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

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Introduction

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- Introduction
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- Results
Hybrid perovskites?

Methylammonium Lead iodide
(MAPbI$_3$)

Perovskite structure $\rightarrow$ ABX$_3$

Applications: Photovoltaics

Methylammonium Lead iodide (MAPbI$_3$)

Perovskite structure $\rightarrow$ ABX$_3$

3D Perovskite

- Low temperature solution synthesis
- PV quantum efficiency (23.3%)
- Instability due to ionic diffusion in the inorganic network
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
• Goldsmich tolerance factor

\[ t = \frac{r_A + r_X}{\sqrt{2(r_B + r_X)}} \]

0.7 > t > 1

2D Perovskite

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

Organic « spacer »

cation

G. Grancini, et al., Nat. Comm. 8 2017
M. Yuan, L. N. Quan et al., Nat. Nanotechnol. 2016
Dimensionality: 3D $\rightarrow$ 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 $\rightarrow$ 2D

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3. Electronic/dielectric confinement

- Stronger excitonic effect
- Larger bandgap (BG)
Dimensionality: 3D $\rightarrow$ 2D

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

$(C_6H_{13}NH_3)_2PbI_4$

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

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

\((C_6H_{13}NH_3)_2PbI_4\)

Monoclinic (P21/a) 258K \(\rightarrow\) 268K

Orthorhombic (Pbca)

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

Orthorhombic (Pbca) 306K \(\rightarrow\) 315K

Monoclinic (P21/a)

Methodology

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

\[ \rightarrow \text{Materials modeling & electronic properties} \]
\[ \rightarrow \text{Density Functional Theory (DFT): Plane Wave basis set (PW)} \]
\[ \rightarrow \text{PBE (GGA functional)} \]

\[
\text{DFT (static, ground state)}
\]

- **Grimme correction:**
  \[
  E_{\text{DFT-\textit{D}}} = E[\rho] + E_{\text{disp}} \quad \text{et} \quad E_{\text{disp}} = -s_6 \sum_{i=j}^{\text{Nat}-1} \sum_{j=i+1}^{\text{Nat}} \frac{C_{ij}^6}{R_{ij}^6} \frac{1}{1 + e^{-d(R_{ij}/R_r - 1)}}
  \]

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 \( E_{disp} = -s_6 \sum_{i=j}^{Nat-1} \sum_{j=i+1}^{Nat} \frac{C_{ij}}{R_{ij}^6} \frac{1}{1 + e^{-d(R_{ij}/R_0 - 1)}} \)

• Spin-orbit coupling (SOC)

• Hybrid functional (PBE0)

Methodology

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

DFT (static, ground state) \[ \rightarrow \] TDDFT (static, excited state)

- **Grimme correction:**
  \[ E_{DFT-D} = E[\rho] + E_{disp} \]
  \[ E_{disp} = -s_6 \sum_{i=j}^{Nat-1} \sum_{j=i+1}^{Nat} \frac{C_{ij}}{R_{ij}^6} \frac{1}{1 + e^{-d(\frac{R_{ij}}{R_{r}} - 1)}} \]

- **Spin-orbit coupling (SOC)**
- **Hybrid functional (PBE0)**
Methodological study

- PBE (GGA) agrees with experimental BG

MAPbI$_3$

Methodological study

MAPbI$_3$

- PBE (GGA) agrees with experimental BG
- GW approximation $\Rightarrow$ BG opening of 1 eV

Methodological study

MAPbI$_3$

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

Methodological study

MAPbI$_3$

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

Compensation of errors

$\Rightarrow$ PBE agrees with SOC-GW and is in good agreement with experimental data

Methodological study

$(\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{PbI}_4$

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

---

Methodological study

\((\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{PbI}_4\)

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

Methodological study

\[(C_6H_{13}NH_3)_2PbI_4\]

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

No compensation of errors
Better Exchange interaction description overcomes SOC correction

