Supporting Information

Bismuth-based perovskite-derivates with thermal voltage exceeding 40 mV/K.

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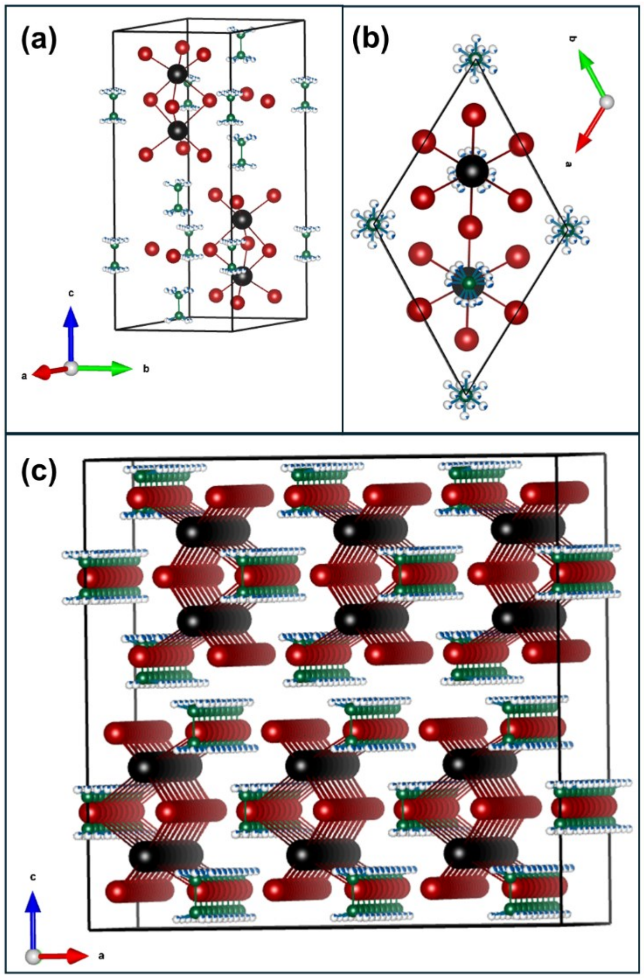

Figure S1. Representation of the crystalline structure of **MABiI**, identified by Kamminga et al.,[1] showing the unit cell in all three directions (**a**), along c (**b**), and a supercell 2 x 2 x 2. Images have been produced by using VESTA software.

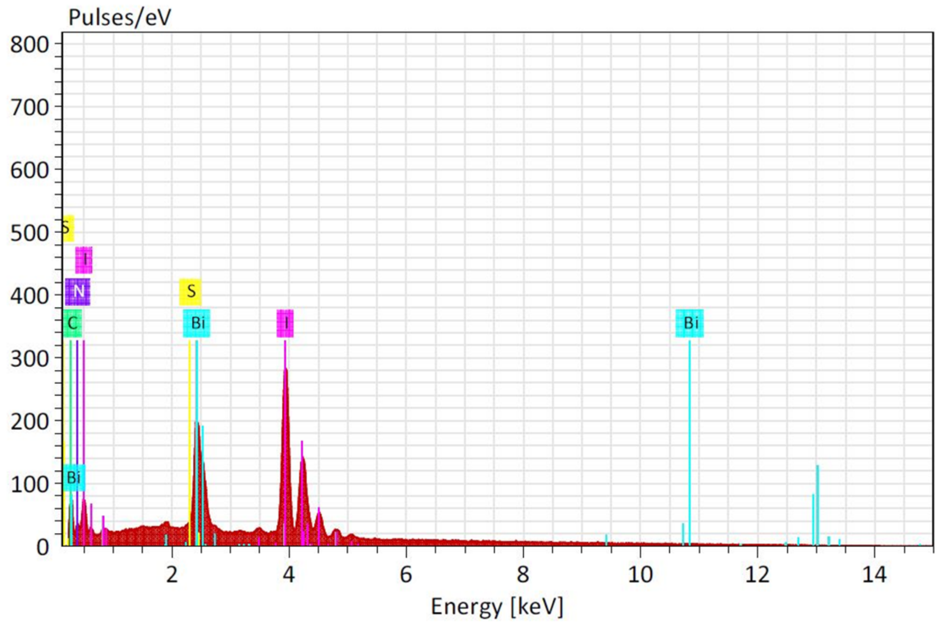

Figure S2. EDS spectrum of sulfur-doped methylammonium bismuth iodide (**S.MABiI**) containing C, N, Bi, I, and S.

