# Domain-dependent Electronic Structure and Optical Absorption Property in Hybrid Organic-inorganic Perovskite

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## Supporting Information Available

### 1. Lattice constant parameters for different domains of $CH_3NH_3PbI_3$

To optimize the crystalline structures with different domains, the $\sqrt{2} \times \sqrt{2}$ supercell, with 8 cations, 8 Pb atoms and 24 I atoms are used. For obtaining the order-arranged conformations, the cations are aligned exactly into the same direction at the initial stage, and locate systematically inside the Pb-I framework, while the crystalline structure is in the cubic phase. Then, both lattices and atomic positions are allowed to be relaxed. In this way, we can achieve the stable configurations of hybrid perovskite with various orders.

The lattice constants for nine kinds of domains of $CH_3NH_3PbI_3$, $CF_3NH_3PbI_3$ and $CH_3SH_2PbI_3$ are listed as Table S1. Here, a, b and c represent the length of lattice vectors $\vec{A}_1$, $\vec{A}_2$ and $\vec{A}_3$, while α, β and γ are the angles between $\vec{A}_2$ and $\vec{A}_3$, $\vec{A}_1$ and $\vec{A}_3$, $\vec{A}_1$ and $\vec{A}_2$, respectively. The tilting angles of $PbI_3$ octahedra are also listed.

| | Domain | a(Å) | b(Å) | c(Å) | α(°) | β(°) | γ(°) | Pb-I angle |
|---|---|---|---|---|---|---|---|---|
| $CH_3NH_3PbI_3$ | **S-FM** | 12.97 | 12.88 | 12.90 | 89.93 | 90.93 | 90.09 | 85.03 |
| | **S-HFM** | 12.80 | 12.86 | 12.95 | 90.02 | 89.33 | 89.97 | 87.08 |
| | **S-AFM** | 12.85 | 12.91 | 12.95 | 90.06 | 90.04 | 89.93 | 85.70 |
| | **P-FM** | 12.87 | 12.99 | 12.72 | 89.88 | 90.27 | 88.64 | 86.89 |
| | **P-HFM** | 12.85 | 12.84 | 12.87 | 90.48 | 89.77 | 89.65 | 86.78 |
| | **P-AFM** | 12.90 | 12.85 | 12.74 | 89.98 | 89.82 | 88.77 | 86.51 |
| | **B-FM** | 12.81 | 12.88 | 12.83 | 91.93 | 88.77 | 88.42 | 88.98 |
| | **B-HFM** | 12.91 | 12.84 | 12.90 | 90.56 | 88.09 | 89.62 | 86.25 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **B-AFM** | 12.81 | 12.85 | 12.82 | 91.72 | 88.90 | 87.40 | 86.25 |
| $CF_3NH_3PbI_3$ | **S-FM** | 13.09 | 12.72 | 13.22 | 89.90 | 90.99 | 89.75 | 85.22 |
| | **S-HFM** | 12.78 | 12.95 | 13.33 | 90.03 | 90.47 | 90.03 | 85.24 |
| | **S-AFM** | 12.80 | 12.89 | 13.18 | 90.12 | 89.73 | 89.95 | 89.86 |
| | **P-FM** | 13.07 | 13.02 | 12.71 | 90.43 | 88.86 | 90.04 | 88.66 |
| | **P-HFM** | 12.97 | 12.97 | 13.10 | 90.09 | 90.05 | 90.84 | 86.34 |
| | **P-AFM** | 14.15 | 12.75 | 12.68 | 89.91 | 92.42 | 89.89 | 88.44 |
| | **B-FM** | 13.01 | 12.96 | 12.87 | 90.72 | 89.31 | 89.10 | 87.08 |
| | **B-HFM** | 13.01 | 12.83 | 13.27 | 90.53 | 89.40 | 90.86 | 89.26 |
| | **B-AFM** | 12.97 | 12.94 | 12.79 | 89.93 | 89.78 | 88.83 | 86.77 |
| $CH_3SH_2PbI_3$ | **S-FM** | 13.06 | 12.79 | 12.95 | 89.80 | 86.53 | 90.02 | 89.74 |
| | **S-HFM** | 12.84 | 12.87 | 13.03 | 89.90 | 89.93 | 90.05 | 84.43 |
| | **S-AFM** | 12.91 | 12.81 | 13.00 | 90.02 | 90.03 | 90.08 | 89.51 |
| | **P-FM** | 13.02 | 12.99 | 12.87 | 90.58 | 90.61 | 87.93 | 84.60 |
| | **P-HFM** | 13.00 | 13.00 | 12.86 | 89.94 | 90.19 | 88.00 | 84.76 |
| | **P-AFM** | 12.99 | 12.99 | 12.88 | 90.06 | 90.43 | 88.68 | 85.00 |
| | **B-FM** | 12.99 | 12.84 | 13.00 | 89.84 | 86.99 | 90.23 | 86.56 |
| | **B-HFM** | 12.96 | 12.82 | 12.97 | 90.01 | 89.94 | 90.44 | 87.65 |
| | **B-AFM** | 12.96 | 12.89 | 12.89 | 89.22 | 89.25 | 89.26 | 87.06 |