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

SOC \rightarrow BG closing of 0.66 eV

PBE0 \rightarrow BG opening of 1.47 eV

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

No compensation of errors
Better Exchange interaction description overcomes SOC correction

Methodological study

\((C_6H_{13}NH_3)_2PbI_4\)

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

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

Methodological study

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

\((\text{C}_6\text{H}_{13}\text{NH}_3)\text{PbI}_4\)

- PBE (GGA) BG does not agree with experimental data (2.7 eV)
- SOC $\Rightarrow$ BG closing of 0.66 eV
- PBE0 $\Rightarrow$ 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

Methodological study

\[(\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{PbI}_4\]

- Effect of SOC mostly on CBE (splitting of \(j=1/2 \text{ and } 3/2\) on Pb)
- Effect on PBE0 on both bands, but more on VBE

- PBE (GGA) BG does not agree with experimental data (2.7 eV)
- SOC \(\rightarrow\) BG closing of 0.66 eV
- PBE0 \(\rightarrow\) 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

Methodological study

\((C_6H_{13}NH_3)_2PbI_4\)

PBE0 calculation

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

## Electronic properties

<table>
<thead>
<tr>
<th>PBE</th>
<th>$E_g$ (eV)</th>
<th>$m^*_h$</th>
<th>$m^*_e$</th>
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<tr>
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<td>2.06</td>
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<td>0.17</td>
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<tr>
<td>C6 (orthorhombic)</td>
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<td>0.17</td>
</tr>
<tr>
<td>C12 (monoclinic)</td>
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<td>0.22</td>
<td>0.17</td>
</tr>
<tr>
<td>C12 (orthorhombic)</td>
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<td>0.40</td>
<td>0.24</td>
</tr>
<tr>
<td>MAPI</td>
<td>1.6</td>
<td>0.15</td>
<td>0.13</td>
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</tbody>
</table>

In (100) direction
Electronic properties

<table>
<thead>
<tr>
<th></th>
<th>$E_g$ (eV)</th>
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<td>0.13</td>
</tr>
</tbody>
</table>

→ Different behaviour of C12 (orthorhombic) → WHY ?

→ Same observations at other levels of theory (SOC – PBE0)

Distance between inorganic layers = length of the organic cation
Structural effect

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<tr>
<th></th>
<th>BG</th>
<th>b₁</th>
<th>b₂</th>
<th>b₃</th>
<th>θ</th>
<th>β₁</th>
<th>β₂</th>
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<td>92</td>
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<td>3.25</td>
<td>154</td>
<td>89</td>
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<td>3.23</td>
<td>3.24</td>
<td>3.24</td>
<td>143</td>
<td>94</td>
</tr>
</tbody>
</table>
Influence from the organic component

Side view

polyethylene

Influence from the organic component

C6 mono

C6 ortho

C12 mono

polyethylene

Side view
Alkyl chains stacked like PE in C12 orthorhombic $\Rightarrow$ tilt of PbI octohedras and increase the BG!
Influence from the organic component

- Alkyl chains stacked like PE in C12 orthorhombic → tilt of PbI octohedras and increase the BG!
**Structural effect**

- Influence of organic component

- Alkyl chains stacked like PE

- Tilt of Pb-I octahedra: BG↗

- Consistant with the literature


### Table

<table>
<thead>
<tr>
<th></th>
<th>BG</th>
<th>$b_1$</th>
<th>$b_2$</th>
<th>$b_3$</th>
<th>$\theta$</th>
<th>$\beta_1$</th>
<th>$\beta_2$</th>
</tr>
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<td>C6</td>
<td>mono</td>
<td>2.06</td>
<td>3.19</td>
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<td>89</td>
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Structural effect

