Supplementary Information for

A two-fold engineering approach based on Bi₂Te₃ flakes towards efficient and stable inverted perovskite solar cells

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Figure S1. XRD pattern of the perovskite film



Figure S2. Photograph of the Bi2Te3 flake dispersions produced by LPE in different solvent (IPA, ACN and IPA:ACN (1:1), after 4 h of gravitational sedimentation.



Figure S3. a) UV-Vis-NIR absorption measurement of the Bi_2Te_3 flakes and b) Tauc plot analysis revealing the negligible band gap of the Bi_2Te_3 flakes.



Figure S4. SEM images and EDX mapping of $PC_{70}BM$ surface in **a**) PSC-Ref and **b**) PSC-Int2. The corresponding EDS maps for Pb ($L\alpha = 10.55 \text{ keV}$) and Bi ($L\alpha = 11.84 \text{ keV}$) are also shown. (c) Comparison of the EDX spectra collected for the reference (black) and two different areas for the PSC-Int2 (blue).



Figure S5. AFM images of the $PC_{70}BM$ surface with the Bi_2Te_3 flakes spin coated (4SC) on top, noted as white spots. The left image spans an area of 20x20 μ m² and the right a 10x10 μ m². Similarly, with SEM images, AFM images capture only the thick flakes due to resolution limitation.



Figure S6. a) SEM image of PC₇₀BM surface in PSC-Dop2 sample. The red circles show Bi₂T₃ flakes in the PC₇₀BM layer. Since we were using only the supernatant resulting from the solvent transfer of the Bi₂T₃ flakes from IPA:ACN to chlorobenzene, only small and scattered flakes embedded into the ETL are visible in agreement with AFM images in Figure S3. **b-c)** SEM images revealing how by increasing the number of SC for the Bi₂T₃ interlayer formation promoted the formation of cracks (pointed out by an arrow) on ETL and/or perovskite layer, leading to low photovoltaic performance for SC>2 (see main text, Table 1).



Figure S7. The forward (FS) and reverse (RS) scan J-V plots of the PSC devices



Figure S8. PL measurements of undoped $PC_{70}BM$ without (red) and with two spin coatings of Bi_2Te_3 interlayer (yellow) on top. Besides, doped $PC_{70}BM$ without (green) and with 2 spin coatings of Bi_2Te_3 interlayer (green) on top. In the inset: PL measurements of perovskite with and without $PC_{70}BM$ on top.



Figure S9. Raw data of TPV measurements of the devices: **a)** PSC-Ref, **b)** PSC-Dop2, **c)** PSC-Int2 and **d)** PSC-Com2. The insets present the voltage rise data.



Figure S10. Raw data of various devices TPC measurements: a) PSC-Ref, b) PSC-Dop2, c) PSC-Int2 and d) PSC-Com2.



Figure S11. Raw data of photo-CELIV measurements used for the drift mobility extraction of the devices: a) PSC-Ref, b) PSC-Dop2, c) PSC-Int2 and d) PSC-Com2. The region near the peak is plotted in the insets.