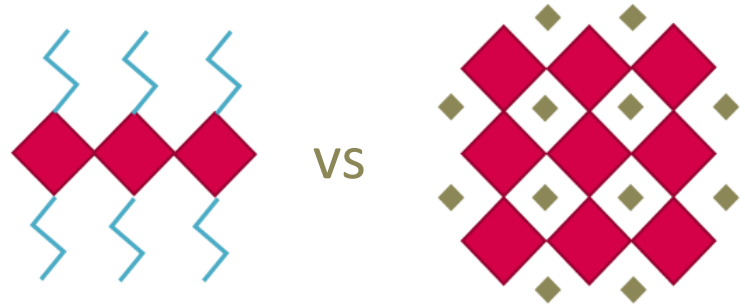
3. Electronic/dielectric confinement

⇨ Stronger excitonic effect

⇨ **Larger bandgap (BG)**



Dimensionality : 3D → 2D



1. Anisotropy

⇨ **Limited ionic diffusion, but also limited electron transport**

2. Chemical flexibility

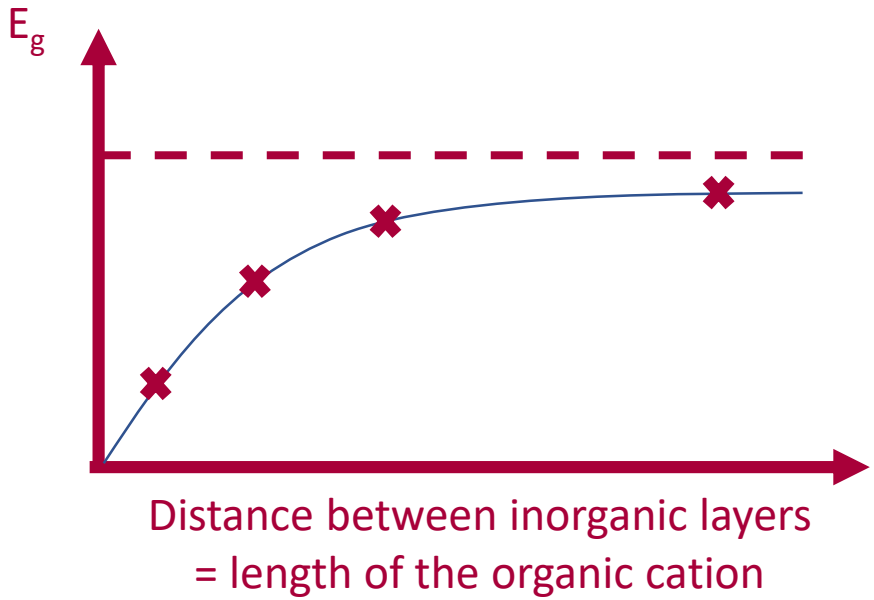
⇨ **Reduced chemical space for 3D components (some cations, Pb, halide)**

↳ Larger number of possibilities for 2D, including the use of functional organic cations

3. Electronic/dielectric confinement

⇨ Stronger excitonic effect

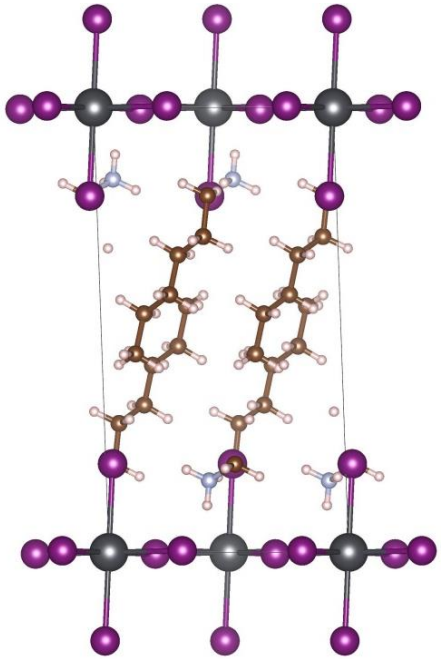
⇨ **Larger bandgap (BG)**



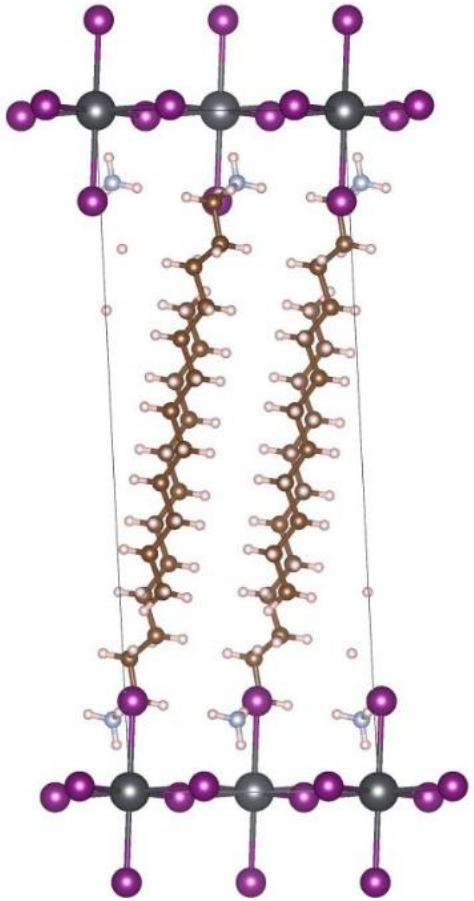
Is it the only effect of the nature (length) of the organic cation?

Studied systems : $(C_nH_{2n+1}NH_3)_2PbI_4$

$(C_6H_{13}NH_3)_2PbI_4$



$(C_{12}H_{25}NH_3)_2PbI_4$

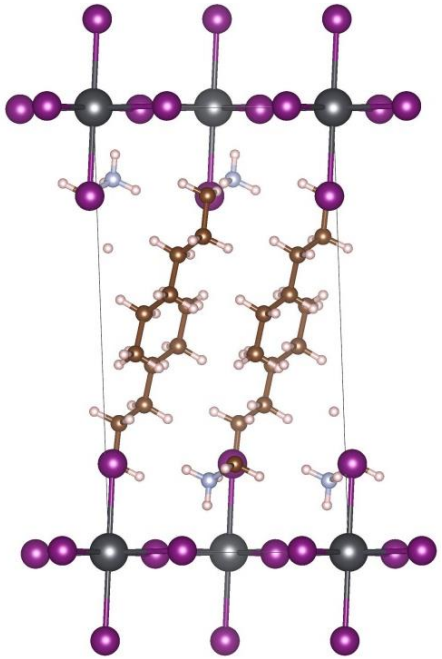


D. G. Billing, A. Lemmerer, *Acta Crystallogr. Sect. B: Struct. Sci.* **2007**

D. G. Billing, A. Lemmerer, *New J. Chem.* **2008**

Studied systems : $(C_nH_{2n+1}NH_3)_2PbI_4$

$(C_6H_{13}NH_3)_2PbI_4$

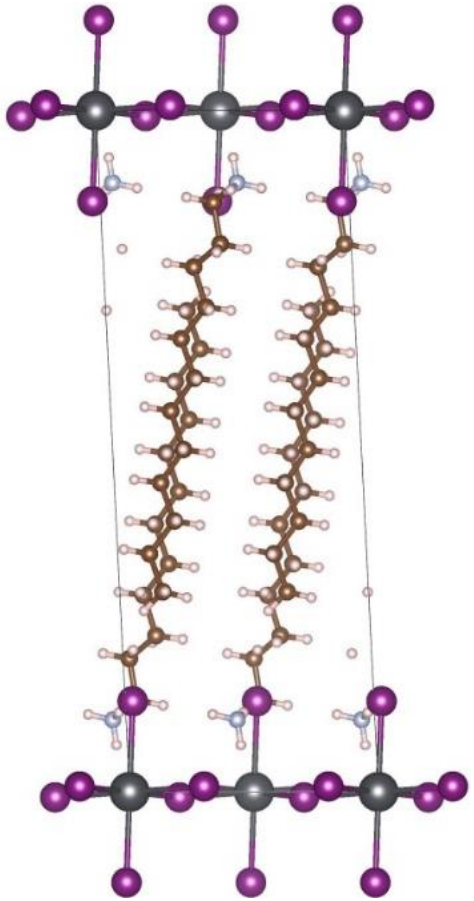


Monoclinic (P21/a)

258K ↑ ↓ 268K

Orthorhombic (Pbca)

$(C_{12}H_{25}NH_3)_2PbI_4$



Orthorhombic (Pbca)

306K ↑ ↓ 315K

Monoclinic (P21/a)

D. G. Billing, A. Lemmerer, *Acta Crystallogr. Sect. B: Struct. Sci.* **2007**

D. G. Billing, A. Lemmerer, *New J. Chem.* **2008**

Methodology

→ **Materials modeling & electronic properties**
→ Density Functional Theory **(DFT)** : **Plane Wave** basis set (PW)
→ **PBE (GGA functional)**

DFT
(static, ground state)

Methodology

→ **Materials modeling & electronic properties**
→ Density Functional Theory **(DFT)** : **Plane Wave** basis set (PW)
→ **PBE (GGA functional)**

DFT
(static, ground state)

- Grimme correction: $E_{DFT-D} = E[\rho] + E_{disp}$ *et* $E_{disp} = -s_6 \sum_{i=j}^{N_{at}-1} \sum_{j=i+1}^{N_{at}} \frac{C_6^{ij}}{R_{ij}^6} \frac{1}{1 + e^{-d\left(\frac{Rij}{R_r}-1\right)}}$

S. Grimme, *Wiley InterScience* (2006)

Methodology

→ **Materials modeling & electronic properties**
→ Density Functional Theory **(DFT)** : **Plane Wave** basis set (PW)
→ **PBE (GGA functional)**

DFT
(static, ground state)

- Grimme correction: $E_{DFT-D} = E[\rho] + E_{disp}$ *et* $E_{disp} = -s_6 \sum_{i=j}^{N_{at}-1} \sum_{j=i+1}^{N_{at}} \frac{C_6^{ij}}{R_{ij}^6} \frac{1}{1 + e^{-d\left(\frac{Rij}{R_r}-1\right)}}$
- Spin-orbit coupling (SOC)
- Hybrid functional (PBE0)

S. Grimme, *Wiley InterScience* (2006)

Methodology

→ **Materials modeling & electronic properties**
→ Density Functional Theory **(DFT)** : **Plane Wave** basis set (PW)
→ **PBE (GGA functional)**

DFT
(static, ground state) → **TDDFT**
(static, excited state)

turbo_dft

- Grimme correction: $E_{DFT-D} = E[\rho] + E_{disp}$ *et* $E_{disp} = -s_6 \sum_{i=j}^{N_{at}-1} \sum_{j=i+1}^{N_{at}} \frac{C_6^{ij}}{R_{ij}^6} \frac{1}{1 + e^{-d\left(\frac{Rij}{R_r}-1\right)}}$
- Spin-orbit coupling (SOC)
- Hybrid functional (PBE0)

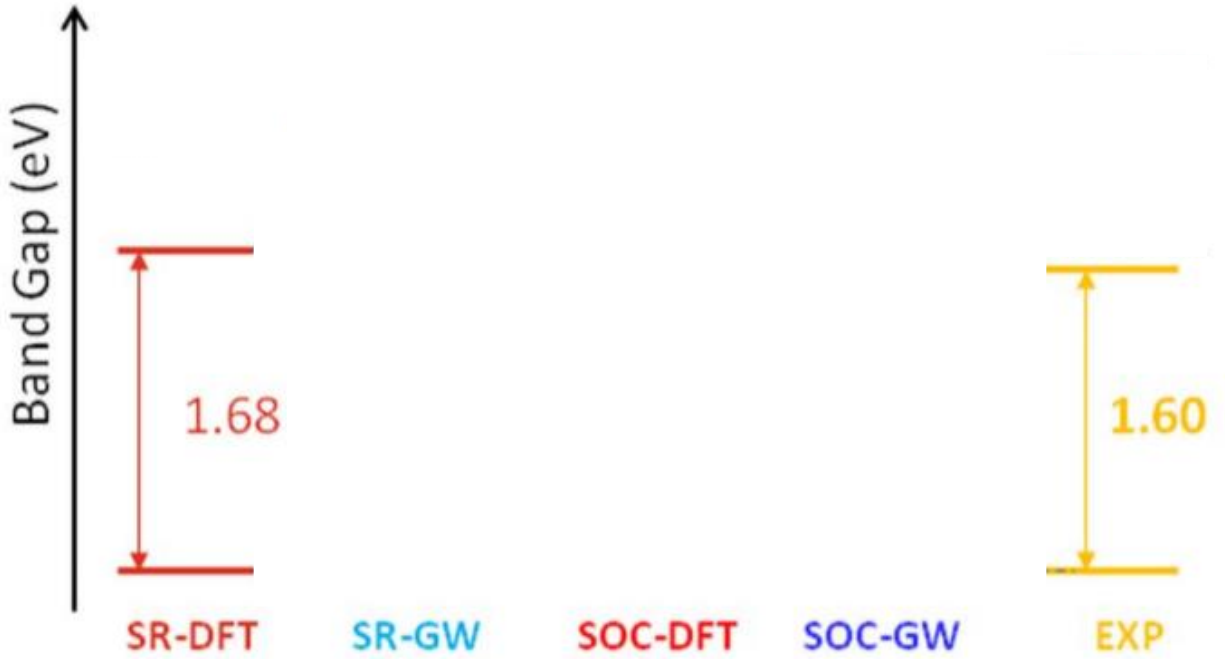
S. Grimme, *Wiley InterScience* (2006)

