A two-fold engineering approach based on Bi$_2$Te$_3$ flakes towards efficient and stable inverted perovskite solar cells

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Perovskite solar cells (PSCs) are currently the leading thin-film photovoltaic technology owing to their high power conversion efficiency (PCE), as well as their low-cost and facile manufacturing process. Two-dimensional (2D) materials have been reported to improve both the PCE and the stability of the PSCs when incorporated across the device’s layered configuration. Hereby, a two-fold engineering approach is implemented in inverted PSCs by using ultra-thin Bi$_2$Te$_3$ flakes, i.e.: (1) to dope the electron transport layer (ETL) and (2) to form a protective interlayer above the ETL. Thorough steady-state and time-resolved transport analyses reveal that our first engineering approach improves the electron extraction rate and thus the overall PCE (+8% vs. reference cells), as a result of the favourable energy level alignment between the perovskite, the ETL and the cathode. Moreover, the Bi$_2$Te$_3$ interlayer through the second engineering approach, facilitates further the electron transport and in addition protects the underlying structure against chemical instability effects leading to enhanced device’s performance and stability. By combining the two engineering approaches, our optimised PSCs reach a PCE up to 19.46% (+17% vs. reference cells) and retain more than 80% of their initial PCE, after the burn-in phase, over 1100 h under continuous 1 Sun illumination. These performances are among the highest reported in literature for inverted PSCs.

Introduction

The incorporation of two-dimensional (2D) materials at different sections of a perovskite solar cell (PSCs) represents an effective approach to enhance both the power conversion efficiency (PCE) and the lifetime stability of such photovoltaic technology. Meanwhile, the exceptional optoelectronic properties of 2D materials and their compatibility with large-scale, solution-processable methods (e.g., roll-to-roll printing techniques) lay the grounds for the direct integration of low-cost and flexible photovoltaic devices in emerging smart and multifunctional technologies. The beneficial impact of graphene and related 2D materials in PSCs has been demonstrated both in mesoporous and inverted planar structures, as well as in their corresponding tandem systems. Beyond graphene and its derivatives various 2D material families have been tested including transition metal dichalcogenides, MXenes, phosphorene and antimonene, just to name a few. The high degree of structural and optoelectronic tunability of 2D materials renders them an ideal choice to form functional layers in PSCs. For example, 2D material films have been proposed as replacements of conventional electron/hole transport layers (ETLs/HTLs) by taking advantage of their optimal charge transport properties, low fabrication cost and chemical inertness. They have been also used as interlayers between the ETL/HTL and the photoactive layers to promote the transport of the photogenerated charges towards the electrodes, while concurrently hindering interfacial charge recombination processes. Recently, 2D materials have been used as additives into the perovskite layer in order to increase the crystal grain size of the latter and to facilitate the extraction rate of the photogenerated charges towards the electrodes. Moreover, the integration of 2D materials in PSCs led to a strong enhancement of the device lifetime due to their morphology-derived protective properties against the diffusion of external agents (e.g., oxygen and moisture) and the metal ion migration, which are both causes of PSCs performance degradation.

In the plethora of layered materials which can be exfoliated into 2D forms, Bi$_2$Te$_3$ belongs to a special material class, namely topological insulators, with exceptional surface states properties originating from their non-trivial topological order protected by time reversal symmetry. Indeed Bi$_2$Te$_3$, as well as other topological insulators, behave as insulators in their interior, while their surface states, featuring a single Dirac cone in their band structure, are electrically conductive and insensitive to carrier’s backscattering. In addition, both Te vacancies and the oxidation level determine the optoelectronic properties of Bi$_2$Te$_3$, which can be engineered to be either metallic or...
Despite the fascinating properties of Bi$_2$Te$_3$, its potential in photovoltaic systems has not been fully rationalized yet, although few studies reported the successful integration of Bi$_2$Te$_3$ in solar cells, including inorganic (CdTe) thin-film solar cells, dye-sensitized solar cells, and PSCs. For example, metallic Bi$_2$Te$_3$ films, produced by thermal evaporation methods, have been used in inverted PSCs as a low-cost counter electrode material to replace expensive noble-metals (e.g., Ag). Beyond economic reasons, Bi$_2$Te$_3$-based counter electrodes can effectively suppress the electron back scattering, thus improving the electron collection. Meanwhile, it can also suppress the metal-induced decomposition of the perovskite layers, increasing the overall device stability. Alternatively, semiconducting Bi$_2$Te$_3$ films have been proposed as interlayers between the perovskite and the HTL in a normal n-i-p cell configuration with three functional roles: 1) to promote the hole extraction via material energy level matching; 2) to reduce the recombination of the photogenerated charges by suppressing the formation of charge trapping interfacial defects and 3) to increase the device stability by providing a barrier against the migration of iodide and silver ions, as well as the diffusion of moisture.

In this work, Bi$_2$Te$_3$ flakes were produced through scalable liquid-phase exfoliation (LPE) of the corresponding crystals and incorporated into the inverted PSCs with a dual functional role. Firstly, Bi$_2$Te$_3$ flakes were used as dopants of the [6,6]-phenyl-C71-butyric acid methyl ester (PC$_{70}$BM)-based ETL. More in detail, the dopant dose was tuned by controlling the relative volume of Bi$_2$Te$_3$ flake dispersion (in CB) added in the initial PC$_{70}$BM solution volume (between 0% and 3% vol/vol). The ETL doped with Bi$_2$Te$_3$ flakes favoured the extraction of the photogenerated electrons through the conductive pathways offered by the surface states of the topological insulator, leading to a PCE increase of 6.6% compared to reference cells (when 2% vol/vol doping was used). Secondly, an interlayer of Bi$_2$Te$_3$ flakes was deposited by consequent spin coatings (SC) below the cathode. The total number of SC was varied from 1 to 3 in order to optimize the Bi$_2$Te$_3$ interlayer. Thanks to the 2D nature of Bi$_2$Te$_3$ flakes, the interlayer acted as a protective barrier increasing the overall device lifetime (+10% vs. reference), when grown at an optimal thickness corresponding to 2 SC processes. Finally, the optimized Bi$_2$Te$_3$-based PSCs combining both engineering approaches (i.e., the PSCs using Bi$_2$Te$_3$-doped PC$_{70}$BM and the Bi$_2$Te$_3$ interlayer), exhibited a PCE of 19.46%, which corresponds to a 15.2% increase compared to the value measured for the Bi$_2$Te$_3$-free reference cell. Our detailed steady-state and time-resolved transport analyses correlated the PCE improvement primarily to an electron extraction rate enhancement and secondarily to the favourable alignment between the Lowest Unoccupied Molecular Level (LUMO) of the PC$_{70}$BM and the work function (W$_f$) of the Ag in the presence of the Bi$_2$Te$_3$ flakes. Moreover, compared to reference cell, our optimized PSCs demonstrated an extended stability, reporting an extrapolated $T_{1000}$ (defined as the time at which the device reach 80% of its initial PCE after the burn-in phase) superior to 1100 h under continuous 1 Sun illumination. The performances achieved by our Bi$_2$Te$_3$-based PSCs are among the highest reported in literature for inverted PSCs.