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<th></th>
<th>BG</th>
<th>$b_1$</th>
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<th>$b_3$</th>
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<th>$\beta_1$</th>
<th>$\beta_2$</th>
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<td>3.18</td>
<td>3.26</td>
<td>152</td>
<td>92</td>
<td>88</td>
</tr>
<tr>
<td>C6 ortho</td>
<td>2.04</td>
<td>3.20</td>
<td>3.20</td>
<td>3.25</td>
<td>154</td>
<td>89</td>
<td>91</td>
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<tr>
<td>C12 mono</td>
<td>2.05</td>
<td>3.22</td>
<td>3.21</td>
<td>3.22</td>
<td>153</td>
<td>88</td>
<td>92</td>
</tr>
<tr>
<td>C12 ortho</td>
<td>2.38</td>
<td>3.23</td>
<td>3.24</td>
<td>3.24</td>
<td>143</td>
<td>94</td>
<td>86</td>
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</tbody>
</table>
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

<table>
<thead>
<tr>
<th>System</th>
<th>Experimental data</th>
<th>Calculations (HF 15%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Excitonic transition (eV)</td>
<td>Exciton binding energy (eV)</td>
</tr>
<tr>
<td>C6</td>
<td>2.37</td>
<td>0.36</td>
</tr>
<tr>
<td>C12</td>
<td>2.57</td>
<td>/</td>
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</table>

Consistant with experimental data

Optical properties

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

Blue shift from C6 to C12 as discussed before.

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 Research Institute for Materials Science and Engineering

• nanoGe Fall Meeting

THANK YOU FOR YOUR KIND ATTENTION
Phase transition

Orthorhombic $\rightarrow$ Monoclinic

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

**THIS IS ACTUALLY THE CASE FOR C10PbI**

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.

<table>
<thead>
<tr>
<th>method</th>
<th>VBE</th>
<th>CBE</th>
<th>Eg</th>
<th>VBE</th>
<th>CBE</th>
<th>Eg</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>C6-monoclinic</td>
<td>C6-orthorhombic</td>
<td>C12-monoclinic</td>
<td>C12-orthorhombic</td>
<td></td>
<td></td>
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<tr>
<td>PBE</td>
<td>-0.34</td>
<td>1.70</td>
<td>2.04</td>
<td>-0.47</td>
<td>1.55</td>
<td>2.02</td>
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<td>PBE+SOC</td>
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<td>1.38</td>
<td>-0.55</td>
<td>0.80</td>
<td>1.35</td>
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<td>PBE0</td>
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<td>3.51</td>
<td>-1.60</td>
<td>1.82</td>
<td>3.42</td>
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<tr>
<td>PBE CORRECT</td>
<td>-1.28</td>
<td>1.57</td>
<td>2.85</td>
<td>-1.68</td>
<td>1.07</td>
<td>2.75</td>
</tr>
<tr>
<td>PBE0+SOC</td>
<td>-1.41</td>
<td>1.32</td>
<td>2.73</td>
<td>-1.41</td>
<td>1.32</td>
<td>2.73</td>
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<tr>
<td>PBE</td>
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<tr>
<td>PBE+SOC</td>
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<td>1.50</td>
<td>-0.37</td>
<td>1.34</td>
<td>1.71</td>
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Electronic properties

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

Figure S2. Atomic Density of State of the C6Pbl and C12Pbl 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 $a (E_g, \text{PBE})$, and structural parameters (bond lengths, $b_1$, $b_2$, $b_3$, and Pb-I-Pb angle $\theta$) for fixed cell and variable cell relaxations.

<table>
<thead>
<tr>
<th>system</th>
<th>$E_g$ (eV)</th>
<th>$b_1$ (Å)</th>
<th>$b_2$ (Å)</th>
<th>$b_3$ (Å)</th>
<th>$\theta$ (°)</th>
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<tr>
<td></td>
<td></td>
<td>fixed cell</td>
<td>variable cell</td>
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<tr>
<td>C6</td>
<td></td>
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<tr>
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Tuning the Optoelectronic Properties of Two-Dimensional Hybrid Perovskite Semiconductors with Alkyl Chain Spacers

Claudio Quarti,* Nadège Marchal, and David Beljonne

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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.