Methodological study

3D CASE

$MAPbI_3$

- PBE (GGA) agrees with experimental BG



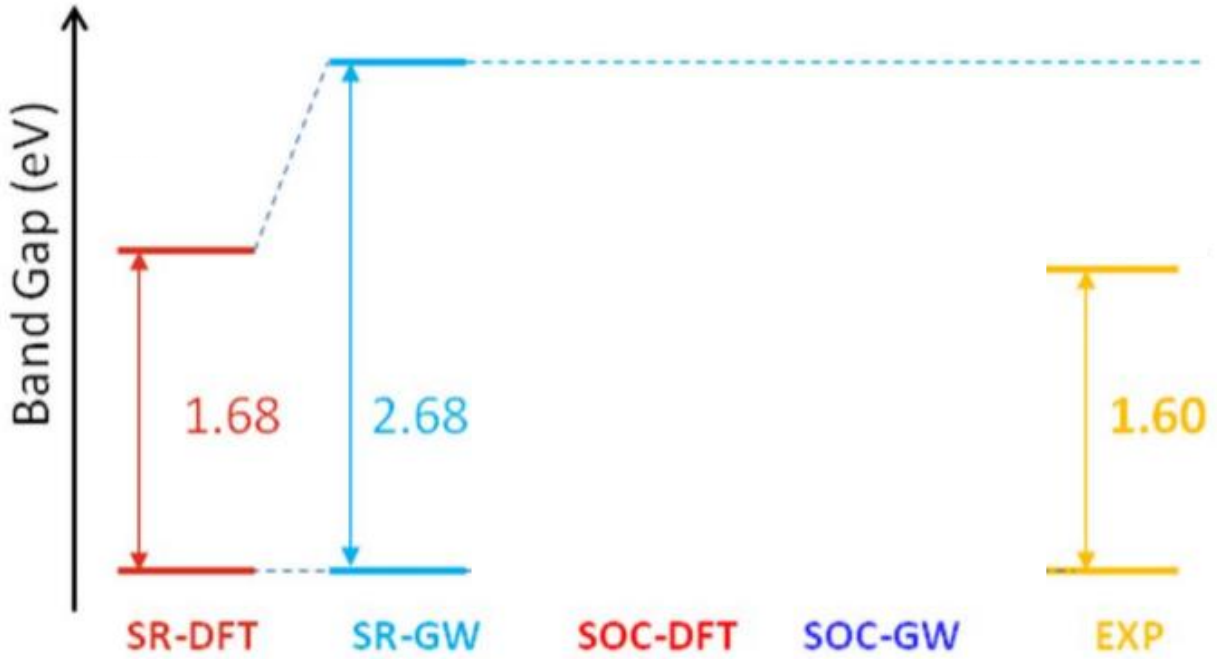
(P. Umari et al., Sci. Rep. 4, 4467, 2014)

Methodological study

3D CASE

$MAPbI_3$

- PBE (GGA) agrees with experimental BG
- GW approximation ➔ BG opening of 1 eV



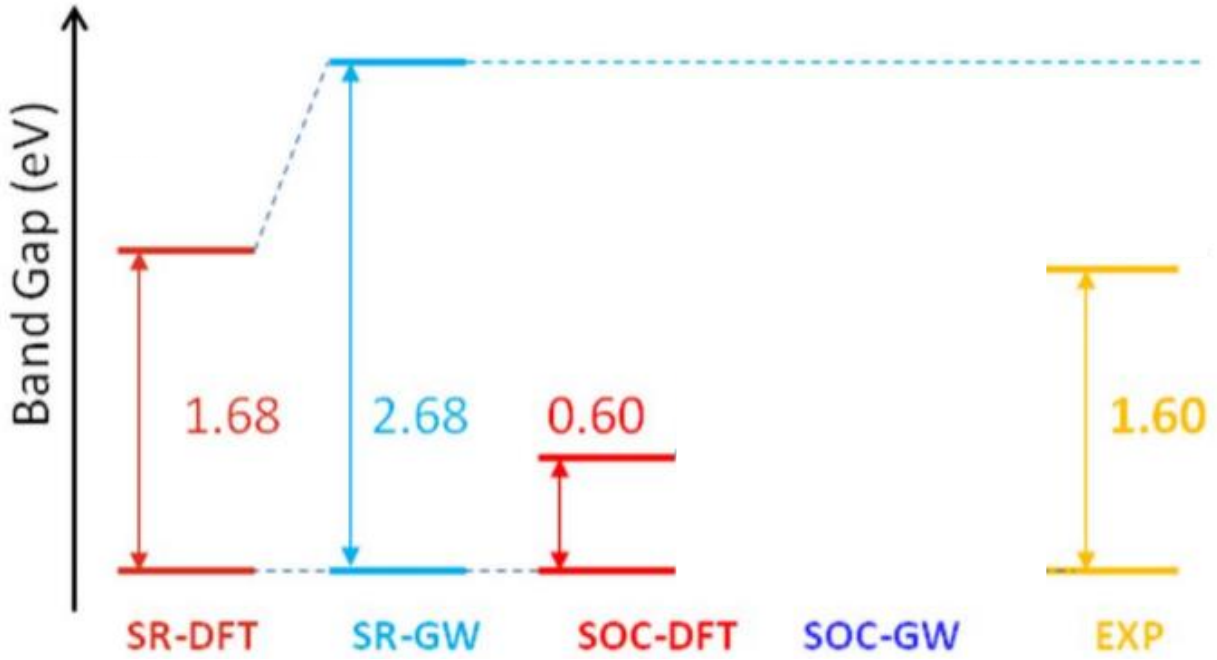
(P. Umari et al., Sci. Rep. 4, 4467, 2014)

Methodological study

3D CASE

$MAPbI_3$

- PBE (GGA) agrees with experimental BG
- GW approximation ➔ BG opening of 1 eV
- SOC ➔ BG closing of 1.1eV



(P. Umari et al., Sci. Rep. 4, 4467, 2014)

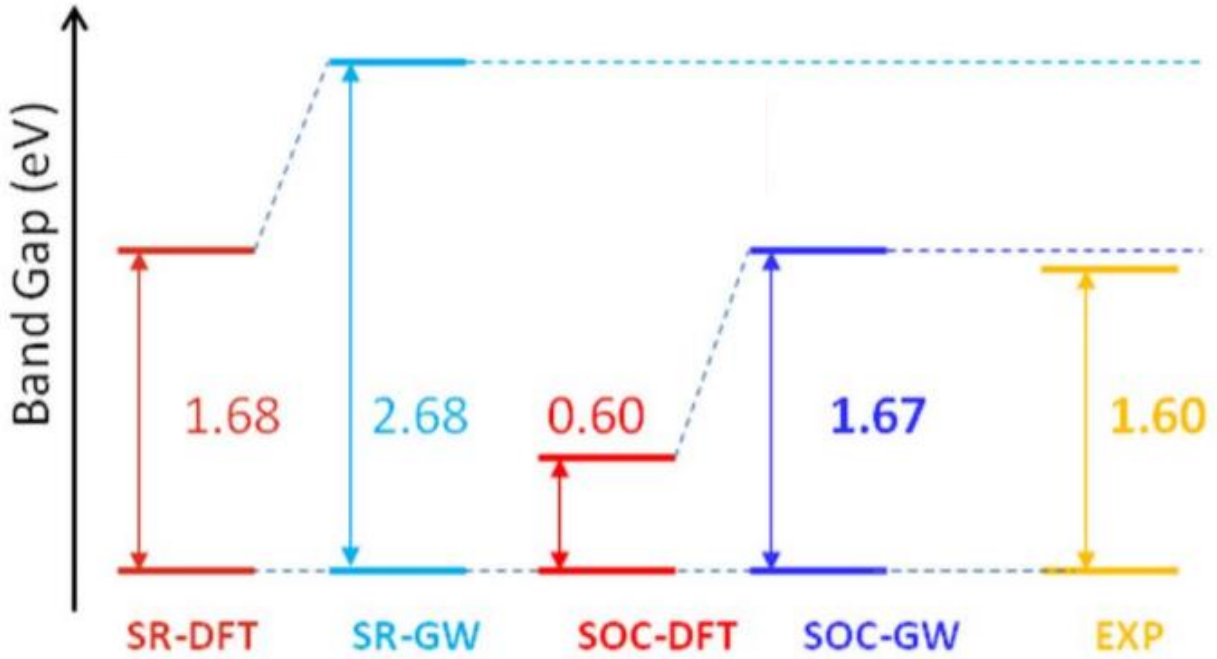
Methodological study

3D CASE

$MAPbI_3$

- PBE (GGA) agrees with experimental BG
- GW approximation ➔ BG opening of 1 eV
- SOC ➔ BG closing of 1.1eV

↳ Compensation of errors



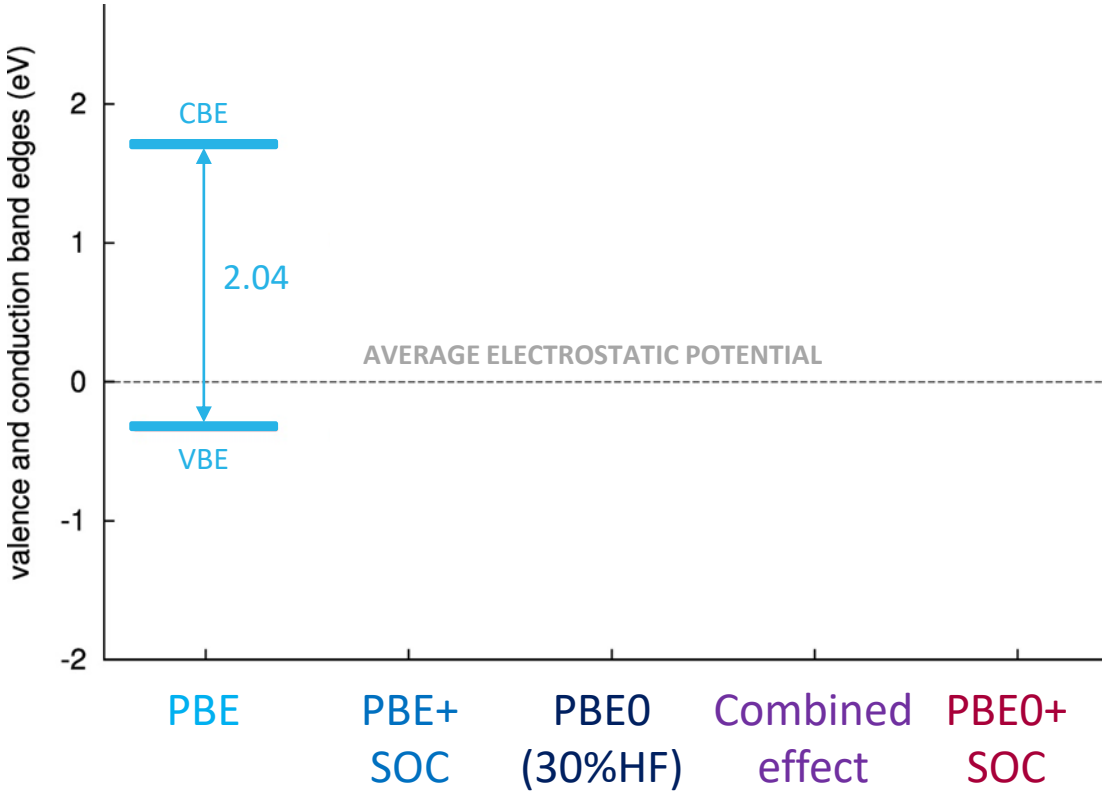
(P. Umari et al., Sci. Rep. 4, 4467, 2014)

