Supporting Information

Molecular Design of Three-Dimensional Metal-Free A(NH$_4$)$_3$X$_3$ Perovskites for Photovoltaic Applications

Jie Bie, Dai-Bei Yang, Ming-Gang Ju, Qiang Pan, Yu-Meng You, Wei Fa, Xiao Cheng Zeng, and Shuang Chen

†Kuang Yaming Honors School, Nanjing University, Nanjing, Jiangsu 210023, China
‡National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing, Jiangsu 210093, China
§School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210023, China
‖School of Physics, Southeast University, Nanjing 211189, China
$Jiangsu$ Key Laboratory for Science and Applications of Molecular Ferroelectrics, Southeast University, Nanjing 211189, China
#Department of Chemistry, University of Nebraska−Lincoln, Lincoln, Nebraska 68588, United States
⊥Institute for Brain Sciences, Nanjing University, Nanjing 210023, China

Emails: chenshuang@nju.edu.cn; xzeng1@unl.edu; wfa@nju.edu.cn
S1. Choice of Density Function Theory (DFT) Functionals for Geometry Optimizations of Three-Dimensional (3D) Metal-Free Perovskites

The PBE-D3, PBEsol, PBEsol-D3, SCAN (meta-GGA), and SCAN-D3 functionals are chosen to optimize the structures of 3D metal-free perovskites, (MDABCO)(NH$_4$)$_3$ (X = Br and I), as benchmark to determine a better functional for our first-principles calculations. To this end, the computed and experimentally measured lattice parameters are summarized in Table S1 for comparison. Notably, we find the lattice parameters, especially for lattice constants, of the benchmark perovskites calculated based on PBEsol-D3 and SCAN-D3 largely deviate from the experimental lattice parameters. Therefore, we focus on the performance of PBE-D3, PBEsol, and SCAN functionals as follows. For the geometry optimization of (MDABCO)(NH$_4$)Br$_3$, these three functionals give comparable performance, and all predict slightly smaller lattice parameters than the experimental ones. Specifically, the optimized lattice constants ($a$, $b$, and $c$) estimated are all about 0.3 Å smaller than the experimental ones, and the lattice angles ($\alpha$, $\beta$, and $\gamma$) respectively estimated by the PBE-D3-, PBEsol-, and SCAN-based geometry optimization are about 0.5°, 0.4°, and 0.8° smaller than the experimental ones. It seems that the PBEsol functional performs a little better than PBE-D3 and SCAN. For the geometry optimization of (MDABCO)(NH$_4$)I$_3$, the SCAN-based geometry optimization predicts the closest lattice parameters to the experimental ones, especially for the lattice constants. The PBE-D3 functional is slightly better than PBEsol due to larger lattice constants than those predicted by PBEsol and nearly the same lattice angles as those predicted by PBEsol and SCAN. Among different DFT functionals considered here, the PBE-D3 functional is selected to perform the geometry optimization due to the less computational resource required.
**Table S1.** Comparison of computed and experimental lattice parameters of 3D metal-free perovskites, (MADABCO)(NH₄)X₃ (X = Br and I).

| Lattice Parameters | Functionals | PBE-D3 | PBEsol | PBEsol-D3 | SCAN | SCAN-D3 | EXP. (298K)**
|-------------------|-------------|--------|--------|-----------|------|---------|---------|
| **(MDABCO)(NH₄)I₃**
| a (Å)             | 7.160       | 7.147  | 7.033  | 7.240     | 7.39 | 7.259(4) |
| b (Å)             | 7.160       | 7.147  | 7.033  | 7.240     | 7.39 | 7.259(4) |
| c (Å)             | 7.160       | 7.147  | 7.033  | 7.240     | 7.39 | 7.259(4) |
| α (°)             | 84.0        | 84.2   | 83.6   | 84.1      | 84.7 | 84.767(4) |
| β (°)             | 84.0        | 84.2   | 83.6   | 84.1      | 84.7 | 84.767(4) |
| γ (°)             | 84.0        | 84.2   | 83.6   | 84.1      | 84.7 | 84.767(4) |
| V (Å³)            | 361.46      | 359.83 | 341.79 | 373.90    | 398.57 | 377.9(5) |
| **(MDABCO)(NH₄)Br₃**
| a (Å)             | 6.875       | 6.883  | 6.749  | 6.881     | 6.749 | 7.195(2) |
| b (Å)             | 6.875       | 6.883  | 6.749  | 6.881     | 6.749 | 7.195(2) |
| c (Å)             | 6.875       | 6.883  | 6.749  | 6.881     | 6.749 | 7.195(2) |
| α (°)             | 84.4        | 84.5   | 83.9   | 84.1      | 83.7 | 84.867(3) |
| β (°)             | 84.4        | 84.5   | 83.9   | 84.1      | 83.7 | 84.867(3) |
| γ (°)             | 84.4        | 84.5   | 83.9   | 84.1      | 83.7 | 84.867(3) |
| V (Å³)            | 320.65      | 321.94 | 302.52 | 321.07    | 302.23 | 368.2(3) |
S2. Electron Localization Function (ELF) Analysis of the Benchmark System (MDABCO)(NH₄)I₃