**Experimental section**

**Materials production**

Bi$_2$Te$_3$ flakes were produced through LPE of the corresponding bulk crystal. Experimentally, 300 mg of Bi$_2$Te$_3$ crystal powder (~325 mesh, 99.99% trace metals basis) were inserted in 50 mL of a mixture of anhydrous isopropanol (IPA) (99.5%, Sigma Aldrich) and acetonitrile (ACN) (99.8%, Sigma Aldrich) (1:1 vol/vol). The resulting mixture was ultrasonicated in an ultrasonication bath (Branson 5800 cleaner, Branson ultrasonics) for 6 h. Subsequently, a sedimentation-based separation (SBS) process was used to separate the exfoliated Bi$_2$Te$_3$ flakes from the unexfoliated material. More specifically, the sample was ultracentrifuged for 20 min at 935g (Sigma 3-16P centrifuge, rotor 19776). Finally, the Bi$_2$Te$_3$ flakes dispersion was obtained by collecting the 80% of the supernatant by pipetting.

Noteworthy, the final dispersion was formulated in low-boiling point solvents, which are compatible with eco-friendly, low-temperature and solution-processed deposition techniques. The handling of the material was carried out inside a N$_2$-filled glovebox to minimize the oxidation occurring when the Bi$_2$Te$_3$ flakes are exposed to ambient environmental conditions. In order to dope the ETL (PC$_{70}$BM) with Bi$_2$Te$_3$ flakes, a solvent exchange approach was used to replace the IPA:ACN mixture with the solvent used to dissolve PC$_{70}$BM, i.e., anhydrous chlorobenzene (CB). A quantitative volume of the pristine Bi$_2$Te$_3$ flakes dispersion in IPA:ACN was added in a pre-weighted empty vial. Subsequently, the sample was dried by evaporating the solvent under mild heating at 45°C. Afterwards, the dried vial was weighted, and an amount of anhydrous CB was added to the Bi$_2$Te$_3$ sediment mass to obtain a Bi$_2$Te$_3$ flake dispersion in CB with a concentration of 1 mg mL$^{-1}$. The so-produced dispersion was sonicated in an ultrasonication bath (Elmasonic S30H) for 60 min followed by an ultracentrifugation for 15 min at 1679g (Hettich Zentrifugen, Universal 320, rotor 1401). A Gilson pipette (PIPETMAN L P100L, 10-100 µL) was then used to collect the supernatant (corresponding to ~95% of the initial volume), which was used without any further treatment. Finally, the sediment was dried and weighted in order to precisely determine the concentration of the collected supernatant, yielding to a final concentration of ~62 µg mL$^{-1}$.

**Materials characterization**
Transmission electron spectroscopy (TEM) characterization of the Bi$_2$Te$_3$ flakes was performed using a JEM 1011 (JEOL) TEM (thermonic W filament), operating at 100 kV. The morphological and statistical analyses were performed by means of ImageJ software (NIH) and OriginPro 9.1 software (OriginLab), respectively. The samples for the TEM measurements were prepared by drop casting the as-produced Bi$_2$Te$_3$ flake dispersion onto ultrathin C-on-holey C-coated Cu grids under N$_2$ atmosphere. The sample were then rinsed with deionized water and subsequently dried overnight under vacuum. The AFM images were acquired with a XE-100 AFM (Park System, Korea) by means of PPPNCHR cantilevers (Nanosensors, Switzerland) having a tip diameter inferior to 10 nm. The images were collected in intermittent contact (tapping) mode over an area of 5×5 μm$^2$ (1024×1024 data points) using a drive frequency of ~330 kHz and keeping the working set point above 70% of the free oscillation amplitude. The scan rate for the acquisition of the images was 0.2 Hz. Gwyddion 2.53 software (http://gwyddion.net/) was used for determining the height profiles, while the statistical analysis of the data was performed using OriginPro 2018 software. The samples were prepared by drop-casting the as-produced Bi$_2$Te$_3$ flake dispersion onto mica sheets (G250-1, Agar Scientific Ltd.) under N$_2$ atmosphere. Then, the samples were heated up to 60 °C for 15 min to dry the samples and remove possible adsorbates. Raman spectroscopy measurements were performed using a Renishaw microRaman Invia 1000 mounting a 50× objective, an excitation wavelength of 633 nm and an incident power on the samples of 0.4 mW. The samples were prepared by drop casting the as-produced Bi$_2$Te$_3$ flake dispersion onto Si/SiO$_2$ substrates under nitrogen atmosphere and subsequently dried under vacuum overnight. Optical absorption spectroscopy (OAS) measurements were performed on the as-produced Bi$_2$Te$_3$ flake dispersion using a Cary Varian 5000 UV–vis spectrometer. Ultraviolet photoelectron spectroscopy (UPS) analysis was performed to estimate the work function (WF) of the Bi$_2$Te$_3$ flakes using a Kratos Axis Ultra spectrometer and a He I (21.22 eV) discharge lamp. The WF was measured from the threshold energy for the emission of secondary electrons during He I excitation. A voltage bias of ~9.0 V was applied to the sample in order to precisely determine the low kinetic energy cut-off. The samples were prepared by drop casting the as-produced Bi$_2$Te$_3$ flake dispersion onto Si substrates.