➔ **PBE agrees with SOC-GW and is in good agreement with experimental data**

Methodological study

2D CASE

$(C_6H_{13}NH_3)_2PbI_4$



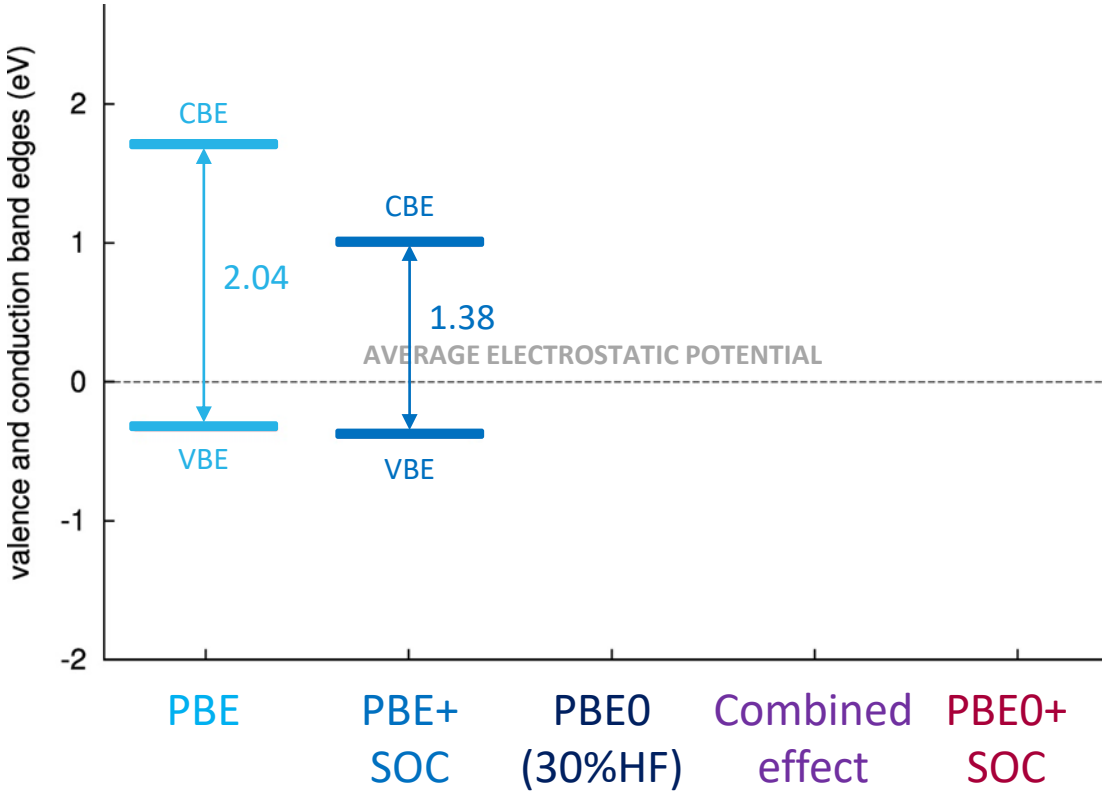
- PBE (GGA) BG does not agree with experimental data (2.7 eV)

K. Tanaka, et al., *Phys. Rev. B* **2005**

Methodological study

2D CASE

$(C_6H_{13}NH_3)_2PbI_4$



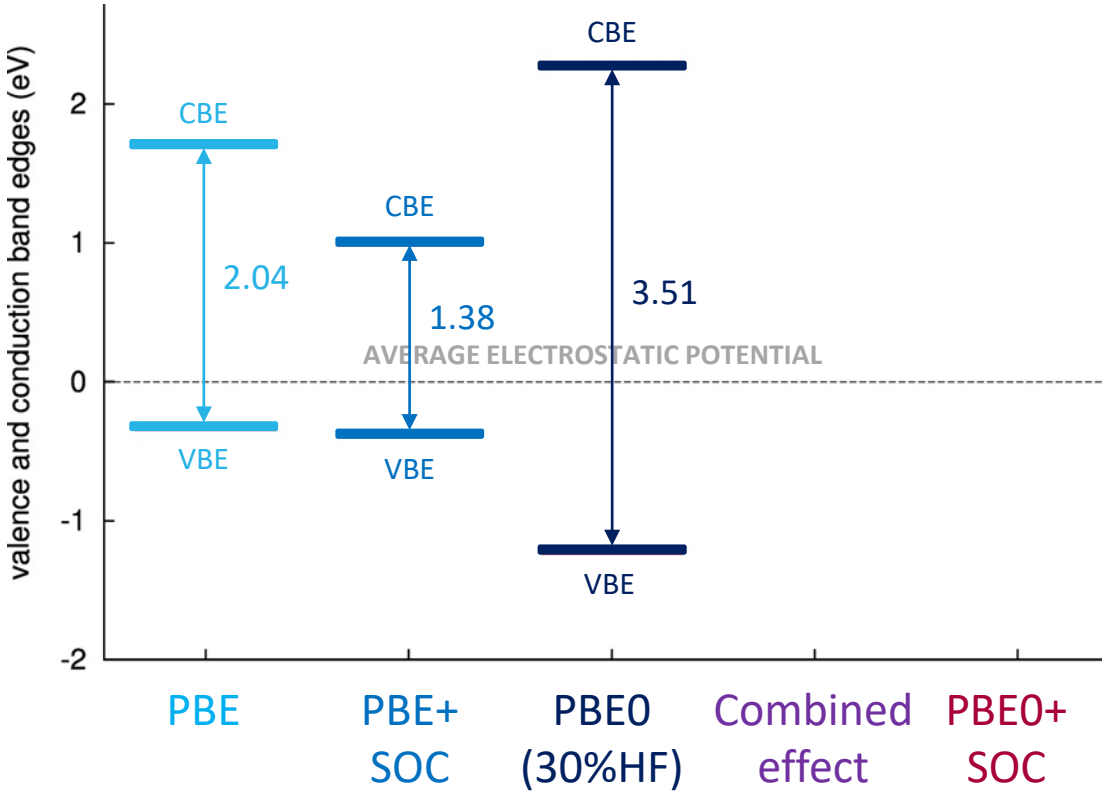
- PBE (GGA) BG does not agree with experimental data (2.7 eV)
- SOC ➔ BG closing of 0.66 eV

K. Tanaka, et al., *Phys. Rev. B* **2005**

Methodological study

2D CASE

$(C_6H_{13}NH_3)_2PbI_4$



- PBE (GGA) BG does not agree with experimental data (2.7 eV)
- SOC ➔ BG closing of 0.66 eV
- PBE0 ➔ BG opening of 1.47 eV

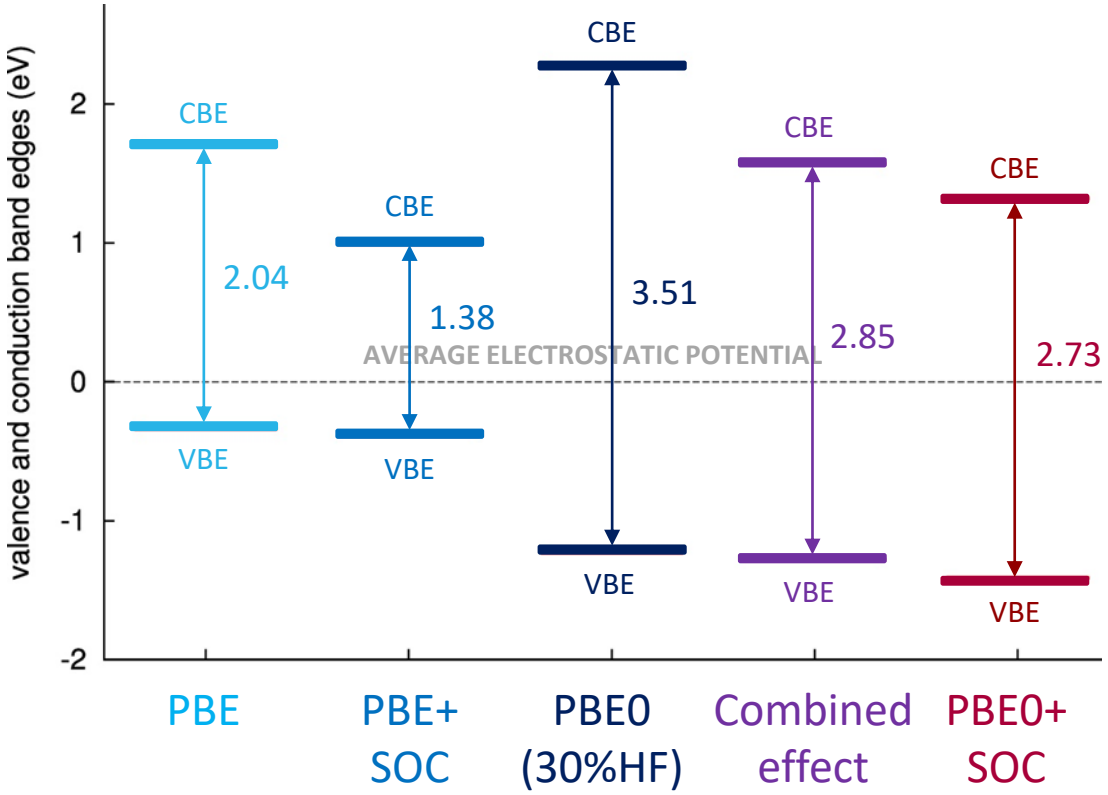
No compensation of errors
Better Exchange interaction description overcomes SOC correction

K. Tanaka, et al., *Phys. Rev. B* **2005**

Methodological study

2D CASE

$(C_6H_{13}NH_3)_2PbI_4$



- PBE (GGA) BG does not agree with experimental data (2.7 eV)
- SOC ➔ BG closing of 0.66 eV
- PBE0 ➔ BG opening of 1.47 eV

No compensation of errors
Better Exchange interaction description overcomes SOC correction

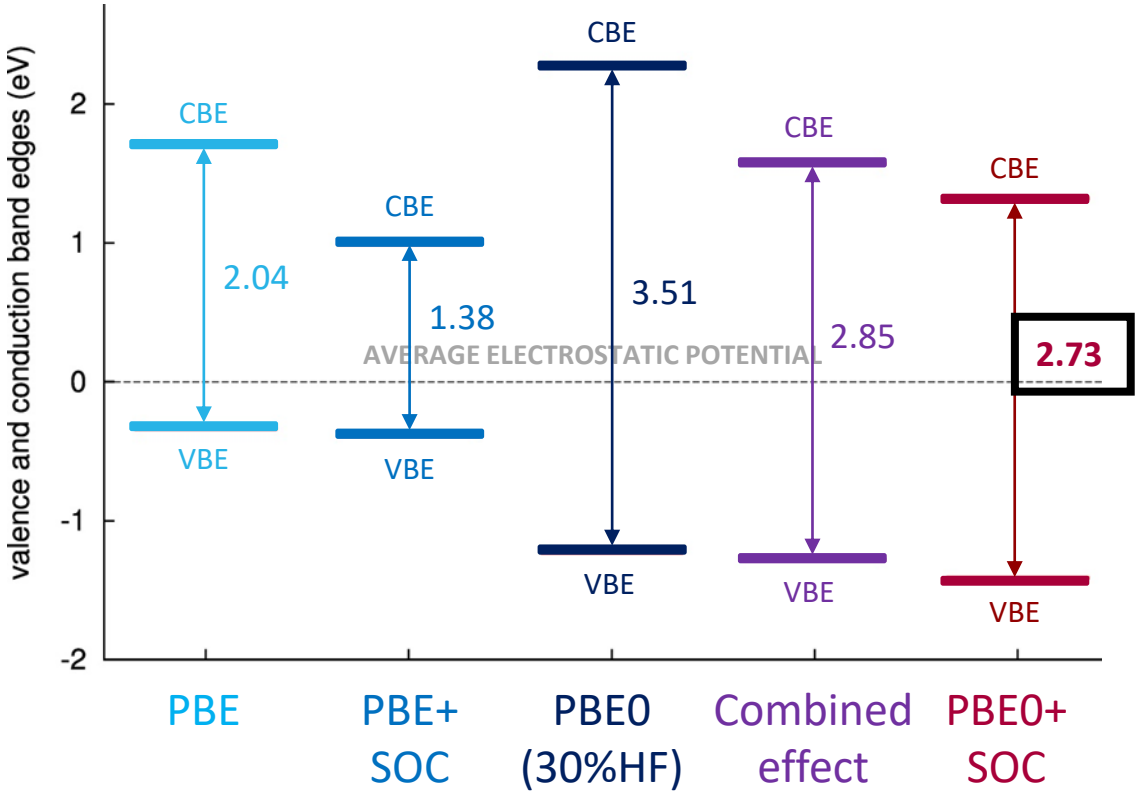
- Calculation with both corrections lead to BG close to the average of the contributions from the separated calculations