The ELF analysis is undertaken for the benchmark system (MDABCO)(NH₄)I₃ perovskite (Figure S1) based on the electronic density calculation method implemented in VASP 5.4.4. This ELF picture is used to locate the possibility of finding a pair of electrons at certain position as a reflection of the bonding nature of materials. Usually for this dimensionless function, the value in a range of 0.5 (green) to 1.0 (red) is considered as a localized electron pair which can be either bonding or nonbonding; while the value in a range of 0 (blue) to 0.5 (green) is viewed as a delocalized electron pair. A normal interval of 0.05 is chosen for Figure S1.

![Figure S1](image.png)

**Figure S1.** ELF analysis of (MDABCO)(NH₄)I₃ perovskite viewed (a) along (001) surface and (b) along (002) surface. NH₄⁺ and I⁻ ions are highlighted in (a) and MDABCO²⁺ and I⁻ ions are highlighted in (b) to distinguish the bonding nature of the benchmark system. A color-bar is given to present ELF values.

The ELF distribution in the (001) plane of the benchmark system (MDABCO)(NH₄)I₃ perovskite is shown in Figure S1a. Those red solid circles indicate distribution region of
the core electrons of $\Gamma^-$ anions. The $\text{NH}_4^+$ cation is also highlighted in Figure S1a, where three red round spots forming a triangle indicate three H atoms that form covalent bonds with N atom. Two $\Gamma^-$ ions, the upper one and the right one, face to two H atoms of $\text{NH}_4^+$ ion respectively. In addition, the outermost green circles of these two $\Gamma^-$ ions are nearly in contact with the outermost green region of $\text{NH}_4^+$ ion. All of these features imply the weak hydrogen bonding between N-H and $\Gamma^-$.

The ELF distribution in the (002) plane of the benchmark system (MDABCO)(NH$_4$I)$_3$ perovskite is shown in Figure S1b. The $\Gamma^-$ anions are still highlighted here, and a quite complex ELF distribution with the outermost green region indicates the MDABCO$^{2+}$ cation. Different from the connective green region between $\Gamma^-$ and $\text{NH}_4^+$ shown in Figure S1a, the region between $\Gamma^-$ and MDABCO$^{2+}$ is purely light blue ($< 0.5$), suggesting nonbonding interaction between $\Gamma^-$ and MDABCO$^{2+}$ here. Based on this ELF analysis, we can conclude that there is still nonbonding interaction between nearby MDABCO$^{2+}$ cations.
**S3. Band Structures of All 3D Metal-Fee Perovskites Considered**

![Band Structures of 3D Metal-Free Perovskites](image)

**Figure S2.** Computed band structures of all the 3D metal-free $A(NH_4)I_3$ perovskites with different $A$-type cations (1-9) shown in Figure 2 of the main text, based on the PBE-D3-functional-based DFT calculations. The Fermi levels are marked by the dotted lines at zero, and the valence and conduction bands are highlighted by the sky-blue and red lines respectively.
S4. Band Structures and Density of States (DOS) of \(A(8)(NH_4)I_3\) and \(A(9)(NH_4)I_3\) by Using HSE06 Functional