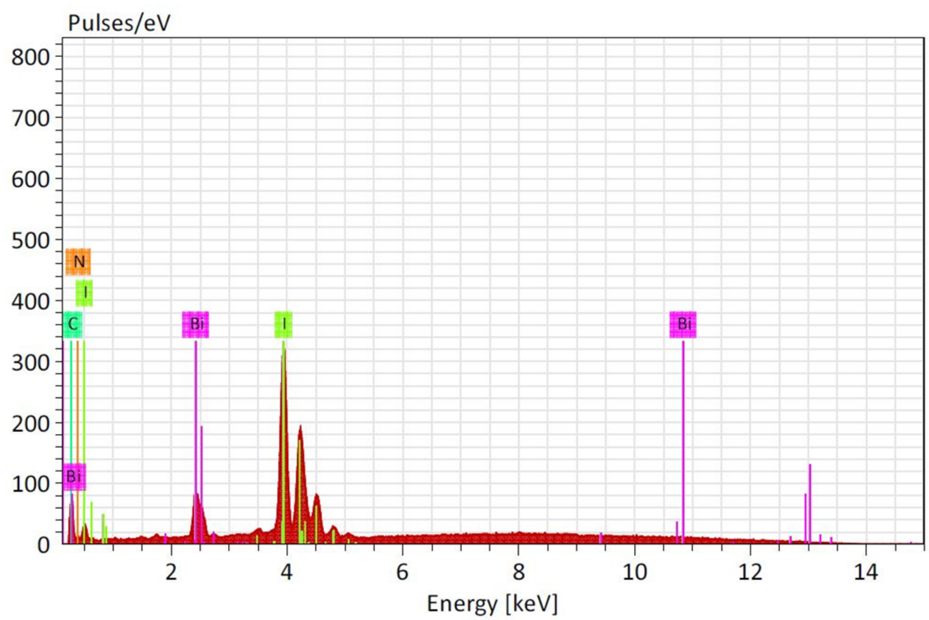

Figure S3. EDS spectrum of undoped methylammonium bismuth iodide (**MABiI**) containing C, N, Bi, I.

Figure S4. Pictures of MABiI (17) and S.MABiI (19) thin films deposited on glass by drop-casting.