K. Tanaka, et al., *Phys. Rev. B* **2005**

Methodological study

2D CASE

$(C_6H_{13}NH_3)_2PbI_4$



- PBE (GGA) BG does not agree with experimental data (2.7 eV)
- SOC ➔ BG closing of 0.66 eV
- PBE0 ➔ BG opening of 1.47 eV

No compensation of errors
Better Exchange interaction description overcomes SOC correction

- Calculation with both corrections lead to BG close to the average of the contributions from the separated calculations

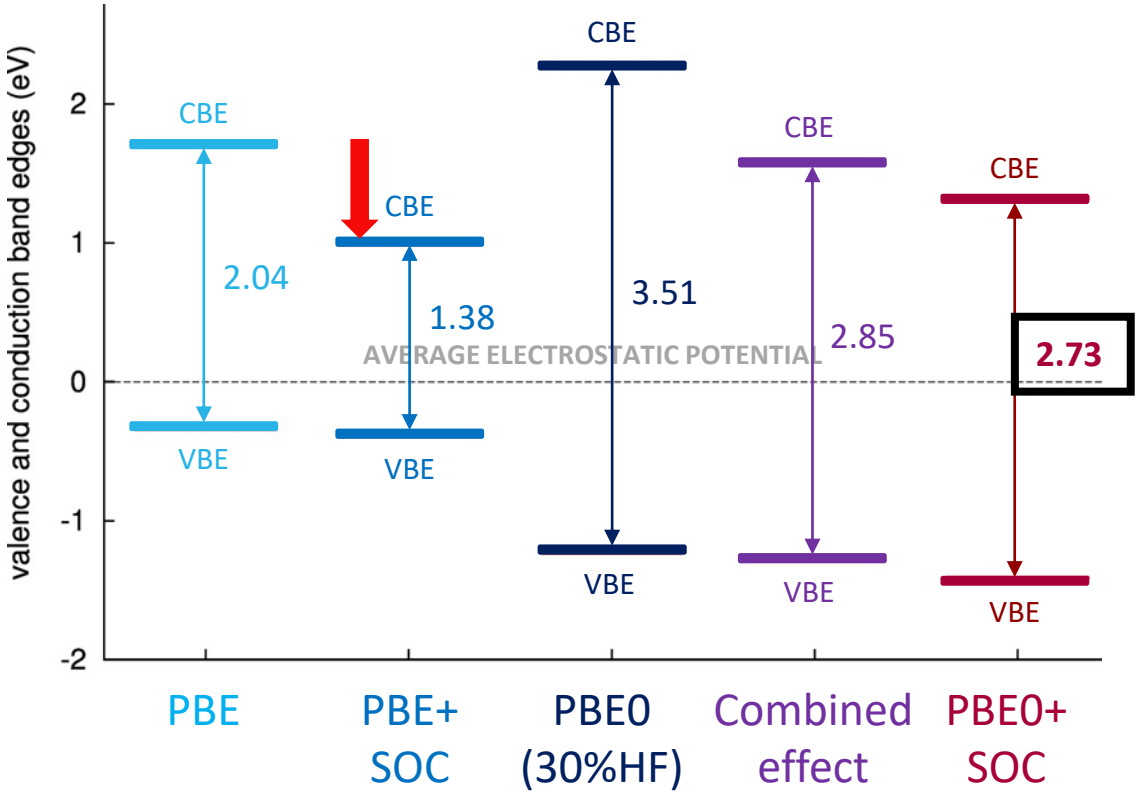
K. Tanaka, et al., *Phys. Rev. B* **2005**

Methodological study

Effect of SOC mostly on CBE (splitting of j=1/2 and 3/2 on Pb)

2D CASE

$(C_6H_{13}NH_3)_2PbI_4$



- PBE (GGA) BG does not agree with experimental data (2.7 eV)
- SOC ➔ BG closing of 0.66 eV
- PBE0 ➔ BG opening of 1.47 eV

No compensation of errors
Better Exchange interaction description overcomes SOC correction

- Calculation with both corrections lead to BG close to the average of the contributions from the separated calculations

K. Tanaka, et al., *Phys. Rev. B* **2005**

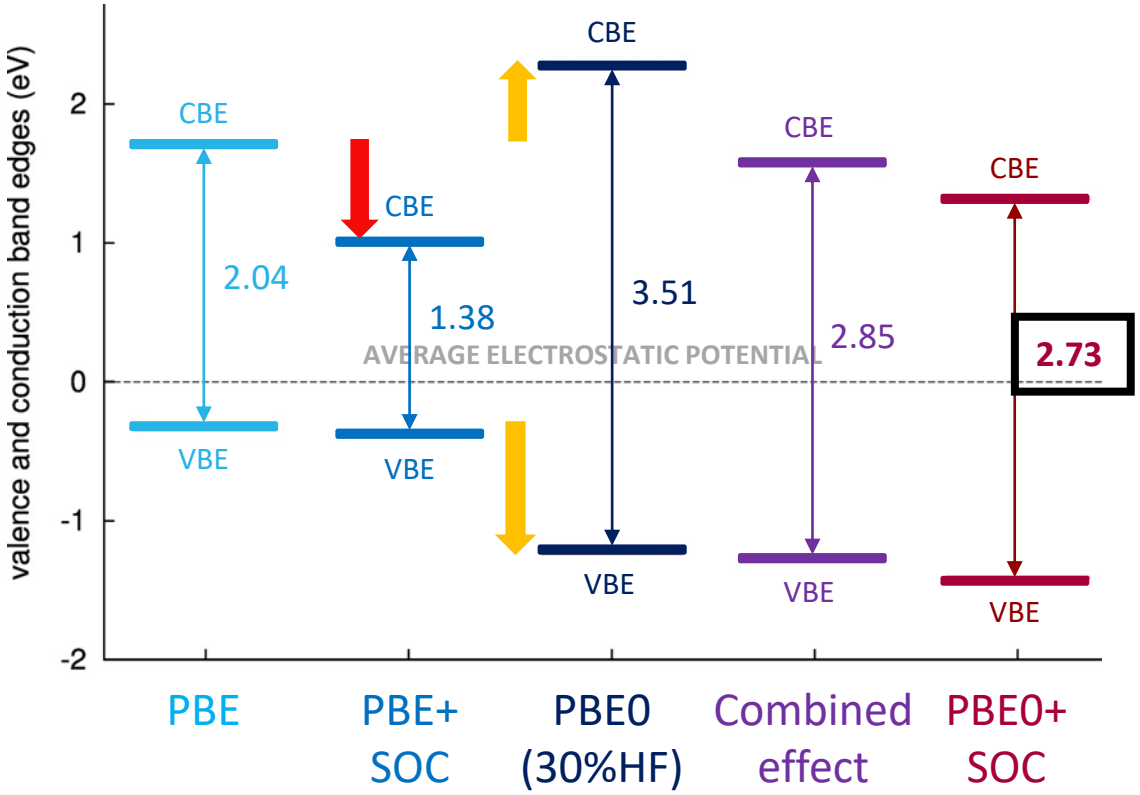
Methodological study

Effect of SOC mostly on CBE (splitting of j=1/2 and 3/2 on Pb)

Effect on PBE0 on both bands, but more on VBE

2D CASE

$(C_6H_{13}NH_3)_2PbI_4$



- PBE (GGA) BG does not agree with experimental data (2.7 eV)
- SOC ➔ BG closing of 0.66 eV
- PBE0 ➔ BG opening of 1.47 eV

No compensation of errors
Better Exchange interaction description overcomes SOC correction

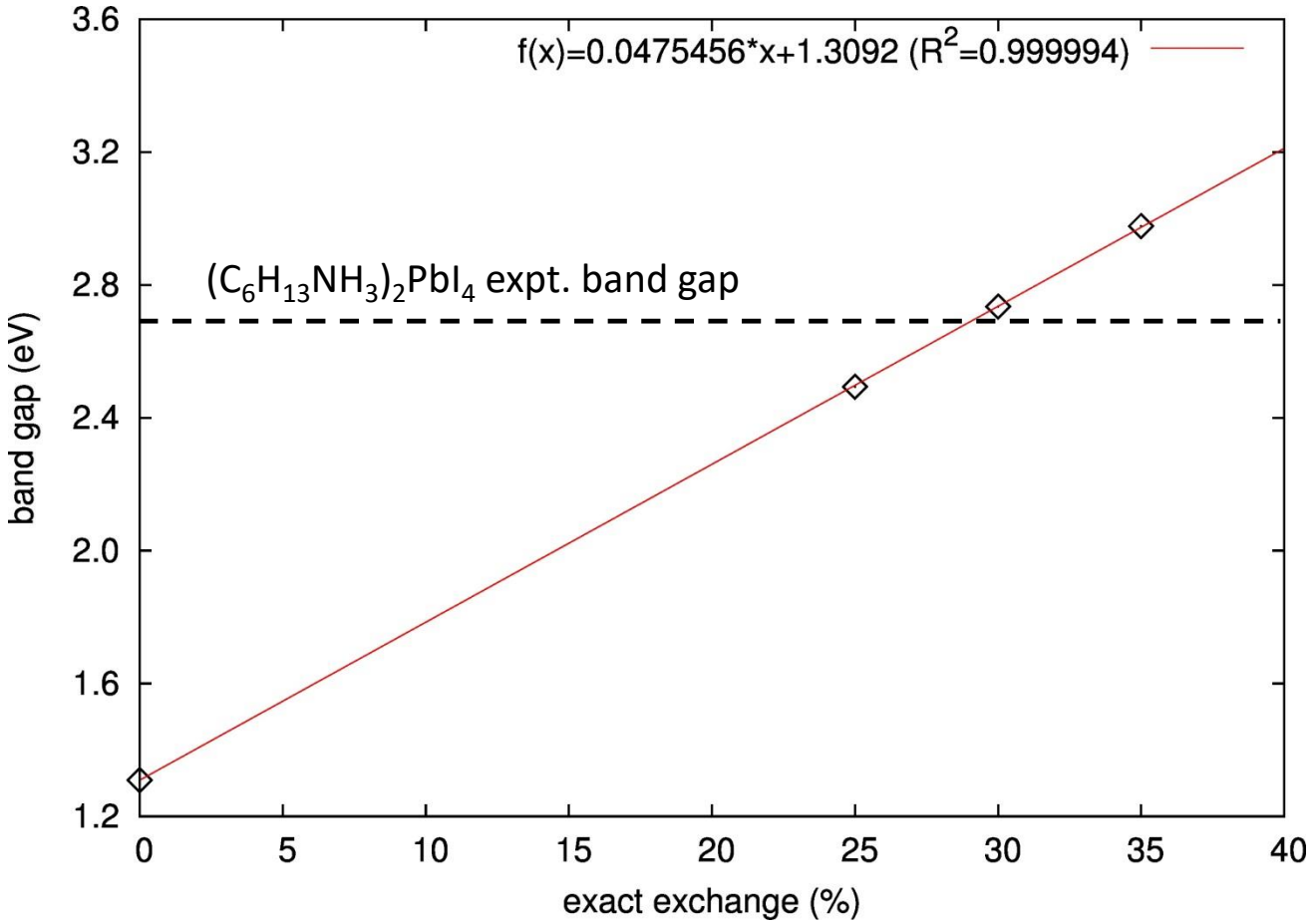
- Calculation with both corrections lead to BG close to the average of the contributions from the separated calculations

K. Tanaka, et al., *Phys. Rev. B* **2005**

Methodological study

2D CASE

$(C_6H_{13}NH_3)_2PbI_4$



PBE0 calculation

➔ The best agreement with the experimental BG (2.7 eV) is at **30% of Hartree-Fock exchange**