**Table S1. The lattice constants for nine kinds of domains of $CH_3NH_3PbI_3$, $CF_3NH_3PbI_3$ and $CH_3SH_2PbI_3$.**

## 2. Various kinds of cations we study

The conformation of various kinds of cations are shown as Figure S1.

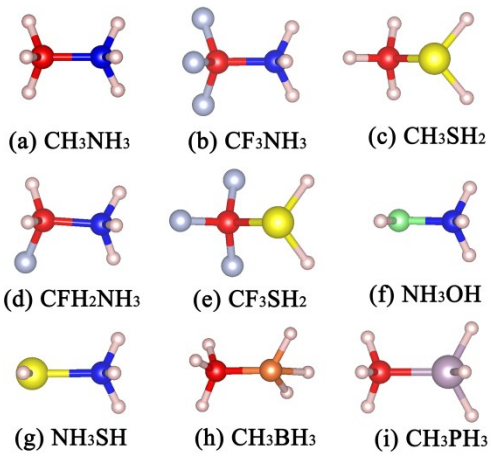


**Figure S1. Conformation of various kinds of cations we have studied.**

### 3. Band structures for different domains of $CF_3NH_3PbI_3$

The band structures for different domains of $CF_3NH_3PbI_3$ are shown as Figure S2.The band gaps are in the region of 1.63 ~ 2.07 eV. Among these domains, P-FM, P-HFM, P-AFM, B-FM, B-HFM, B-AFM exhibit direct gap feature, while S-FM, S-HFM and S-AFM show indirect gap feature.