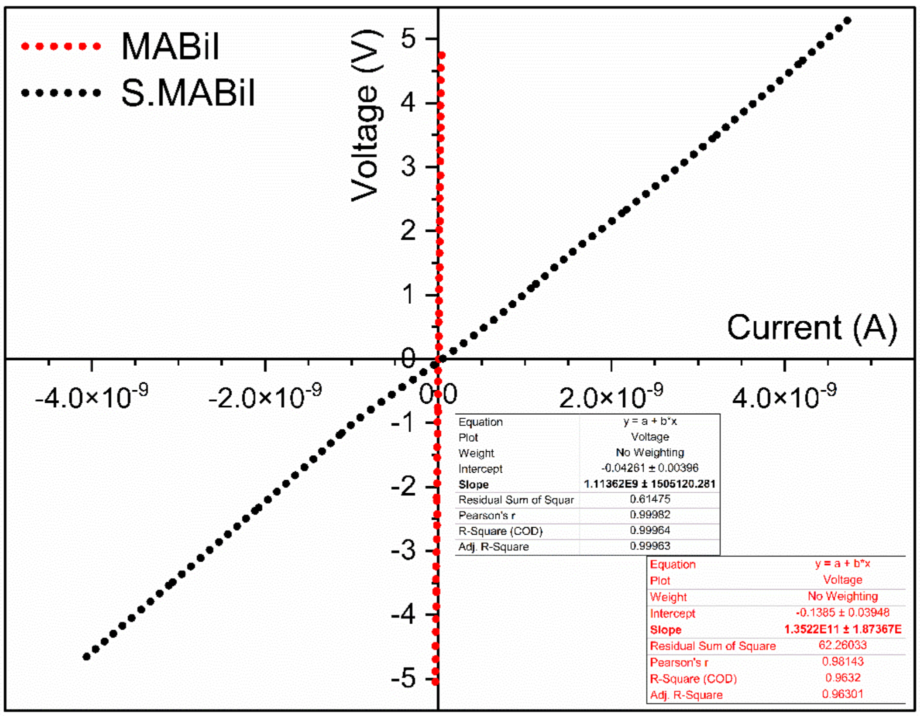

Figure S5. Electrical resistance measurement of methylammonium bismuth iodide (**MABiI**) and sulfur-doped methylammonium bismuth iodide (**S.MABiI**).

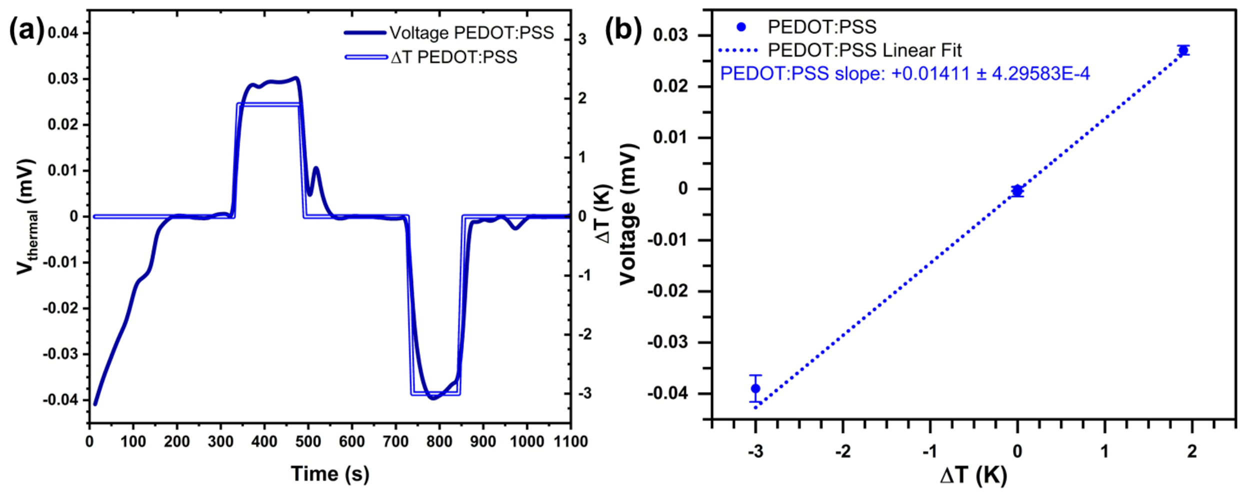

Figure S6. (a) Measured $V_{thermal}$ and temperature difference, ΔT, between two Au electrodes contacting a **PEDOT:PSS** thin film. (b) Linear fitting of $V_{thermal}$ varying the temperature difference, ΔT. The linear fit gives a Seebeck coefficient of 14.1 μV K^{-1}.