K. Tanaka, et al., *Phys. Rev. B* **2005**

Electronic properties

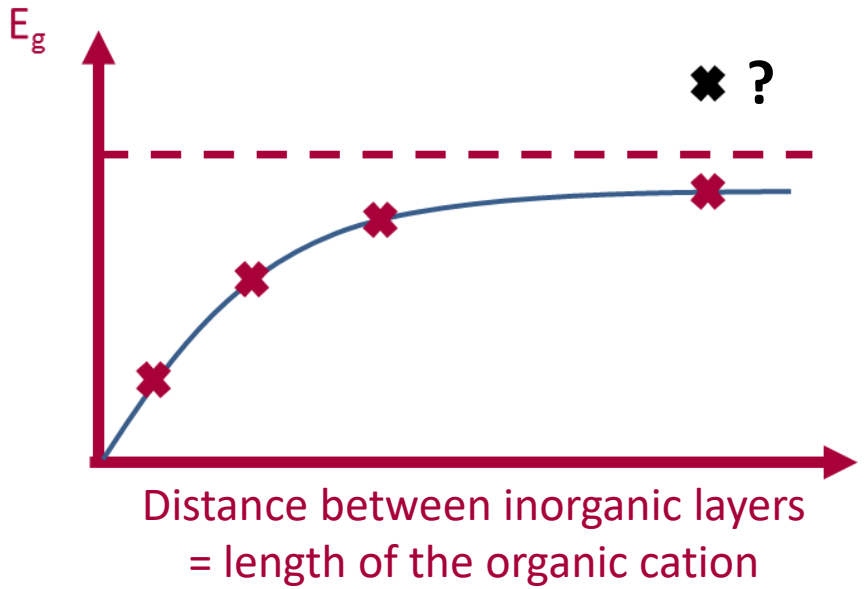
In (100) direction

PBE	E_g (eV)	m^*_h	m^*_e
C6 (monoclinic)	2.06	0.24	0.17
C6 (orthorhombic)	2.04	0.24	0.17
C12 (monoclinic)	2.05	0.22	0.17
C12 (orthorhombic)	**2.38**	**0.40**	**0.24**
MAPI	1.6	0.15	0.13

Electronic properties

In (100) direction

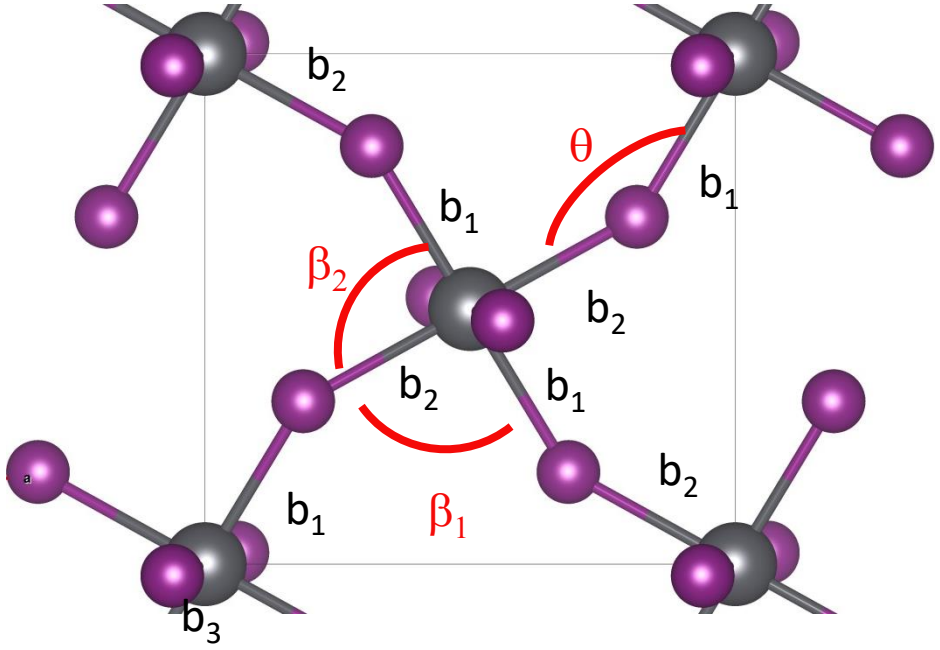
PBE	E_g (eV)	m^*_h	m^*_e
C6 (monoclinic)	2.06	0.24	0.17
C6 (orthorhombic)	2.04	0.24	0.17
C12 (monoclinic)	2.05	0.22	0.17
C12 (orthorhombic)	**2.38**	**0.40**	**0.24**
MAPI	1.6	0.15	0.13



➔ **Different behaviour of C12 (orthorhombic) ➔ WHY ?**

➔ Same observations at other levels of theory (SOC – PBEO)

Structural effect



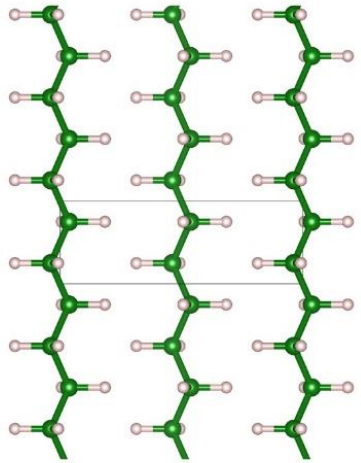
out-of-plane

		BG	b_1	b_2	b_3	θ	β_1	β_2
C6	mono	2.06	3.19	3.18	3.26	152	92	88
	ortho	2.04	3.20	3.20	3.25	154	89	91
C12	mono	2.05	3.22	3.21	3.22	153	88	92
	ortho	**2.38**	3.23	3.24	3.24	**143**	**94**	**86**

Influence from the organic component

Side view

polyethylene

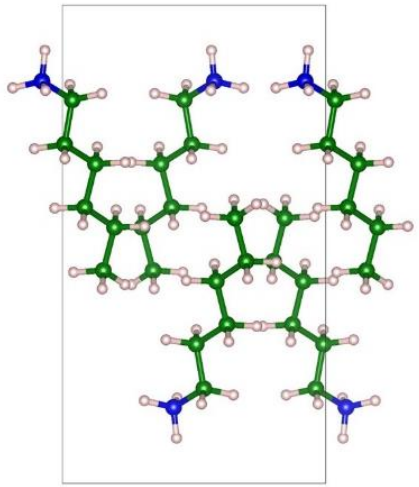


G. Avitabile, et al., *J. Polym. Sci. Lett. Ed.,* **1975**

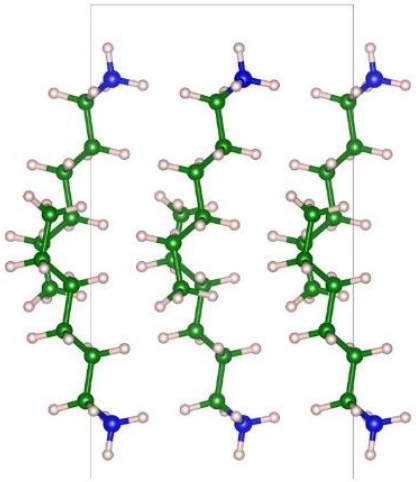
Influence from the organic component

Side view

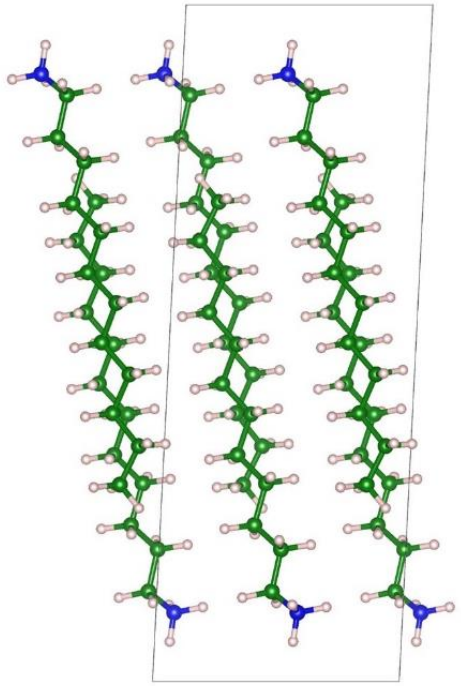
C6 mono



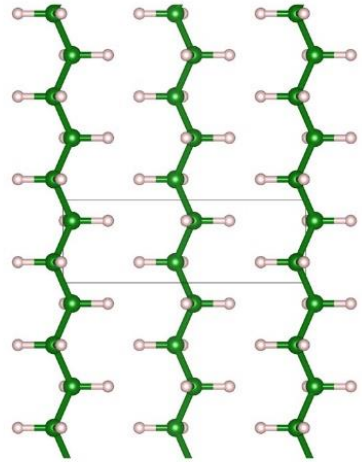
C6 ortho



C12 mono



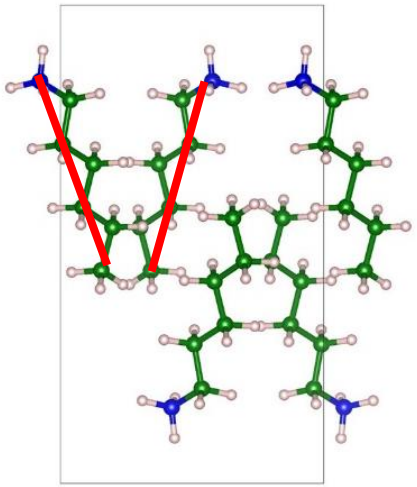
polyethylene



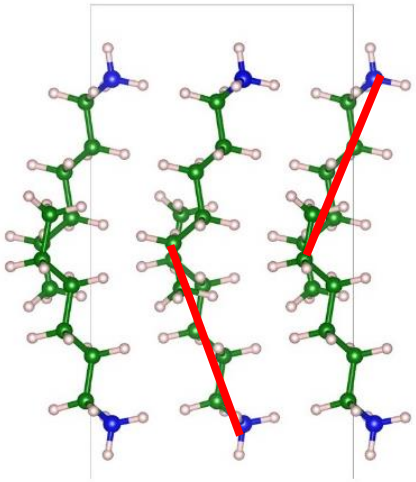
Influence from the organic component

Side view

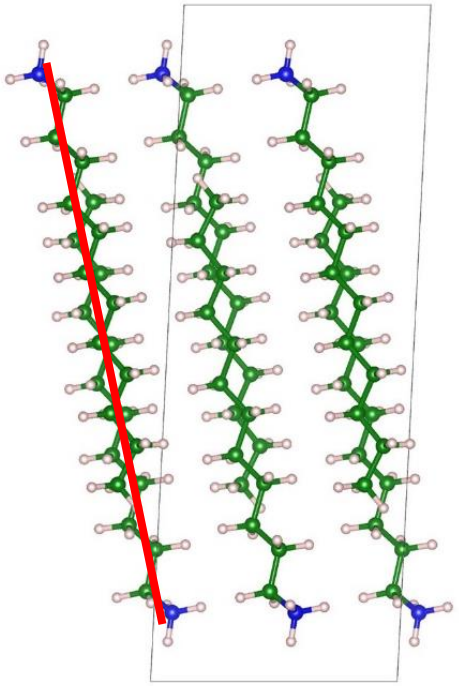
C6 mono



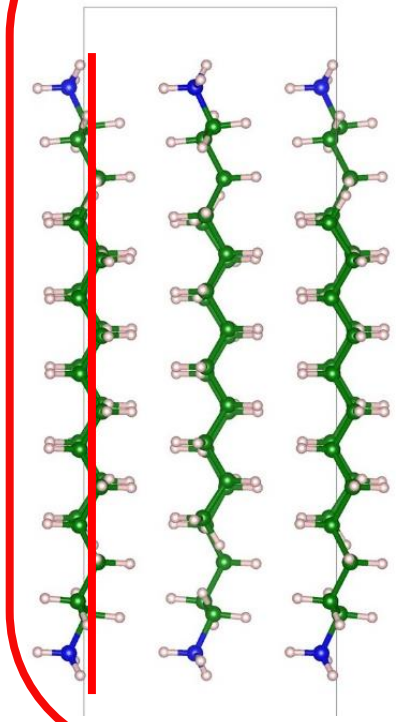
C6 ortho



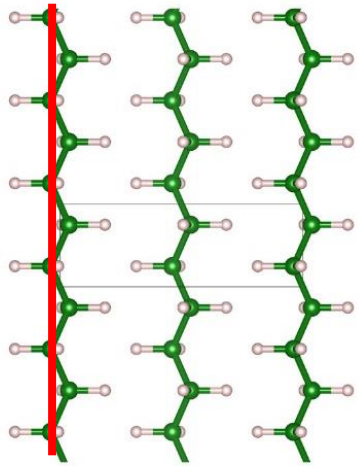
C12 mono



C12 ortho



polyethylene

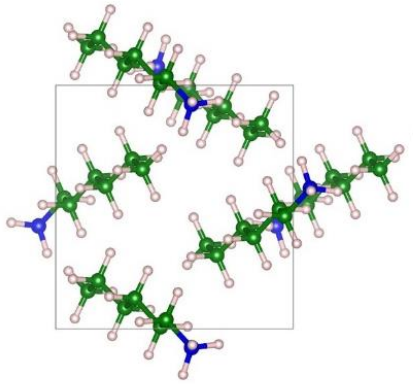


➔ Alkyl chains stacked like PE in C12 orthorhombic → tilt of PbI octohedras and increase the BG!