**Figure S3.** Computed band structures and density of states (DOS) projected onto \(A^{2+}\), \(NH_4^+\), and \(I^-\) components of the \(A(NH_4)I_3\) perovskites where \(A = (a)\ A(8)\) and \(b)\ A(9)\), based on the HSE06-functional-based DFT calculations. The Fermi levels are marked by the dotted lines at zero, and the valence and conduction bands are highlighted by the sky-blue and red lines respectively.
S5. Comparison of Computed Optical Absorption Spectra by using $G_0W_0$/BSE and Time-Dependent Density Functional Theory (TDDFT) Methods

The optical absorption coefficients calculated by using $G_0W_0$/BSE and TDDFT methods (as shown in Figure S4) refer to the PBE Kohn-Sham (KS) eigensystem. It is known that both Pb and I are heavy elements and the valence and conduction bands of MAPbI$_3$ should entail significant relativistic effects.$^{55-6}$ In other words, more reliable electronic band structure of MAPbI$_3$ would be obtained if the spin-orbit coupling (SOC) effect is considered in the first-principles calculations.$^{55-7}$ For the Pb-containing prevailing organohalide lead perovskite, MAPbI$_3$, the SOC effect is considered in the $G_0W_0$/BSE calculations. However, the bandgap of MAPbI$_3$ calculated by using the HSE06 functional without considering SOC effect seems to be still in reasonable agreement with the experimental results due to certain cancellation of errors.$^6$ In order to save the computational resource, we estimate the optical spectrum of MAPbI$_3$ in our TDDFT calculations without considering SOC effect in Figure S4.

Note that our solid-state UV/vis diffuse reflectance spectroscopy measurement in Figure S4 shows that the onset absorption peak of MAPbI$_3$ is at the photo energy of $\sim$1.5 eV. Compared to this experimental result, the $G_0W_0$/BSE method with SOC effect predicts a slightly blue-shifted onset optical bandgap of $\sim$1.67 eV, while the TDDFT method predicts a poor onset optical bandgap, i.e., a large red-shift value of $\sim$1.0 eV. Taking the prevailing MAPbI$_3$ as a benchmark, we also computed optical absorption spectra of the newly designed 3D metal-free perovskite A(8)(NH$_4$I)$_3$ for comparison. Here, its difference in the predicted onset optical bandgaps between $G_0W_0$/BSE and TDDFT computation is even larger than that for MAPbI$_3$. The TDDFT method predicts abruptly increasing absorption intensity for MAPbI$_3$, finally larger than the experimental one and the $G_0W_0$/BSE-computed one. However, TDDFT predicts really small absorption intensity for A(8)(NH$_4$I)$_3$, quite different from the $G_0W_0$/BSE one. It appears that the performance of PBE-based
TDDFT method is poor to compute the optical absorption spectra as far as the 3D metal-free perovskites are concerned.

**Figure S4.** Computed optical absorption spectra by using $G_0W_0$/BSE (dashed lines) and TDDFT (solid lines) methods for MAPbI$_3$ and A(8)(NH$_4$)$_3$ perovskites. The blue dotted line is the experimental optical absorption spectrum of MAPbI$_3$ taken from the solid-state UV/vis diffuse reflectance spectroscopy measurement.
S6. Dipole Transition Matrix Elements of the Newly Designed $A(8)(\text{NH}_4)I_3$ and $A(9)(\text{NH}_4)I_3$ Perovskites

For the newly designed 3D metal-free $A(8)(\text{NH}_4)I_3$ and $A(9)(\text{NH}_4)I_3$ perovskites, their high transition probabilities between the valence-band maximums and the conduction-band minimums around the $T$ and $L$ points are shown respectively via the calculated sum of the square of the dipole transition matrix element, $P^2$, at various $k$ points, as shown in Figure S5. Although these $P^2$ values are provided in arbitrary unit, the values of different structures can be directly compared.\textsuperscript{88} Compared to the previous study on inorganic lead-free metal halide perovskites and double perovskites,\textsuperscript{88} the transition matrix values of the $A(8)(\text{NH}_4)I_3$ (about 88 a.u.) and $A(9)(\text{NH}_4)I_3$ (about 56 a.u.) perovskites here are really large, suggesting their good optical absorption behavior.