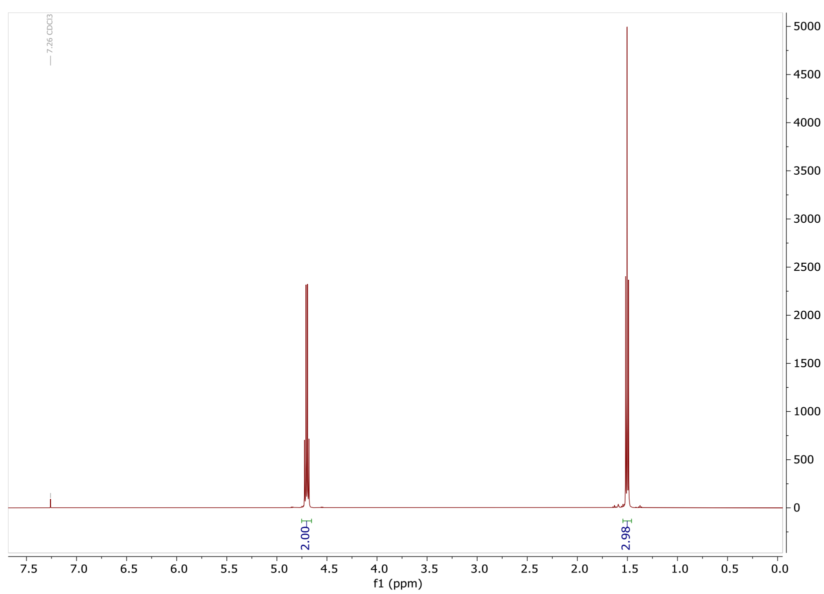

Figure S7. ^{1}H NMR spectrum of the synthesized $(C_2H_5OCS_2)_3Bi$ (**Bi(xt)$_3$**) powder. Chemical shifts (δ) are reported in parts per million (ppm), using the residual solvent peaks as the internal standard ($CDCl_3$ δ = 7.26).

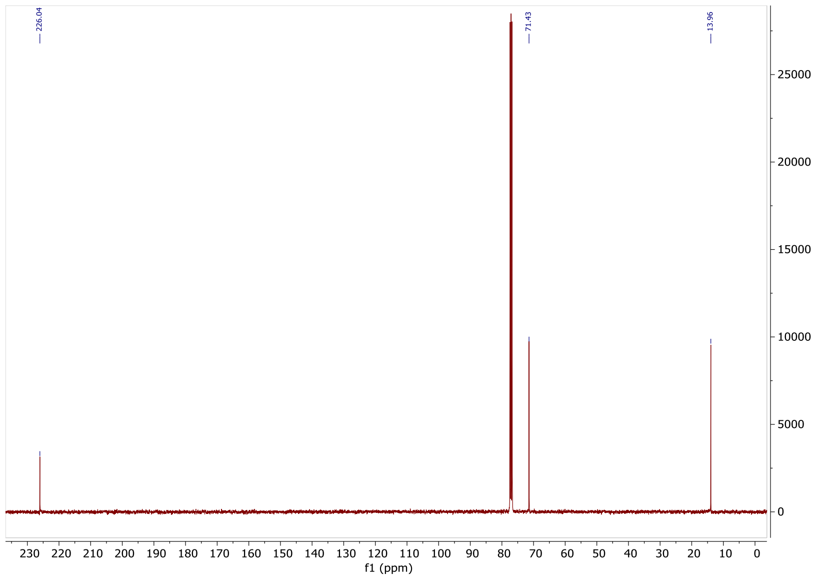

Figure S8. ^{13}C NMR spectrum of the synthesized $(C_2H_5OCS_2)_3Bi$ (**Bi(xt)$_3$**) powder. Chemical shifts (δ) are reported in parts per million (ppm), using the residual solvent peaks as the internal standard ($CDCl_3$ δ = 77.16).

(1) Kamminga, M. E.; de Wijs, G. A.; Havenith, R. W. A.; Blake, G. R.; Palstra, T. T. M. The Role of Connectivity on Electronic Properties of Lead Iodide Perovskite-Derived Compounds. *Inorganic Chemistry* **2017**, *56* (14), 8408-8414. DOI: 10.1021/acs.inorgchem.7b01096.