Top-view and cross-sectional scanning electron microscopy (SEM) analysis of the devices was carried out using a FEI® Helios Nanolab 450S microscope provided with dual-beam focused ion beam (FIB)/ SEM. The microscope operated at 5 kV and 0.2 nA for the top-view imaging, while the cross-sectional imaging was performed with the FIB on top of a metal contact using 30 kV and 0.8 nA for the exposure. Scanning electron microscopy coupled to energy dispersive X-Ray spectroscopy (SEM-EDS) measurements of the devices were carried out in a FEI® Quanta 250 FEG microscope operating at 30 kV.

Device fabrication

Pre-patterned 2.5 × 1.5 cm$^2$ ITO substrates (Naranjo substrates) with a sheet resistance of ~20 Ω sq$^{-1}$ were cleaned through a four-step process consisting of subsequent washings with 5% liquid soap solution, deionized water, acetone and isopropanol, and performing 10 min sonication for each step. After drying with N$_2$ flow, the substrates were transferred to a N$_2$-filled glovebox, where they underwent a UV-Ozone treatment (15 min at 1.2 mW cm$^{-2}$). Thin (~10 nm) layers of poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine (PTAA) (Solaris Mw = 20-70 kDa) were prepared by uniformly spreading 65 μL of a 2 mg mL$^{-1}$ solution in toluene (Honeywell Research chemicals, ≥99.7%) on ITO substrates and spinning at an angular speed of 6000 rpm and an acceleration of 750 rpm $s^{-1}$ for 30 s. Then, the so-obtained PTAA layers were annealed at 110 °C for 10 min and left to cool down for 5 min before the next step. The quadruple cation perovskite (Rb$^+$, Cs$^+$, MA$^+$, FA$^+$, with: MA = methylammonium; FA = formamidinium) was formulated by following previous protocols reported by Saliba et al$^{[1]}$. Initially, a (MA$_{0.15}$FA$_{0.85}$)PbI$_{0.85}$Br$_{0.15}$ perovskite solution (hereafter simply named MAFA) was prepared containing 0.2 M MABr (GreatCell Solar), 1.14 M FAI (GreatCell Solar), 0.2 M PbBr$_2$ (TCI America) and 1.24 M PbI$_2$ (TCI America) in 4:1 V/V anhydrous dimethylformamide (DMF) (99.8%, Sigma Aldrich):dimethyl sulfoxide (DMSO) (≥99.9%, Sigma Aldrich). Stock solutions of 1.5 M CsI (99.999% trace metal basis, Sigma Aldrich) in DMSO and 1.5 M RbI (99.8% metals basis, Sigma Aldrich) in DMF:DMSO (4:1 vol/vol) were prepared and heated at 150 °C until the powders were completely dissolved. Afterwards, the stock solutions were left to cool down for 40 min. The (RbPbI$_3$)$_{0.04}$(CsPbI$_3$)$_{0.96}$[(FAPbI$_3$)$_{0.85}$(MAPbBr$_3$)$_{0.15}$]$_{0.81}$ perovskite (hereafter simply named RbCsMAFA) solution was prepared by adding 5 vol% of CsI stock solution and 4 vol% of RbI stock solution to the MAFA precursor, and the solution was left under stirring for 12 h. The perovskite layer was deposited by dynamically spin coating 45 μL of the RbCsMAFA solution on the PTAA film at an angular speed of 6000 rpm for 45 s. Ten seconds prior to the spin coating process, the samples were washed with 200 μL of anhydrous CB (99.8%, Sigma Aldrich) used as antisolvent. Subsequently, the samples were immediately annealed for 45 min on a preheated hotplate at 100 °C. The XRD pattern of the perovskite layer is presented in Figure S1. The XRD peak around 14.25° corresponds to RbCsMAFA perovskite phase, while no peaks related with PbI$_2$ nor a yellow-phase peak are evident.

The PC$_70$BM (99%, Solenne) layers were deposited onto perovskite by spinning 45 μL of a 20 mg mL$^{-1}$ PC$_70$BM solution in anhydrous CB (99.8%, Sigma Aldrich), stirred at least 12 h at 70 °C, at an angular speed of 1000 rpm and an acceleration of 333 rpm $s^{-1}$ for 60 s. In order to dope the PC$_70$BM with the Bi$_2$Te$_3$ flakes, the 62 μg mL$^{-1}$ Bi$_2$Te$_3$ flake dispersion in anhydrous CB was added to the initial PC$_70$BM solution upon stirring for 3 h at 70 °C. The doping of the PC$_70$BM solution with the Bi$_2$Te$_3$ flake dispersion in CB was varied between 0% to 3% v/v. For the devices incorporating a Bi$_2$Te$_3$ interlayer above the PC$_70$BM, the Bi$_2$Te$_3$ flake were deposited onto PC$_70$BM through consecutive SCs (up to three) of the corresponding dispersion in IPA:ACN. Afterwards, 45 μL of 0.5 mg mL$^{-1}$
bathocuproine (BCP) (96%, Sigma Aldrich) in IPA (99.5% extra dry, ACROS Organics,) were spin coated on PCBM layer (Bi2Te3-doped or not) or on Bi2Te3 interlayer (in case of samples incorporating the interlayer) at an angular speed of 4000 rpm and an acceleration of 333 rpm s⁻¹ for 45 s. Finally, a 100 nm-thick Ag top electrode was deposited by thermal evaporation at a base pressure of 10⁻⁶ mbar.

**Device characterization**

The PSCs were tested under inert atmosphere using an ABB solar simulator (Oriel) equipped with a 450W Xenon lamp and a AM1.5 G filter. The intensity was calibrated at 100 mW cm⁻² by a KG5-window Si reference cell. The J-V curves were recorded at a constant scan rate of 20 mV s⁻¹ using a multiplexor test board system (Ossila), and no device preconditioning was applied before the measurements. A black metallic aperture mask was used during each measurement to fix the active area of the fabricated devices close to 0.04 cm² and to reduce the influence of the scattered light. The external quantum efficiency (EQE) spectra were recorded using a QE-T system from Enlitech. A chopping frequency of 65 Hz was used. The calibration of the light intensity was performed using a quartz-window Si solar cell. The integrated current density was calculated by integrating the product between the spectral response of the test cell and the AM1.5G spectrum, correcting the result by multiplying them with the spectral mismatch factor. The topography of samples was evaluated through AFM by means of a XE7 AFM (Park Systems) operating in non-contact mode, as described in Material characterization.