**Figure S5.** Computed band structures and corresponding dipole transition matrix elements for 3D metal-free (a) $A(8)(\text{NH}_4)I_3$ and (b) $A(9)(\text{NH}_4)I_3$ perovskites based on PBE-D3 computations. The valence and conduction bands are highlighted by the sky-blue and red lines respectively.
S7. Strain-Induced Bandgap Change for A(9)(NH₄)I₃ Perovskite

For A(9)(NH₄)I₃ perovskite, we apply either the uniaxial or biaxial compressive/tensile strain to it to examine the strain-induced bandgap tuning (see Figure 4 in the main text). As shown in Figure S6, the strain-induced indirect to direct bandgap transition in A(9)(NH₄)I₃ perovskite can be observed here. Under the small strain considered here, the A(9)(NH₄)I₃ perovskite nearly maintains the indirect bandgap. After applying the uniaxial −2.5% strain along the b axis and the biaxial +2.5% strain along a and c axes, the valence and conduction bands of A(9)(NH₄)I₃ perovskite generally keep their shapes and overall shift down, while the valence bands decrease notably at the Γ points compared to corresponding bands without the strain (see Figure S6b and S6d), finally leading to the indirect to direct bandgap transition.

![Energy band diagrams](image-url)
**Figure S6.** Computed electronic band structures of 3D metal-free A(9)(NH₄)I₃ perovskite without and with uniaxial strain (a) along the a axis or (b) along the b axis, or biaxial strain (c) along a and b axes or (d) along a and c axes based on the PBE-D3-functional DFT calculations. The bands are plotted in blue (at −2.5% compressive strain), black (with zero strain), and red (at 2.5% tensile strain), respectively, for clear inspection of possible indirect to direct bandgap transition.
Supporting References

S1. Csonka, G. I.; Perdew, J. P.; Ruzsinszky, A.; Philipsen, P. H. T.; Lebègue, S.; Paier, J.; Vydrov, O. A.; Ángyán, J. G., Assessing the performance of recent density functionals for bulk solids. Phys. Rev. B 2009, 79 (15), 155107.

S2. Sun, J.; Ruzsinszky, A.; Perdew, J. P., Strongly Constrained and Appropriately Normed Semilocal Density Functional. Phys. Rev. Lett. 2015, 115 (3), 036402.

S3. Ye, H.-Y.; Tang, Y.-Y.; Li, P.-F.; Liao, W.-Q.; Gao, J.-X.; Hua, X.-N.; Cai, H.; Shi, P.-P.; You, Y.-M.; Xiong, R.-G., Metal-free three-dimensional perovskite ferroelectrics. Science 2018, 361 (6398), 151-155.

S4. Becke, A. D.; Edgecombe, K. E., A simple measure of electron localization in atomic and molecular systems. J. Chem. Phys. 1990, 92 (9), 5397-5403.

S5. Frost, J. M.; Butler, K. T.; Brivio, F.; Hendon, C. H.; van Schilfgaarde, M.; Walsh, A., Atomistic Origins of High-Performance in Hybrid Halide Perovskite Solar Cells. Nano Lett. 2014, 14 (5), 2584-2590.

S6. Ye, Y.; Run, X.; Hai-Tao, X.; Feng, H.; Fei, X.; Lin-Jun, W., Nature of the band gap of halide perovskites ABX₃ (A= CH₃NH₃, Cs; B= Sn, Pb; X= Cl, Br, I): First-principles calculations. Chin. Phys. B 2015, 24 (11), 116302.

S7. Amat, A.; Mosconi, E.; Ronca, E.; Quarti, C.; Umari, P.; Nazeeruddin, M. K.; Grätzel, M.; De Angelis, F., Cation-induced band-gap tuning in organohalide perovskites: interplay of spin–orbit coupling and octahedra tilting. Nano Lett. 2014, 14 (6), 3608-3616.

S8. Meng, W.; Wang, X.; Xiao, Z.; Wang, J.; Mitzi, D. B.; Yan, Y., Parity-Forbidden Transitions and Their Impact on the Optical Absorption Properties of Lead-Free Metal Halide Perovskites and Double Perovskites. J. Phys. Chem. Lett. 2017, 8 (13), 2999-3007.