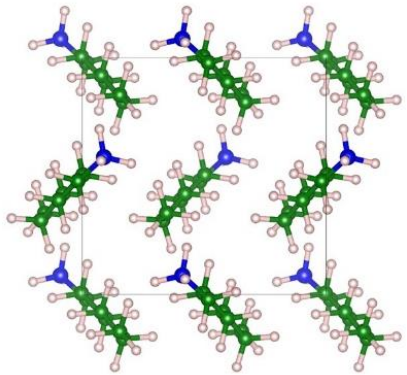
Influence from the organic component

Top view

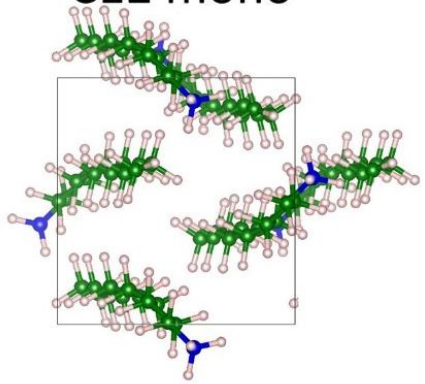
C6 mono



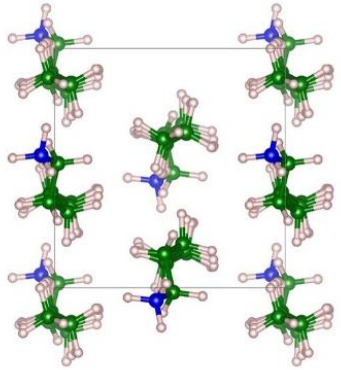
C6 ortho



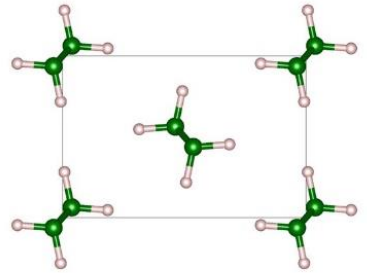
C12 mono



C12 ortho

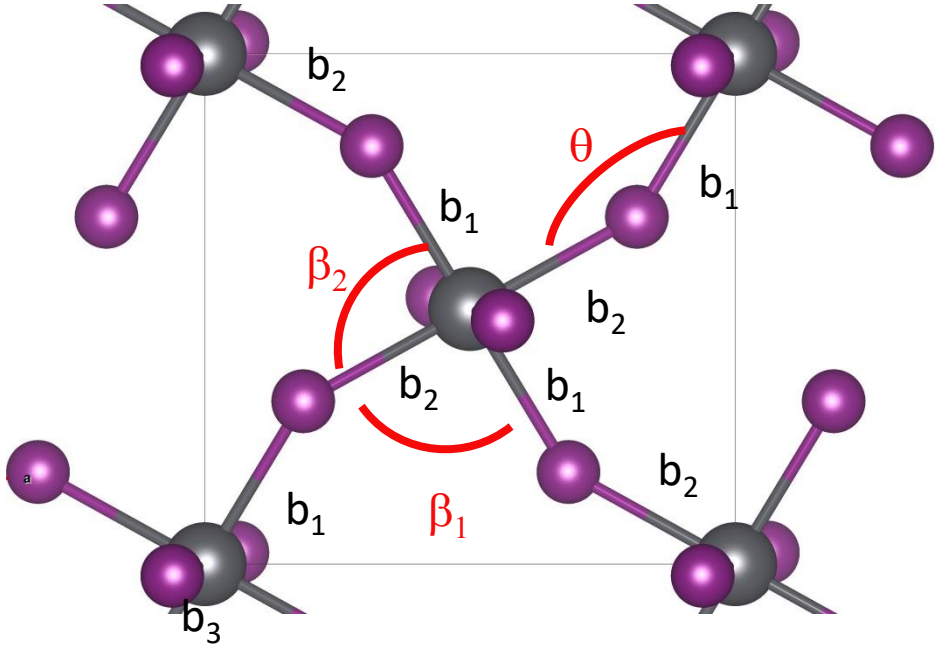


polyethylene



➔ Alkyl chains stacked like PE in C12 orthorhombic → tilt of PbI octohedras and increase the BG!

Structural effect



out-of-plane

➔ Influence of organic component

↳ **Alkyl chains stacked like PE**

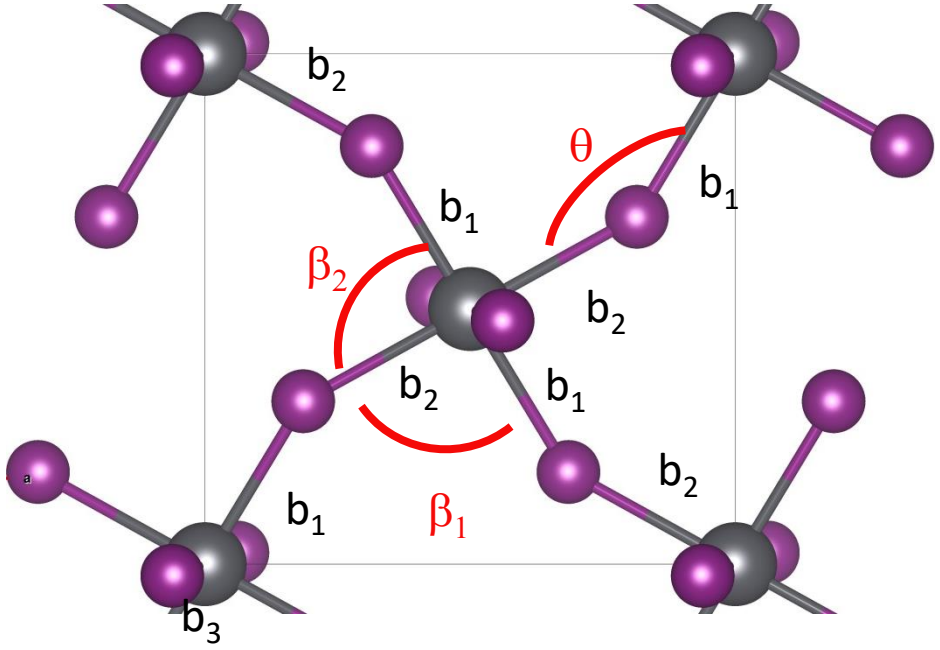
↳ **Tilt of Pb-I octahedra: BG↗**

➔ Consistant with the literature

Amat, *Nano Lett.*, 14,p. 3608–3616 (2014)

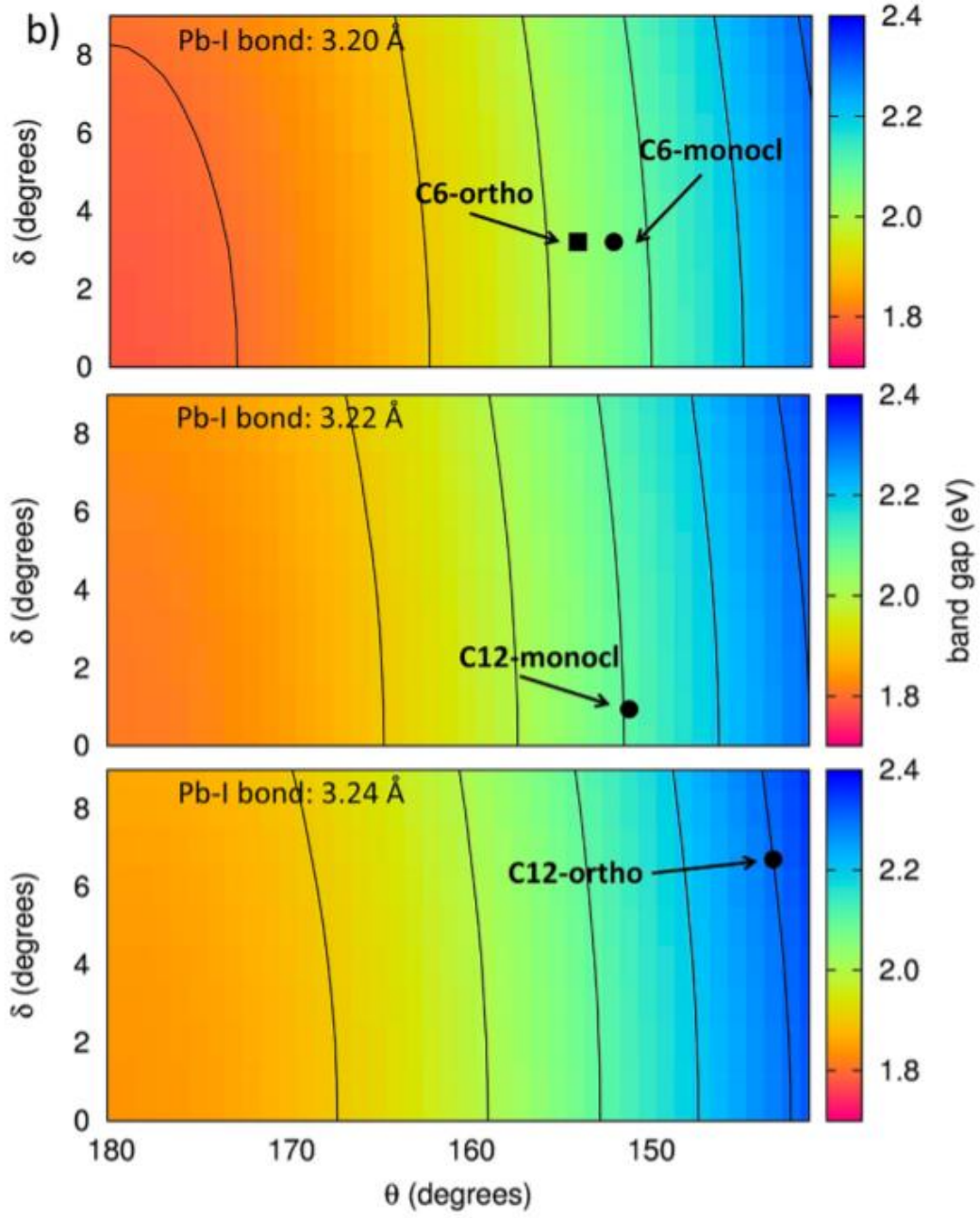
		BG	b_1	b_2	b_3	θ	β_1	β_2
C6	mono	2.06	3.19	3.18	3.26	152	92	88
	ortho	2.04	3.20	3.20	3.25	154	89	91
C12	mono	2.05	3.22	3.21	3.22	153	88	92
	ortho	**2.38**	3.23	3.24	3.24	**143**	**94**	**86**

