

Supplementary Data

Computational Details

All calculation on the $[\text{H}_2\text{mela}]\text{PbBr}_4$ materials and $\text{H}_2\text{melaBr}_2$ salt were carried out using Quantum Espresso program package.¹ Geometry optimization were performed using ultra soft fixed experimental cell parameters with plane wave cutoff of 25/200 Ry along with PBE³ function and ultrasoft pseudo potential with electrons from I 5s, 5p; N, C, O 2s, 2p; H 1s; Pb, 6s, 6p, 5d shells explicitly included in calculations. For the isolated $\text{H}_2\text{melaBr}_2$ salt a 20x20x20 Å cubic box was adopted to avoid interaction with the replicants. DOS calculation has been carried out using the exact exchange through the HSE06 functional⁴ ($\alpha=0.43$), following the previous approach.⁵ Hybrid calculations, spin orbit coupling included, have been carried out at the relaxed PBE geometries using norm conserving pseudopotential with 22 valence electrons for Pb has been used, by including the Pb 5s and 5p states, which ensures an accurate reproduction of MAPbI_3 band gap and band edges against GW calculations.⁶ For the other elements, pseudopotentials with the same number of valence electrons as in the US case have been used. To reduce the computational effort, hybrid SOC calculations have been performed by using a plane wave cutoff of 40 Ry, without affecting the accuracy of the calculations.

The simulation of the triplet state of the $\text{H}_2\text{melaBr}_2$ salt was carried out at scalar relativistic level because of with non-collinear calculation is not possible to impose the multiplicity, however, while SOC is fundamental for the description of the inorganic part, the SOC effects on the organic molecules are negligible. In particular, to further confirm this aspect we compare the HOMO-LUMO gap of the non-interacting organic part at the singlet state with scalar relativist approach and with SOC alternatively and we obtain exactly the same band gap value.

1. Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I.; Corso, A. D.; de Gironcoli, S.; Fabris, S.; Frates, G.; Gebauer, R.; Gerstmann, U.; Gougoussis, C.; Kokalj, A.; Lazzeri, M.; Martin-Samos, L.; Marzari, N.; Mauri, F.; Mazzarello, R.; Paolini, S.; Pasquarello, A.; Paulatto, L.; Sbraccia, C.; Scandolo, S.; Sclauzero, G.; Seitsonen, A. P.; Smogunov, A.; Umari, P.; Wentzcovitch, R. M., QUANTUM ESPRESSO: A Modular and Open-Source Software Project for Quantum Simulations of Materials. *J. Phys.: Condens. Matter* **2009**, *21*, 395502.
2. Cortecchia, D.; Neutzner, S.; Srimath Kandada, A. R.; Mosconi, E.; Meggiolaro, D.; De Angelis, F.; Soci, C.; Petrozza, A., Broadband Emission in Two-Dimensional Hybrid Perovskites: The Role of Structural Deformation. *J. Am. Chem. Soc.* **2017**, *139* (1), 39-42.
3. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865-3868.
4. Heyd, J.; Scuseria, G. E.; Ernzerhof, M., Hybrid Functionals Based on a Screened Coulomb Potential. *J. Chem. Phys.* **2003**, *118* (18), 8207-8215.
5. (a) Du, M.-H., Density Functional Calculations of Native Defects in $\text{CH}_3\text{NH}_3\text{PbI}_3$: Effects of Spin-Orbit Coupling and Self-Interaction Error. *J. Phys. Chem. Lett.* **2015**, *6* (8), 1461-1466; (b) Meggiolaro, D.; Motti, S.

G.; Mosconi, E.; Barker, A. J.; Ball, J.; Andrea Riccardo Perini, C.; Deschler, F.; Petrozza, A.; De Angelis, F., Iodine chemistry determines the defect tolerance of lead-halide perovskites. *Energy Environ. Sci.* **2018**, *11* (3), 702-713.

6. Umari, P.; Mosconi, E.; De Angelis, F., Relativistic GW Calculations on $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{SnI}_3$ Perovskites for Solar Cell Applications. *Sci. Rep.* **2014**, *4*, 4467.