Optoelectrical characterization was performed with a transient module of a commercially available measurement platform, ARKEO (Cicci Research s.r.l.). Transient photovoltage spectroscopy (TPV) experiments were performed in small perturbation mode by confining the intensity of the light pulse to less than 10% of the background voltage. Thus, the equilibrium of the field induced by the background bias remained undisturbed. By doing so, the voltage decay of the measured devices follows a first order behaviour and directly reflects the lifetime of the charge carriers. Transient photocurrent (TPC) experiments were performed in both large and small perturbation regimes. Large perturbations were induced over 200 µs under 0.8 duty cycle, while small perturbations were loaded at 0.001 cycle and passed through an external circuit of a 50 Ω resistance. Both the signals of open circuit voltage (for TPV) and short circuit current (for TPC) were monitored after passing them through voltage and impedance amplifiers. In order to observe the photoinduced charge extraction through linearly increasing voltage (photo-CELIV) measurements, a 470 nm fast LED source driven by 100mA current and exhibiting a Lambertian radiation pattern was used. Relaxation pulse width was set to 20 µs, charged by 50000 V s⁻¹ ramp, following 13 µs delay after injection pulse. Collected signals were processed through a transimpedance amplifier and passed through a 100 MHz bandwidth digitizer running in single shot mode.

The lifetime behaviour of the solar cells was monitored using the ISOS testing laboratory from InfinityPV in ISOS-L2 operation mode. The devices were first encapsulated with a piece of glass and a UV-curable epoxy as adhesive (Ossila E132). Then, the devices were placed inside the test chamber and exposed to continuous illumination. The apparatus was equipped with a solar simulator employing a metal halide light source simulating the AM1.5G spectrum in the range 300-900 nm. The light intensity was calibrated at 100 mW cm⁻² using a Si reference cell. The humidity in the test chamber was below 15%, while the temperature was over 65 °C.

**RESULTS AND DISCUSSION**

**Production and characterization of Bi2Te3 flakes**

The Bi2Te3 flakes were produced through the LPE of the corresponding bulk crystal in IPA:ACN followed by a SBS process to remove the unexfoliated material. Noteworthly, the use of IPA:ACN as the exfoliating solvent circumvents any issue related to: a) the use of toxic and/or high boiling point solvents (e.g., 1-cyclohexyl pyrrolidine (CHP) or N-methyl-2-pyrrolidone (NMP), which have been previously used to exfoliate Bi2Te3,⁵¹,⁵³ b) material’s handling with special precautions (e.g., the use of controlled atmosphere or fume hood) and c) the high temperature (≥ 100 °C) processing for the solvent removal. In addition, the choice of the IPA:ACN mixture is advantageous compared to the use of single IPA or ACN. In fact, as shown in Figure S2, the LPE in IPA leads to instable Bi2Te3 flake dispersions, while the LPE in ACN results in stable dispersions only at very low material’s concentration (<1 mg L⁻¹, weight estimated by weighting the residual mass after the evaporation of the solvent). Contrary, the LPE in IPA:ACN (1:1) results in stable flake dispersions even after centrifugation. We tentatively attribute the stabilization of the Bi2Te3 flakes in LPE in IPA:ACN (1:1) to a possible matching of Hansen solubility parameters of the solvent with the HSPs of Bi2Te3.

The morphology of the Bi2Te3 flakes was characterized by TEM and AFM to determine their lateral size and thickness distributions, respectively. Figure 1a shows a TEM image of representative Bi2Te3 flakes, which show irregular and wrinkled geometries. Noteworthily, a single-layer of Bi2Te3 consists of five monoatomic planes of Te–Bi–Te–Bi–Te, which result in the so-called quintuple structure with a thickness of ~1 nm.⁵⁴,⁵⁵ Therefore, the flakes shown in the AFM image of Figure 1b refer to few-layer (or few-quintuple) Bi2Te3 flakes. Statistical TEM analysis shows that the flakes lateral size follows a log-normal distribution with a mode value of 33 nm (Figure 1c). Besides, the statistical AFM analysis shows that the flakes thickness is mainly distributed between 1
and 13 nm, following a log-normal fit peaking at ~3 nm (Figure 1d). The structural properties of the Bi$_2$Te$_3$ flakes were evaluated through Raman spectroscopy measurements. Belonging to the space group R3m ($D_{3d}^3$)\textsuperscript{56}, the rhombohedral crystal structure of bulk Bi$_2$Te$_3$ exhibits 15 lattice vibration modes, namely 3 acoustic modes ($A_{2u} + E_u$) and 12 optical modes ($2A_{1g} + 2E_g + 2A_{1u} + 2E_u$). Because of the inversion symmetry of Bi$_2$Te$_3$ space group, the optical modes are exclusively Raman- or IR-active.\textsuperscript{57,58} In particular, the Raman-active modes are two-fold degenerate in-plane modes ($E_2^g$ and $E_2^u$) and two-fold degenerate out-of-plane modes ($A_1^g$ and $A_1^u$). However, additional Raman modes, i.e., $A_{1u}$ and $A_{2u}$ (odd parity modes), show up in low-dimensional structures, including single-/few-layer flakes and thin films, due to the breaking of the crystal symmetry along the c-axis.\textsuperscript{59,60} Figure 1e shows the comparison between the Raman spectra of the bulk Bi$_2$Te$_3$ (native crystals) and the Bi$_2$Te$_3$ flakes. An excitation power on the sample as low as 0.4 mW was used to avoid local heating and/or oxidation effects of the Bi$_2$Te$_3$ materials.\textsuperscript{54} The bulk Bi$_2$Te$_3$ shows two main peaks at 103.7 cm$^{-1}$ and 135.0 cm$^{-1}$ attributed to $E_2^g$ and $A_1^g$, respectively. In the Bi$_2$Te$_3$ flakes, $A_1^g$ retains the same position, while $E_2^g$ is slightly blueshifted (by 1.3 cm$^{-1}$), in agreement with previous studies.\textsuperscript{61,62} In addition, $A_{1u}$ is also evidenced, confirming the successful exfoliation of the material. Ultraviolet photoelectron spectroscopy (UPS) measurements were performed to determine the Fermi level energy ($E_F$), i.e., the work function ($W_f$), and the valence band maximum (VBM) energy ($E_{VBM}$) of the Bi$_2$Te$_3$ flakes. As shown in Figure 1f, the secondary electron cut-off (threshold) energies of the He I (21.22 eV) UPS spectra of Bi$_2$Te$_3$ bulk and flakes are both ~17.0 eV. These values correspond to a $W_f$ of 4.2 eV. Such low values can be likely attributed to a n-type doping, which originates in presence of chalcogen vacancies, as found for several chalcogenides.\textsuperscript{14} Moreover, the presence of parasitic oxides, which form on the native Bi$_2$Te$_3$ powder after ambient exposure, can also lower the $W_f$ of the Bi$_2$Te$_3$ flakes.\textsuperscript{63} Figure 1g shows the UPS spectrum region near the $E_F$. These data evidence a non-negligible signal, decreasing to zero at the low binding energy region, corresponding to the position of the Fermi level. This behaviour is typical of metal-like materials, and likely arise from the metallic surface of Bi$_2$Te$_3$. Optical absorption spectroscopy (OAS) measurements of the Bi$_2$Te$_3$ flakes shows a weak broad band in the UV-visible-NIR range (Figure S3a), in agreement with previous studies on Bi$_2$Te$_3$ used for broadband non-linear optical processes.\textsuperscript{64,65} In addition, the Tauc plot analysis presented in Figure S3b, reveals the negligible band gap of the surface state of Bi$_2$Te$_3$ flakes.