Structural effect

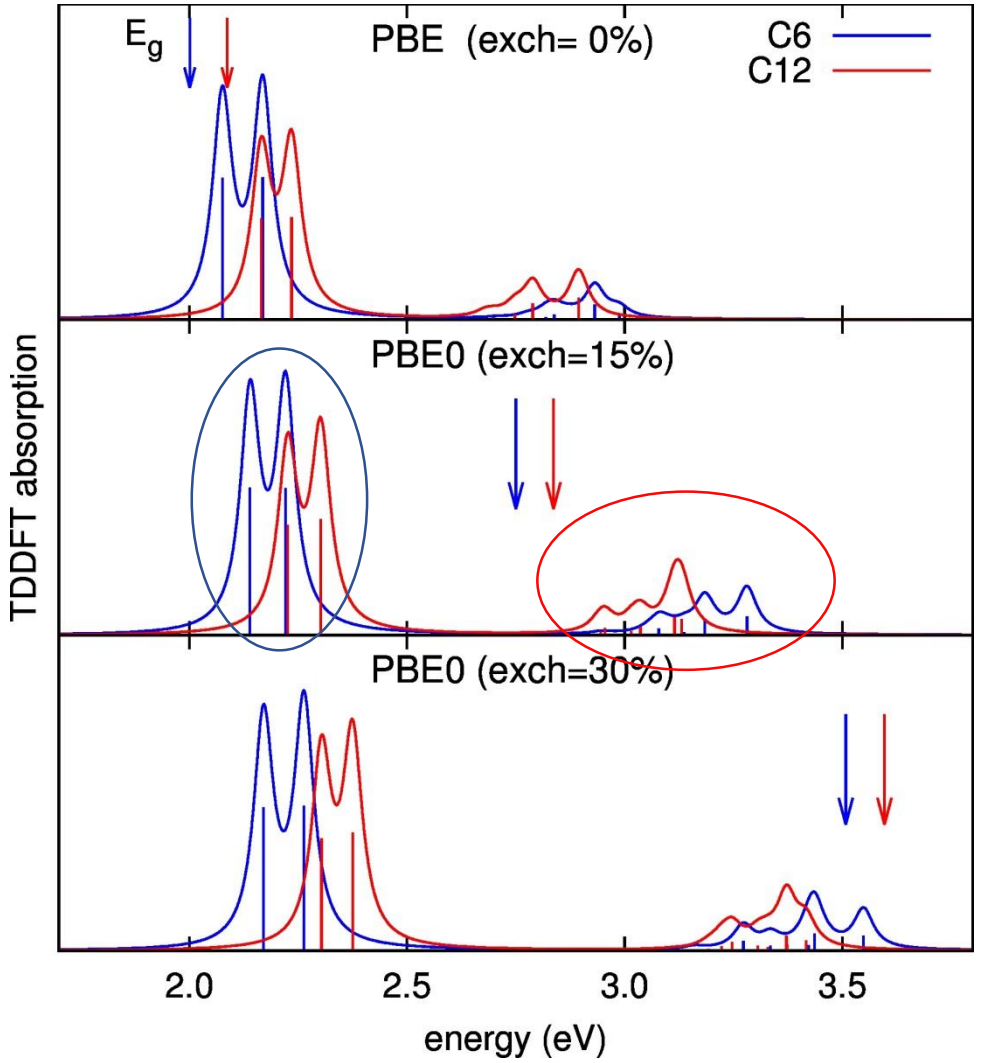


out-of-plane

		BG	b_1	b_2	b_3	θ	β_1	β_2
C6	mono	2.06	3.19	3.18	3.26	152	92	88
	ortho	2.04	3.20	3.20	3.25	154	89	91
C12	mono	2.05	3.22	3.21	3.22	153	88	92
	ortho	**2.38**	3.23	3.24	3.24	**143**	**94**	**86**



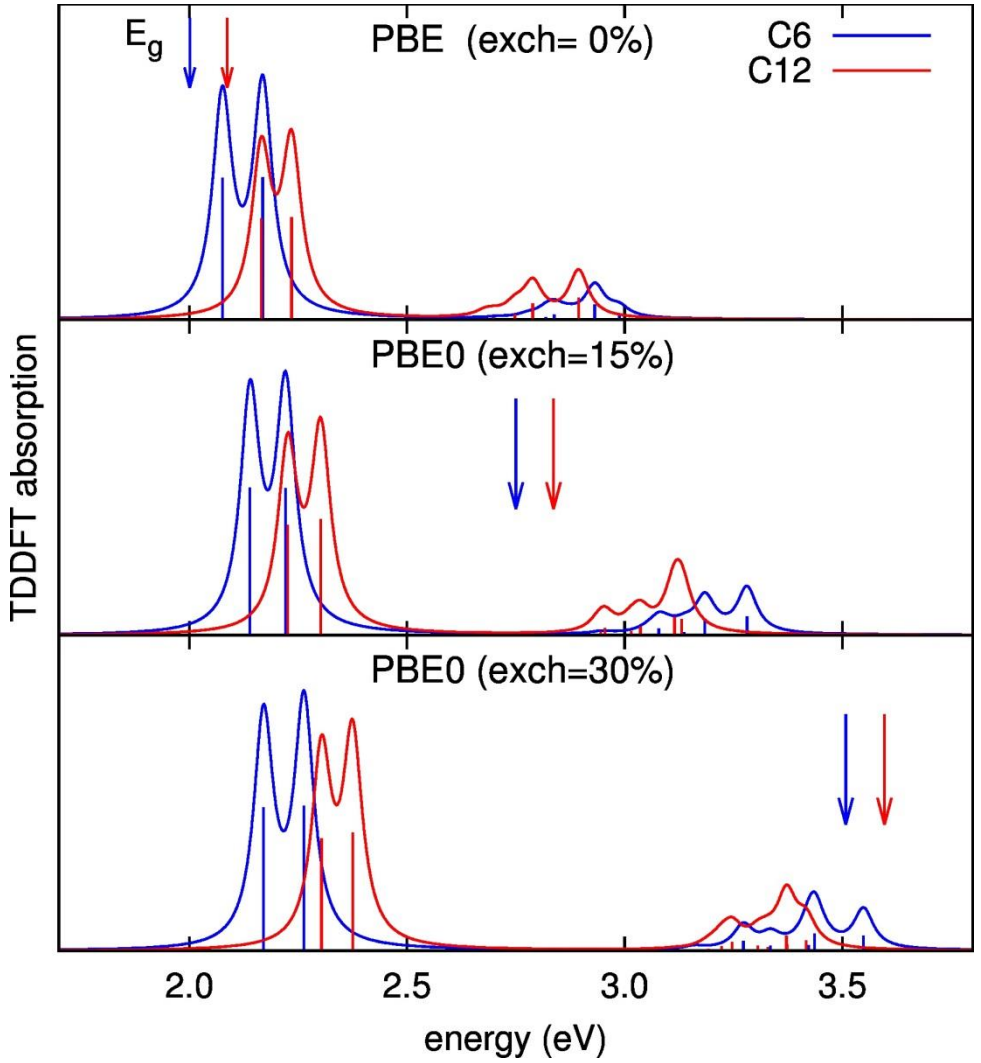
Optical properties



Energy of the excited states

BG of the 2 systems at different level of theory

Optical properties



Energy of the excited states

BG of the 2 systems at different level of theory

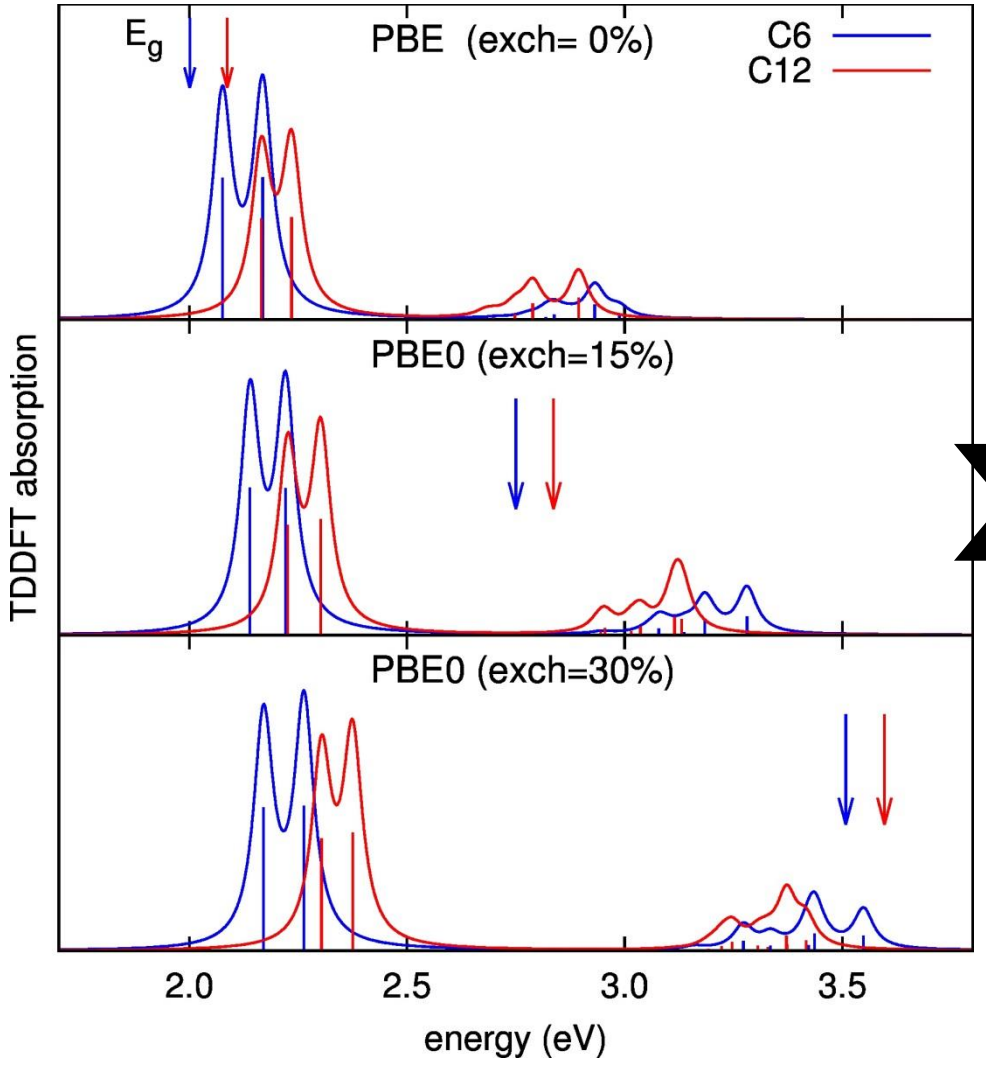
	Experimental data		Calculations (HF 15%)	
	Excitonic transition (eV)	Exciton binding energy (eV)	Excitonic transition (eV)	Exciton binding energy (eV)
C6	2.37	0.36	2.14-2.22	0.6
C12	2.57	/	2.18-2.31	/

→ **Consistant with experimental data**

E. P. Booker, et al., *J. Am. Chem. Soc.* **2017**

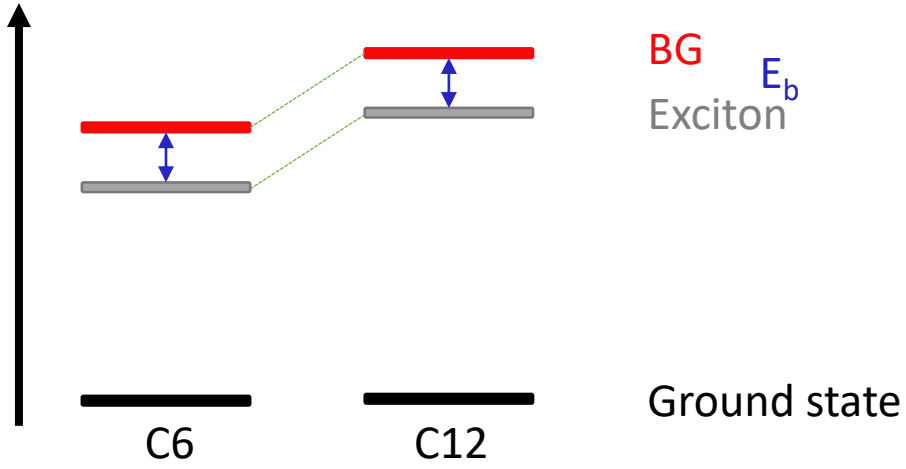
K. Tanaka, et al., *Phys. Rev. B* **2005**