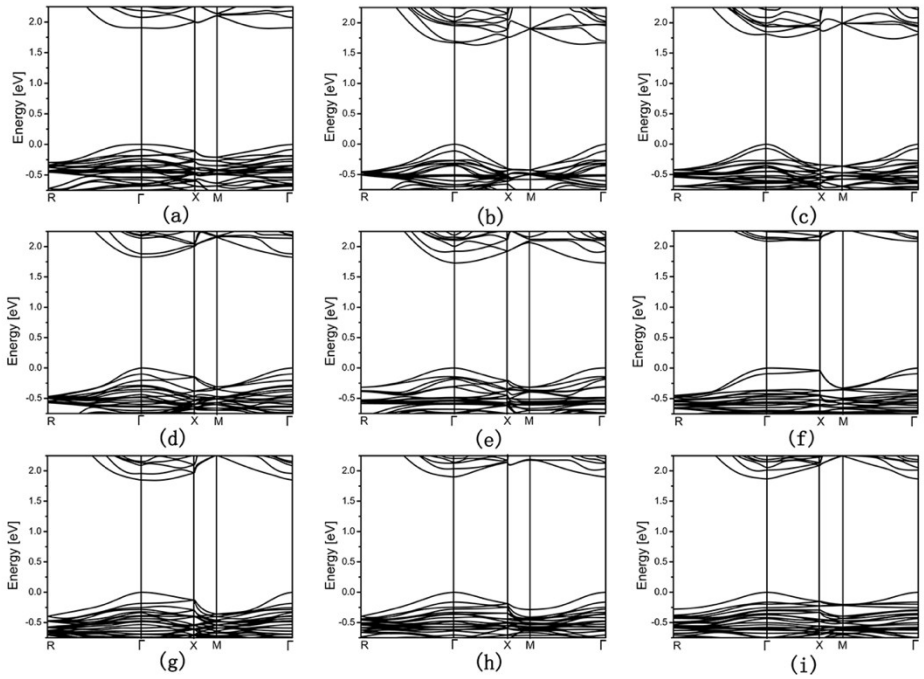


**Figure S2. The band structures of $CF_3NH_3PbI_3$ for various domains. From (a) to (i), they are in order of different domain, S-FM, S-HFM, S-AFM, P-FM, P-HFM, P-AFM, B-FM, B-HFM and B-AFM. For band structure simulations, the k-points we selected are along the line of R→Γ→X→M→Γ. R: (0.5, 0.5, 0.5), Γ: (0,0,0), X: (0.5, 0,0), M: (0.5, 0.5, 0).**

### 4. Band structures for different domains of $CH_3SH_2PbI_3$

The band structures for different domains of $CH_3SH_2PbI_3$ are shown as Figure S3. The band gaps between different domains are similar, in the region of ~ 1.66 eV. Furthermore, all the domains exhibit direct gap feature.

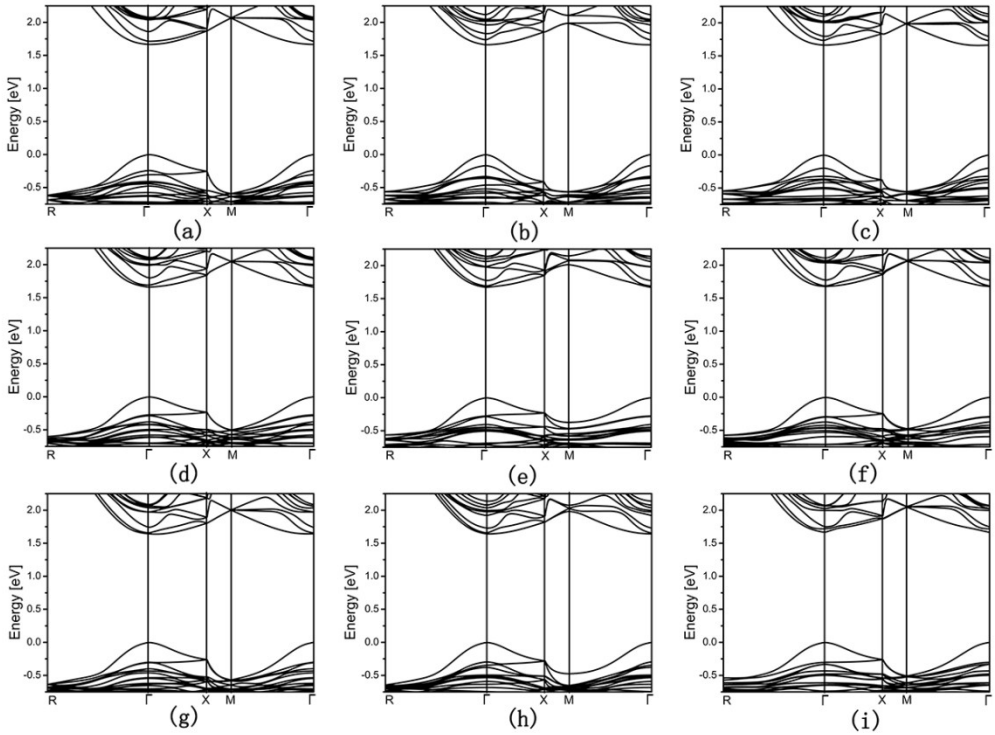


**Figure S3. The band structures of $CH_3SH_2PbI_3$ for various domains. From (a) to (i), they are in order of different domain, S-FM, S-HFM, S-AFM, P-FM, P-HFM, P-AFM, B-FM, B-HFM and B-AFM. For band structure simulations, the k-points we selected are along the line of R→Γ→X→M→Γ. R: (0.5, 0.5, 0.5), Γ: (0,0,0), X: (0.5, 0,0), M: (0.5, 0.5, 0).**