Structural and morphological characterization of PSCs

A schematic illustration of an inverted PSC is shown in Figure 2a, consisting of glass/ITO/PTAA/Perovskite/PC$_{70}$BM/BCP/Ag material stack. The positions 1 and 2 in which Bi$_2$Te$_3$ flakes have been incorporated as ETL dopants and interlayer films, respectively, are also depicted in Figure 2a. Based on the aforementioned spectroscopic characterization, the sketch of the materials energy diagram is graphically presented in Figure 2b, revealing that the $W_F$ of the Bi$_2$Te$_3$ flakes is between the LUMO of the PC$_{70}$BM (~4 eV)\textsuperscript{66} and the $W_F$ of the Ag (~4.3 eV).\textsuperscript{67} This finding, in combination with the metallic character of the material surface states, propelled our efforts towards the use of Bi$_2$Te$_3$ flakes in PSCs to fulfill a dual function: 1) to dope the PC$_{70}$BM ETL in order to accelerate the electron transport through conductive pathways offered by the metallic surface states of the flakes while suppressing the electron backscattering and the associated recombination at the perovskite/ETL interface; 2) to form an ultra-thin interlayer between the ETL and the Ag to further align the energy levels of the overall structure and to suppress various chemical instability effects by blocking the migration of iodide and silver ions, as well as the diffusion of oxygen and moisture towards the PC$_{70}$BM and the perovskite.\textsuperscript{68-71}

Hereafter, the cells using pristine PC$_{70}$BM is named PSC-Ref. The cells using doped PC$_{70}$BM are named PSC-Dop2 and PSC-Dop3 for the Bi$_2$Te$_3$ flake dispersion doping of the PC$_{70}$BM solution of 2% and to 3% v/v, respectively. The cells incorporating the Bi$_2$Te$_3$ interlayer are named PSC-Int1, PSC-Int2 and PSC-Int3 having an interlayer respectively formed by 1 Sc, 2 Scs and 3 Scs of the Bi$_2$Te$_3$ flake dispersion onto PC$_{70}$BM. Finally, the cells incorporating both engineering approaches are named PSC-Com1, PSC-Com2 and PSC-Com3, having an interlayer formed by 1 Sc, 2 Scs and 3 Scs, respectively, while all incorporating 2% v/v PC$_{70}$BM doping.

Representative top-view and cross-section SEM images of the PSC-Ref are presented in Figure 3a and 3b respectively. In particular, Figure 3a shows the perovskite surface, evidencing crystal grain sizes of approximately 250nm. Figure 3b depicts a typical cross-section of a complete reference device, well showing its layered structure. Top-view and cross-section SEM images of PSC-Com2 are shown in Figure 3c and d, respectively. Notably, since most of the flakes have thickness around 3 nm or below (see TEM and AFM data in Figure 1), only the thicker Bi$_2$Te$_3$ flakes can be detected by the SEM imaging shown in Figure 3c). However, SEM-EDX analysis (Figure S4) and AFM measurements (Figure S5) confirmed the presence of Bi$_2$Te$_3$ flakes onto the PC$_{70}$BM surface, as well as inside the doped PC$_{70}$BM (Figure S6a). The Bi$_2$Te$_3$ interlayer positioned onto the PC$_{70}$BM surface passivates shunt pathways by covering both cracks and pinholes (for details see the extended discussion regarding the J-V analysis in the next section). Moreover, the Bi$_2$Te$_3$ flake doping does not affect the morphology of the PC$_{70}$BM, which is similar to the one reported in previous works.\textsuperscript{19} Finally, as shown by the cross-sectional SEM imaging (Figure 3d), the insertion of the Bi$_2$Te$_3$ interlayer does not affect the device morphology, indicating that the solvent (CB) used to disperse the Bi$_2$Te$_3$ flakes is compatible with both the PC$_{70}$BM and the perovskite layer. A perovskite layer thickness of approximately 400 nm is determined for both device types.
Steady state photovoltaic characterization of PSC devices

The photovoltaic performance of the PSCs was initially evaluated by incorporating different levels of Bi$_2$Te$_3$ doping in the PC$_{70}$BM ETL. As shown in Figure 4a, the optimal photovoltaic performance was achieved for 2% v/v doping, namely PSC-Dop2. More in detail, the incorporation of Bi$_2$Te$_3$ flakes increased the PCE of champion devices from 16.89% (PSC-Ref) to 18.0%, corresponding to a ~6.6% enhancement (see Table 1). However, by further increasing the amount of doping to 3% v/v (PSC-Dop3), the PCE decreased to 17.4%. Nevertheless, this value is still superior to the reference cell.