Optical properties



Energy of the excited states

BG of the 2 systems at different level of theory



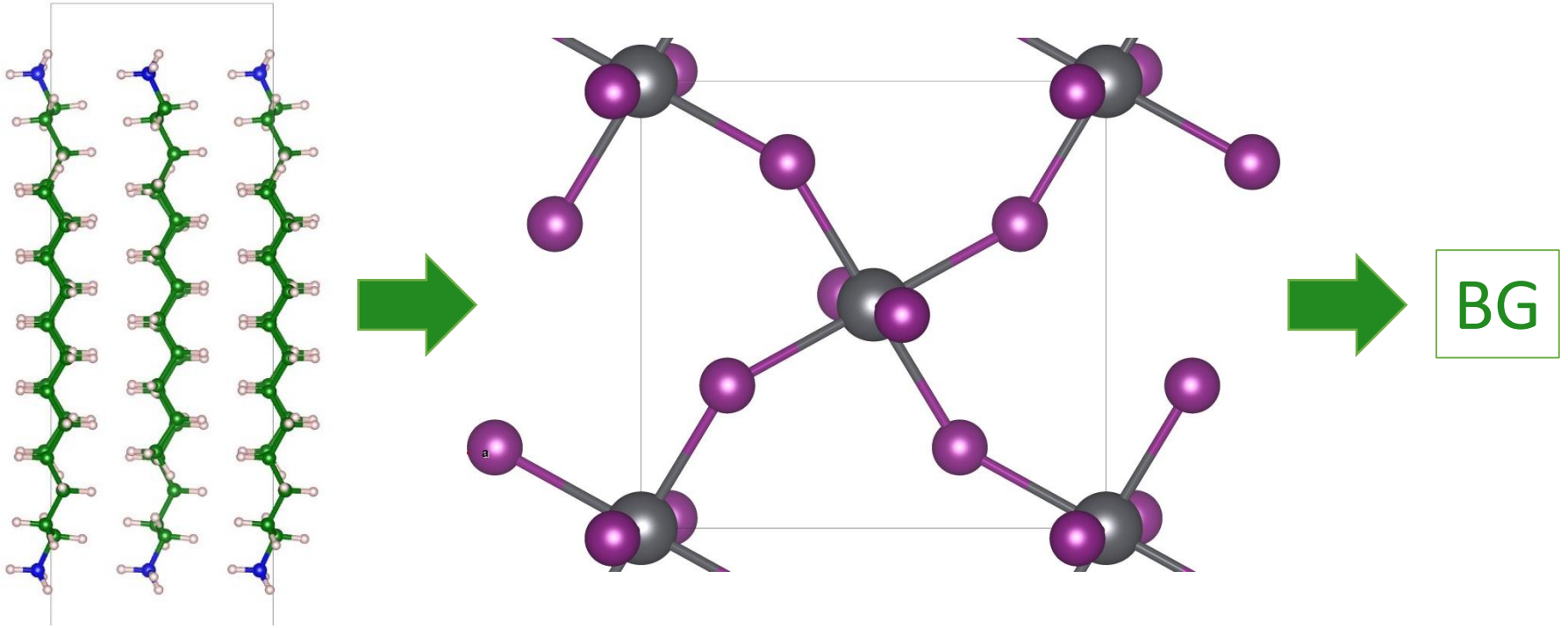
➔Blue shift from C6 to C12 as discussed before

➔The length of the cation has an effect on optical response via the BG, no effect on exciton binding energy E_b

Summary

- Methodology ➔ PBE0 30% of HF exchange + SOC lead to a good description of the electronic properties
  ➔ PBE0 15% HF seems to be better for optical properties (without SOC)

- Even if **the organic part is not directly involved in the description of the frontier crystaline orbitals**, it has **an indirect effect** on the electronic structure, namely the value of the bandgap! Same effect on the optical gap, no significant change on the exciton binding energy



Acknowledgement

- Laboratory for Chemistry of Novel Materials

UMONS Université de Mons

CMN

- UMONS Research Institute for Materials Science and Engineering

materials
UMONS RESEARCH INSTITUTE FOR MATERIALS SCIENCE AND ENGINEERING

nG

- nanoGe Fall Meeting

THANK YOU FOR YOUR KIND ATTENTION

Phase transition

Orthorhombic → Monoclinic

In C12PbI perovskites with should be accompanied by a sudden change in the band gap!!!

THIS IS ACTUALLY THE CASE FOR C10PbI

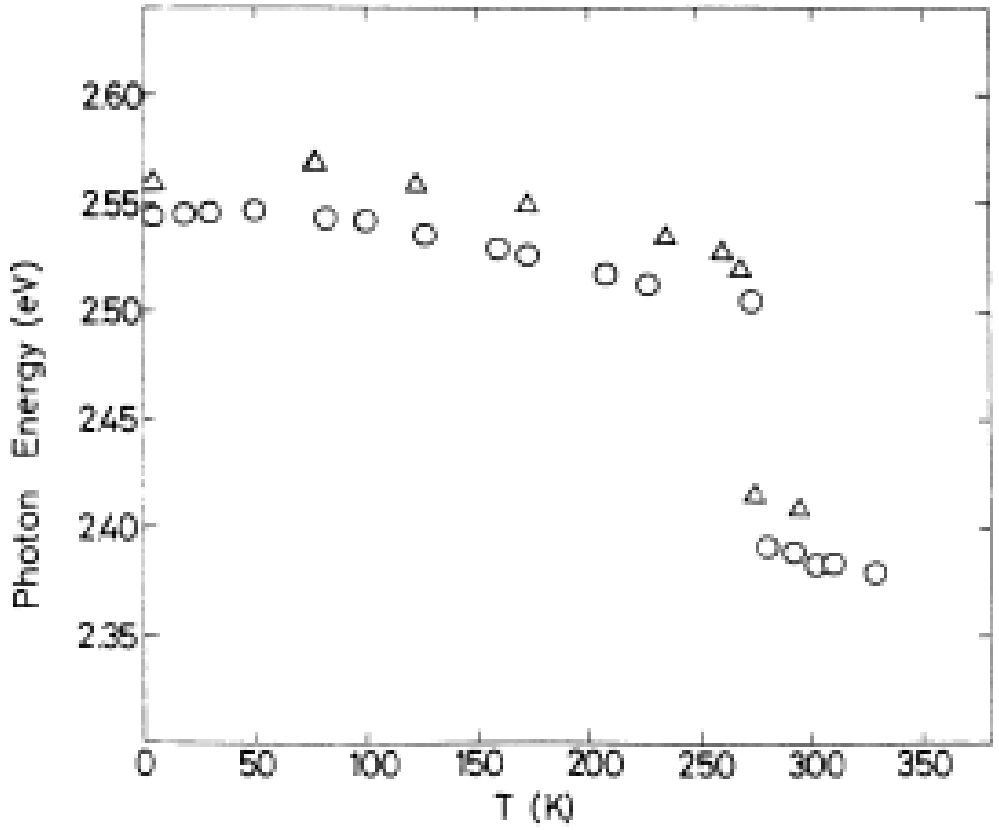


FIG. 7. Energies of absorption (Δ) and luminescence peaks (○) in a single crystal of $(C_{10}H_{21}NH_3)_2PbI_4$ as a function of temperature.

Phys. Rev. B, 42, 11099 (1990)

Electronic properties

Energy of the valence and conduction band edge for the C6 and C12 polymorphs

Table S1. Energy of the valence band edge (VBE) and conduction band edge (CBE) and band gap (Eg), computed for the monoclinic and orthorhombic polymorphs of C6 and C12, using the various computational approaches. All energies are referred to the averaged electrostatic potential of the crystal cell, computed using the various methods. Data in eV.

method	VBE	CBE	Eg	VBE	CBE	Eg
		C6-monoclinic			C6-orthorhomib	
PBE	-0.34	1.70	2.04	-0.47	1.55	2.02
PBE+SOC	-0.39	0.99	1.38	-0.55	0.80	1.35
PBE0	-1.23	2.28	3.51	-1.60	1.82	3.42
PBE CORRECT	-1.28	1.57	2.85	-1.68	1.07	2.75
PBE0+SOC	-1.41	1.32	2.73	-1.41	1.32	2.73
		C12-monoclinic			C12-orthorhombic	
PBE	-0.45	1.72	2.17	-0.23	2.12	2.44
PBE+SOC	-0.50	1.00	1.50	-0.37	1.34	1.71
PBE0	-1.57	2.03	3.60	-1.46	2.43	3.89
PBE CORRECT	-1.68	1.07	2.93	-1.46	1.65	3.11
PBE0+SOC	-1.45	1.42	2.87			

Electronic properties

Density of States (DOS) of the C6 and C12 polymorphs

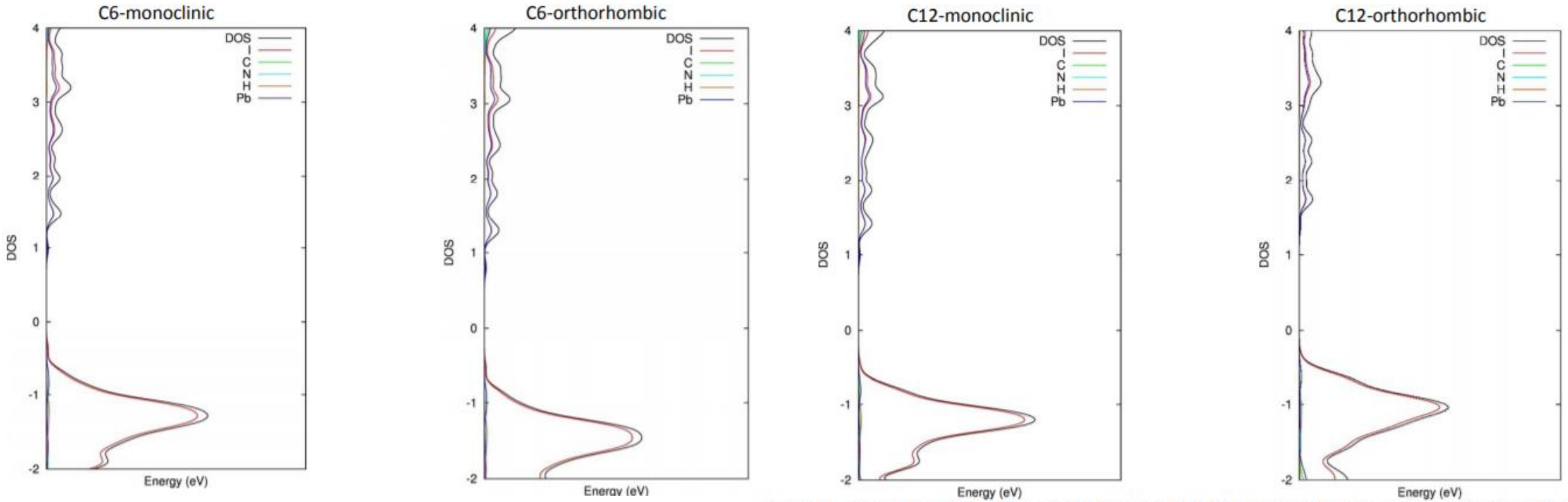


Figure S2. Atomic Density of State of the C6PbI and C12PbI polymorphs. The contribution from the different chemical elements is listed. Electronic structure obtained with the PBE functional for the description of the exchange-correlation interaction, including spin-orbit coupling.

Variable cell

Comparison of the results for fixed cell and variable cell calculation

Table S3. Comparison of the band gap a (E_g, PBE), and structural parameters (bond lengths , b_1, b_2, b_3, and Pb-I-PB angle θ) for fixed cell and variable cell relaxations.

system		E_g (eV)	b_1 (Å)	b_2 (Å)	b_3 (Å)	θ (°)
			fixed cell			
C6	mono	2.04	3.18	3.19	3.26	152.3
	ortho	2.02	3.20	3.19	3.25	153.8
C12	mono	2.17	3.22	3.21	3.23	153.4
	ortho	2.44	3.24	3.23	3.23	143.4
			variable cell			
C6	mono	1.98	3.09	3.09	3.23	148.8
	ortho	2.04	3.10	3.10	3.23	146.5
C12	mono	2.00	3.07	3.08	3.23	146.3
	ortho	2.33	3.07	3.09	3.22	138.9

THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Letter

pubs.acs.org/JPCL

Tuning the Optoelectronic Properties of Two-Dimensional Hybrid Perovskite Semiconductors with Alkyl Chain Spacers

Claudio Quarti,* Nadège Marchal, and David Beljonne

Laboratory for Chemistry of Novel Materials, University of Mons, Place du Parc, 20, B-7000 Mons, Belgium

Supporting Information

ABSTRACT: Layered two-dimensional organo-metal halide perovskites are currently in the limelight, largely because their versatile chemical composition offers the promise of tunable photophysical properties. We report here on (time-dependent) density functional theory [(TD)DFT] calculations of alkyl-ammonium lead iodide perovskites, where significant changes in the electronic structure and optical properties are predicted when using long versus short alkyl chain spacers. The mismatch between the structural organization in the inorganic and organic layers is epitomized for dodecyl chains that adopt a supramolecular packing similar to that of polyethylene, at the cost of distorting the inorganic frame and, in turn, opening the electronic band gap. These results rationalize recent experimental data and demonstrate that the optoelectronic properties of layered halide perovskite semiconductors can be modified through the use of electronically inert organic saturated chains.