### 5. Activation barrier between FM domain and AFM domain in $CF_3NH_3PbI_3$

Here, we study the activation barrier transfer from FM domain to AFM domain by climbing-image nudged elastic band (CI-NEB) method, the energy evolution profile is shown as Figure S4. According to our simulation, the transfer between FM domain and AFM domain should experience an activation barrier of 1.15 eV. Comparing with the rotation barrier of cation in $CH_3NH_3PbI_3$ achieved in previous work, the rotation in $CF_3NH_3PbI_3$ is much more difficult, which means that the rotation in $CF_3NH_3PbI_3$ can be much harder, and the ordered domain and overall polarization effect has a much higher probability to achieve against the thermal fluctuation.

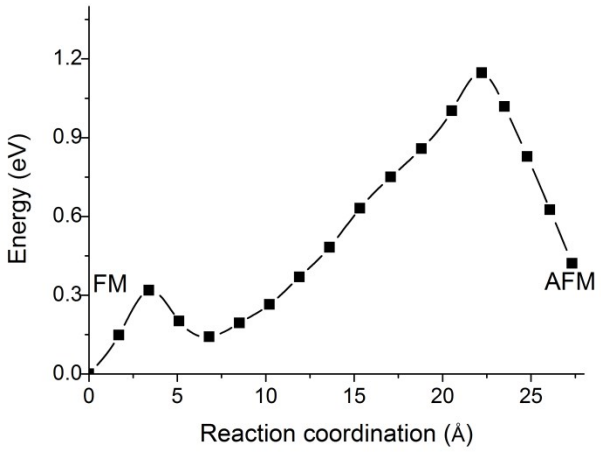


**Figure S4. Energy profile when the domain transfers from FM into AFM in $CF_3NH_3PbI_3$.**

### 6. Lattice constant for various kinds of MAPbI3 with different MA

In Table S2, we list the lattice constant for various kinds of MAPbI3 with MA= $CFH_2NH_3^+$, $CF_3SH_2^+$, $NH_3OH^+$, $NH_3SH^+$, $CH_3BH_3^+$, $CH_3PH_3^+$. It can be seen that all of these kinds of materials can be viewed as hybrid perovskite with approximately cubic structures.

| Structure | a(Å) | b(Å) | c(Å) | α(°) | β(°) | γ(°) |
|---|---|---|---|---|---|---|
| **$CFH_2NH_3PbI_3$** | 12.94 | 12.90 | 12.94 | 89.51 | 88.90 | 88.41 |
| **$CF_3SH_2PbI_3$** | 13.28 | 12.68 | 13.11 | 89.94 | 89.00 | 90.02 |
| **$NH_3OHPbI_3$** | 12.72 | 12.78 | 13.06 | 90.02 | 86.18 | 89.92 |
| **$NH_3SHPbI_3$** | 12.86 | 12.91 | 13.01 | 90.00 | 89.21 | 90.04 |
| **$CH_3BH_3PbI_3$** | 13.35 | 12.97 | 13.04 | 98.36 | 86.64 | 85.27 |
| **$CH_3PH_3PbI_3$** | 13.73 | 12.85 | 12.92 | 89.96 | 88.01 | 89.95 |

**Table S2 Lattice constant for various kinds of MAPbI3 with different MA**

## References:

(5) Wang, J. T. W.; Ball, J. M.; Barea, E. M.; Abate, A.; Alexander-Webber, J. A.; Huang, J.; Saliba, M.; Mora-Sero, L.; Bisquert, J.; Snaith, H. J.; Nicholas, R. J. *Nano Lett.* **2013**, 14, 724-730.