A similar investigation was performed by tuning the number of consequent SCs (from 0 up to 3) of the Bi$_2$Te$_3$ flake dispersion in IPA:ACN on top of the undoped PC$_{70}$BM (Figure 4b). The maximum photovoltaic performance was achieved after 2 consequent SCs (PSC-Int2), in a PCE as high as 18.6% (+10% vs. PSC-Ref). The further increase of the number of the SCs to 3 (PSC-Int3), significantly reduced the resulting photovoltaic performance, resulting in a PCE close to 15%. This behaviour is likely due to the enhanced electrons’ scattering rate as the interlayer thickness increases, as well as to the possible negative effect of the excessive deposition of the underlying layers to IPA:ACN solvent (see SEM analysis in Figure S6b and S6c). Although the simplicity of spin coating deposition is effective for preliminary lab-scale studies, the use of automated methods to deposit 2D materials based inks on large scale, e.g., spray coating, could overcome any issue related to the spin coating deposition of Bi$_2$Te$_3$ flakes and further increase the current device performance.

Table 1 summarizes the main devices’ photovoltaic parameters extracted from the J-V curves, i.e., the PCE, the Voc, the Jsc and the fill factor (FF). All devices exhibited negligible hysteresis as proved by Figure S7, where forward and reverse J-V scans are presented and by Table 1, where all devices’ characteristics are listed. Moreover, the steady-state PCE behaviour of the devices was excellent as shown in Figure 4d, where the maximum power point tracking plot of PSC-Com2 PCE for 250 s is depicted (below 1% difference).

Figure 5b displays the EQE spectrum of representative PSC-Int2 and PSC-Com2 devices. The EQE curves shows a wide photoresponse in a spectral region from 300 to 830 nm, which is consistent with the absorption spectrum of the perovskite film. From the high-wavelength edge of the EQE spectrum, the band gap of the perovskite is estimated to be ~1.6 eV. The integrated current densities for PSC-Int2 and PSC-Com2 are 21.01 and 22 mA cm$^{-2}$, respectively, which deviate less than 3% compared to the Jsc values measured in the J-V curve (Figure 5a).

Photoluminescent (PL) measurements were also performed to support role the Bi$_2$Te$_3$ flakes in improving the performance of the PSCs. Noteworthy, PL analysis represent an effective tool to qualitatively detect changes of carrier extraction rates at the various interfaces of the PSCs. As shown in Figure S8, our PL measurements corroborate the beneficial role of Bi$_2$Te$_3$ flakes acting either as ETL dopant or as interlayer in inverted PSCs. Indeed, although a significant quenching of the PL intensity occurs after the deposition of PC$_{70}$BM layer on top the perovskite (inset of Figure S8), the maximum PL quenching is observed in the PSC-Com2. Therefore, these data clearly indicate that the PSC-Com2 shows an optimal charge extraction, in agreement with its highest photovoltaic performance among those measured for the investigated PSCs.

In summary, the incorporation of Bi$_2$Te$_3$ flakes either as PC$_{70}$BM dopants or as interlayer, the photovoltaic performance can be significantly improved, suggesting an active role of the flakes to enhance the electron extraction dynamics. More in particular, the Bi$_2$Te$_3$-basedPSCs exhibited higher Voc, Jsc and FF values compared to reference cell as a direct consequence of: 1) the favourable energetic alignment between the LUMO of the PC$_{70}$BM and the Wf of the Ag in the presence of the Bi$_2$Te$_3$ flakes, and 2) the enhanced carrier extraction induced by conductive paths within the PC$_{70}$BM layer originated from the surface states of Bi$_2$Te$_3$ flakes.

Transient photovoltaic characterization of PSCs

Transient photovoltage and TPC measurements were performed to further support the physical mechanism of the reported performance enhancement when the Bi$_2$Te$_3$ flakes were incorporated into the PSCs. Figure 6a shows the comparison between the photovoltage decay curves of PSC-Int2, PSC-Com2 and PSC-Ref. Small perturbation TPV decays followed a single exponential trend, which can result from either a charge carrier annihilation or a three-body recombination. Since the excitons in perovskites dissociate after 2 ps upon generation and our measurement cover a µs-scale, we can safely disregard the potential exciton contribution. Hence, the measured decay curves are the consequence of the electron-hole recombination, and the transient tail
can directly yield the carrier lifetimes. The data indicate that the devices incorporating Bi$_2$Te$_3$ flakes exhibit a V$_{oc}$ decay slower than the one of reference device. In particular, TPV results show that the Bi$_2$Te$_3$ flakes reduce the charge recombination rate and increase the charge carriers’ lifetime (Figure 6b), which is consistent with the highest V$_{oc}$ of Bi$_2$Te$_3$-based devices measured through the J-V characterization (see Figure 5a and Table 1). Furthermore, the addition of the Bi$_2$Te$_3$ flakes does not significantly affect the distribution of shallow defect states, as seen from the voltage rise times shown in the inset of Figure S9 (panels a to d), clearly demonstrating a negligible change between reference and the Bi$_2$Te$_3$-based PSCs. On the other hand, PSC-Int2 and PSC-Com2 devices are less sensitive to capacitive contributions (low bias conditions in Figure S9). This is due to the spatially divided distribution of charge carriers and shunts pathways, which means that the Bi$_2$Te$_3$-based PSCs are less affected by electrically injected / background carriers. Transient photocurrent experiments in charge extraction mode demonstrated that the use of Bi$_2$Te$_3$ flakes increases the overall extracted charge density, especially in PSC-Com2 device (blue data in Figure 6c). This data suggests that the metallic character of the Bi$_2$Te$_3$ flakes improve the charge extraction efficiency. The measurements performed in high perturbation regime (0.8 duty cycle) show the absence of deep trap states in all the tested samples (see supplementary TPC data in Figure S10). By doping the PC$_{70}$BM with the Bi$_2$Te$_3$ flakes, the charge transport was slightly slowed down, as evidenced by the calculated transit times (Figure 6d), obtained under low perturbation conditions. However, this is compensated in the optimal device case (PSC-Com2 device), which showed a higher extraction rate compared to reference device. The extrapolated charge carrier transfer times are in the order of 10$^{-7}$ s in all the investigated devices. These values are about ten times higher than the bimolecular recombination lifetime measured by TPV (tens of μs). Therefore, we can reasonably assume that the charge recombination and extraction processes are non-competitive, which is consistent with the high PCE achieved by our PSCs.

The drift mobility of electrons/holes was probed using charge extraction by linearly increasing voltage (photo-CELIV) under various light pulse delay points. More in detail, the drift mobility was derived from the extracted charge represented by the part of the transient superimposed over the displacement current level (Figure S11). Taking into account the fact that perovskites are not highly disordered materials and according to the equation proposed by Lorrmann et al. mobility can be derived.$^{73}$

$$\mu = \frac{L}{2At_{max}^2} \left[ \frac{1}{6.2 \left( 1 + 0.002 \frac{\Delta V}{V_0} \right)} + \frac{1}{\left( 1 + 0.12 \frac{\Delta I}{I_0} \right)^2} \right]$$

where L is active layer thickness, A is the ramp of the extraction voltage, t$_{max}$ is the point of transient measurement where current reaches its peak and ΔV/I$_0$ ratio corresponds to the level of charge accumulation. As shown by Figure 6e, both PSC-Int2 and PSC-Com2 demonstrated improved charge carrier mobility compared to the reference device by approximately half an order of magnitude. This effect results in a more efficient charge transfer, which agrees with the TPC results. Notably, the delay of the photogeneration pulses does not affect the drift mobility, which means that the charge carrier transport is well balanced. Additionally, the PSC-Int2 devices were characterized by the complete absence of transient peak shift, suggesting that both charge mobility and electrical conductivity in Bi$_2$Te$_3$-doped PC$_{70}$BM are improved compared to the reference device. These effects likely impede the charge transport to become dispersive (Figure S11).

**Lifetime stability measurements of PSCs**

The stability of the PSCs is also a crucial performance parameter for addressing typical commercial standards in photovoltaic technologies. Several reports have identified oxygen and moisture as external degradation agents along with the diffusion of metal species from the top electrode towards the perovskite layer and the escaping of organic molecules from the perovskite crystal.$^{66,69}$ Hereby, the evaluation of the lifetime of the investigated PSCs was performed by implementing the ISOS-L2 protocol, in which the samples are tested under continuous 1 Sun illumination at temperature above 65 °C. As shown in Figure 7a, the PCE of the PSC-Ref exhibited a drop of its initial PCE by 50% after 15 h (T$_{50}$), and below 20% after 100 h. The PSC-Int1 reported a moderate stability performance, showing a lifetime T$_{50}$ of ca. 70 h. Notably, PSC-Int2 significantly improved the device stability, displaying a T$_{70}$ superior to 600 h. The stability of PSC-Int2 can be explained by the optimal coverage of the PC$_{70}$BM with the Bi$_2$Te$_3$ flake interlayer optimized in its thickness. It has been already reported that the PC$_{70}$BM is the main path for the migration of the metal species towards the perovskite.$^{74,75}$ We attribute the exceptionally stability of the PSC-Int2 to the Bi$_2$Te$_3$ interlayer which passivates the PC$_{70}$BM pin-holes and its imperfections. Besides, Bi$_2$Te$_3$ interlayer acts as a barrier against the of the Ag ions migration towards the perovskite, while suppresses the escaping rate of both cations and anions from the perovskite (mainly MA).$^{72}$ On the other hand, PSC-Int3 device exhibited an enhanced stability compared to the reference retaining 40% of its initial PCE after 400 h. However, its stability was lower than PSC-Int2 device. This can be attributed to the washing out of the previously formed films when the number of consecutive SCs exceed two, and/or the negative impact of the solvent of the Bi$_2$Te$_3$ flake dispersion over the underlying PC$_{70}$BM and perovskite layers.
A typical lifetime stability measurement of the best performing PSCs-Int2 reveals a burn-in phase lasting for about 100 h. During this phase, the device retained 70% of its initial PCE. Thereafter, a stabilized behaviour is followed with a slow linear drop. In accordance to the updated ISOS protocols that specifically address the testing protocol for PSCs, the time at the end of burn-in phase can be noted as $T_{\text{burn-in}}$, while the time at which the PCE is dropped by 20% compared to this value is referred as $T_{80}$. A linear fit was performed in the temporal region corresponding to a stable PSC behaviour enabling the estimation of the degradation rate. The degradation slope was found to be $-0.017 \%\text{PCE h}^{-1}$. Conversely, following this approach we estimated a $T_{80}$ to be approximately 1100 h under continuous 1 Sun illumination.

**Conclusions**

Ultrathin flakes of Bi$_2$Te$_3$ were produced through LPE method to be incorporated via solution-processed techniques, in two distinct positions across inverted planar PSCs. In particular, the Bi$_2$Te$_3$ flakes were evaluated as dopants of the PC$_{70}$BM and as interlayer between the PC$_{70}$BM and the Ag. The combination of these two engineering approaches led to an increase of both device efficiency and stability. The optimal doping of PC$_{70}$BM with Bi$_2$Te$_3$ flakes was found to be 2\% v/v, which resulted in a PCE of 18.0\%. This value corresponds to an increase of 6.6\% compared to the values measured for the reference device. An optimal interlayer was achieved by performing 2 SCs of the Bi$_2$Te$_3$ flake dispersion onto the PC$_{70}$BM, leading to a PCE of 18.6\%. This value corresponds to a 10\% improvement, while this protective interlayer notably enhanced the stability and lifetime of the devices under ISOS-L2 protocols. By combining these two engineering approaches, PCE values of champion devices (PSC-Com2) were reported up to 19.46\%, corresponding to an improvement of 15.2\% compared to reference device. Furthermore, PSC-Com2 device retained 80\% of its initial PCE, after the burn in phase, for more than 1100 h, resulting in one of the highest stability performances reported for inverted PSCs to date. Transient transport measurements, structural and optical characterization supported that this combined engineering approach increases the carrier lifetimes, the extracted charge density and the carrier effective mobilities.

**Conflicts of interest**

In accordance with our policy on Conflicts of interest please ensure that a conflicts of interest statement is included in your manuscript here. Please note that this statement is required for all submitted manuscripts. If no conflicts exist, please state that “There are no conflicts to declare”.

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**Notes and references**

Figure 1. a) Representative TEM image of Bi$_2$Te$_3$ flakes. b) Representative AFM image of Bi$_2$Te$_3$ flakes. Height profiles of the indicated sections are also shown. c) Lateral size and d) thickness statistical analyses for Bi$_2$Te$_3$ flakes. e) Raman spectra of Bi$_2$Te$_3$ bulk crystals and flakes. f) Secondary electron threshold region of He-I UPS spectrum of the Bi$_2$Te$_3$ flakes. g) The He-I UPS spectrum region near the E$_F$ of the Bi$_2$Te$_3$ flakes.
Figure 2. (a) Schematic illustration (not in scale) of a typical inverted p-i-n perovskite device consisting of the following material stack: glass/ITO/PTAA/Perovskite/PC$_{70}$BM/BCP/Ag. A two-fold engineering approach is implemented by doping the ETL, PC$_{70}$BM (position 1), with Bi$_2$Te$_3$ flakes (flakes dispersion in CB) and by forming an interlayer on top of the ETL (position 2) using multiple spin coatings of Bi$_2$Te$_3$ flakes (pristine flakes dispersion in IPA:ACN). (b) A graphical presentation of material’s stack energy levels.
Figure 3. Representative top view and cross-section SEM images of PSC-Ref (panels a, b) and PSC-Com2 (panels c, d). a) Top view of perovskite surface prior to PC$_{70}$BM deposition in PSC-Ref. b) Cross-section SEM image of PSC-Ref. c) Top view of interlayer surface in PSC-Com2. d) Cross-section SEM image of PSC-Com2. False colouring was used for the different layers of the structure: ITO/PTAA/perovskite (PSK)/PC$_{70}$BM/Ag. For clarity the top view SEM images were collected in areas outside of the contacts and in the case of the reference before the PC$_{70}$BM coating.
Figure 4. Device performance statistics of each engineering approach implemented separately or combined at various material conditions. a) Device performance statistics of PSC-Ref (black), PSC-Dop2 (red) and PSC-Dop3 (blue). b) Device performance statistics of PSC-Ref (black), PSC-Int1 (red), PSC-Int2 (blue) and PSC-Int3 (purple). The number of SC was 1, 2 and 3, respectively. c) Device performance statistics of PSC-Dop2 (red), PSC-Int2 (blue), as well as PSC-Com2 (purple). d) Maximum power point tracking plot of PSC-Com2 for 250 s showing enhanced stability of steady state PCE.
Figure 5. J-V characteristics at 1 Sun illumination of each engineering approach and EQE spectrum of representative device. 

a) J-V curves of PSC-Ref (black), PSC-Dop2 (red), PSC-Int2 (green), and PSC-Com2 (blue). b) Representative EQE of PSC-Int2 and PSC-Com2. The integrated current density of the device’s spectral response with the AM1.5G photon flux spectrum is depicted in the right axis.
Figure 6. Estimation of carriers’ lifetime, device extracted charge density and transit time, as well as effective carriers’ mobility based on transient measurements. (a) Normalized $V_{oc}$ decay of PSC-Ref (black), PSC-Dop2 (red) and PSC-Com2 (blue). The lines represent fittings with an exponential decay function. (b) Extracted corresponding lifetimes from TPV decay measurements at different bias conditions. (c) Charge density and (d) transit time extracted from TPC measurement. The lines in panels b-d) represent linear fittings. (e) Drift mobility estimation from photo-CELIV technique.
Figure 7. a) Long term ISOS-L2 stability measurements of PSC-Ref (black), PSC-Com1 (purple), PSC-Com2 (red) and PSC-Com3 (blue). b) Further analysis of the long term stability measurement of PSC-Com2. All the devices were encapsulated. The red line is a linear fit of the experimental points in the stabilized region extrapolated to 1200 hrs. $T_{\text{burn-in}}$ marks the end of the burn-in phase and $T_{s80}$ denotes the time which the initial PCE is dropped by 20% in the stabilized region. The inset shows the linear region of the lifetime measurements.
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<th>Rsh (Ohm cm$^{-2}$)</th>
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Table 1. Photovoltaic parameters of champion PSCs of each engineering approach extracted from the J-V forward (FS) and Reserve (RS) scans.
Figure S1. XRD pattern of the perovskite film
**Figure S2.** Photograph of the Bi$_2$Te$_3$ 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$_2$Te$_3$ flakes and b) Tauc plot analysis revealing the negligible band gap of the Bi$_2$Te$_3$ flakes.
corresponding EDS maps for Pb (\(\text{L}_{\alpha} = 10.55\) keV) and Bi (\(\text{L}_{\alpha} = 11.84\) 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\(_2\)Te\(_3\) flakes spin coated (4SC) on top, noted as white spots. The left image spans an area of 20x20 \(\mu\)m\(^2\) and the right a 10x10 \(\mu\)m\(^2\). Similarly, with SEM images, AFM images capture only the thick flakes due to resolution limitation.
Figure S6. a) SEM image of PC\textsubscript{70} BM surface in PSC-Dop2 sample. The red circles show Bi\textsubscript{2}Te\textsubscript{3} flakes in the PC\textsubscript{70} BM layer. Since we were using only the supernatant resulting from the solvent transfer of the Bi\textsubscript{2}Te\textsubscript{3} 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 Bi\textsubscript{2}Te\textsubscript{3} 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.

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Figure S8. PL measurements of undoped PC$_{70}$BM without (red) and with two spin coatings of Bi$_2$Te$_3$ interlayer (yellow) on top. Besides, doped PC$_{70}$BM without (green) and with 2 spin coatings of Bi$_2$Te$_3$ 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.