New fullerene derivative as an n-type material for highly efficient, flexible perovskite solar cells of a p-i-n configuration

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Metal halide perovskites have raised huge excitement amongst emerging photovoltaic technologies. The possibility of fabricating perovskite solar cells on light-weight, flexible substrates, with facile processing methods, provides very attractive commercial perspectives. Nevertheless, efficiency values for flexible devices reported in literature typically are falling short in comparison to rigid, glass-based architecture. Here, a solution-processable fullerene derivative, [6,6]-Phenyl C61 butyric acid hexyl ester (PCBC6), is reported as a highly efficient alternative to the commonly used n-type materials in perovskite solar cells. The cells with the PCBC6 layer deliver a power conversion efficiency of 18.4%, fabricated on a polymer foil, with an active area of 1 cm². Compared to the PCBM benchmark, significantly enhanced photovoltaic performance is obtained, which is primarily attributed to the improved layer morphology. It results in a better charge extraction and reduced non-radiative recombination at the perovskite/ETM interface. Solution-processed PCBC6 films were uniform, smooth and displayed conformal capping of perovskite layer. Additionally, a scalable processing of PCBC6 layers is demonstrated with an ink-jet printing technique, producing flexible PSCs with efficiencies exceeding 17%, which highlights the prospects of using this material in an industrial process.

1. Introduction

Perovskite solar cells (PSCs) garnered a lot of attention within the scientific community over the last couple of years, thanks to their attractive commercial prospects.^[1] The power conversion efficiency reported for lab-scale devices recorded unprecedented progress, improving within one decade from a mere 3% to over 25%.^[2,3] One of the great advantages of the perovskite technology over conventional photovoltaics (PV) is the possibility to fabricate PSCs on light-weight and flexible substrates.^[4] This allows to attain very high specific powers and enables versatile, low-cost manufacturing methods.^[5] New value propositions available for PSCs position this technology

as a tangible solution for the emerging and rapidly growing PV markets, such as building-integrated PV (facades, windows, rooftops), automotive (vehicle integration), or internet-of-things (autonomous sensors, Industry 4.0).^[6,7]

As PSCs are rapidly moving towards the industrial phase, there are still open questions about the prevailing architecture, choice of materials (including charge selective layers) and processing methodologies. In a commonly employed planar heterojunction perovskite solar cell architecture, perovskite film is sandwiched between two charge selective contacts – electron transporting material (ETM) and hole transporting material (HTM). Detrimental defects tend to form at both of these interfaces with the perovskite layer, which leads to an increase of non-radiative recombination losses and deterioration of a solar cell performance.^[8] Suitable chemical functionalization of perovskite's surface (different groups of ionic or covalent character) can eliminate or passivate some of these interfacial defects.^[9] Additionally, interface chemistry can trigger various degradation mechanisms, and it thus may affect device long term stability.^[10] Therefore, charge selective contacts can be seen as pivotal PSC ingredients and their appropriate chemical design and layer formation are of fundamental importance for the optimal device operation and stability. So-called 'inverted' PSC architecture (planar heterojunction of p-i-n configuration) is a popular option for fabricating devices on flexible, polymeric substrates.^[11,12] This is primarily due to possibility of facile, solution-based processing, without high temperature annealing steps, and wide range of available charge selective materials. A range of different organic and inorganic materials have been used for electron extraction in PSCs.^[13–15] Fullerene (C₆₀) and various fullerene derivatives were widely applied in efficient p-i-n devices due to their demonstrated effective electron extraction from the perovskite layer. Additionally, these organic materials allow low temperature thin film processing from solution on top of perovskite material,

without causing any damage to the active layer. It was also reported that fullerene derivatives can play a passivating role in iodide-rich trap sites on the surface of perovskite layer.^[16] Solution-processed fullerenes conformally cover the surface and permeate into the perovskite layer through the pinholes and grain boundaries, effectively reducing surface recombination. Xu et al. showed that mobile ions can interact with fullerene moiety and form a fullerene-halide adduct, which is thought to suppress the field-induced anion migration in the perovskite film.^[17]

Phenyl-C61-butyric acid methyl ester (PCBM) is the most commonly used ETM in the perovskite solar cells of p-i-n configuration.^[18] However, the PCBM-based contact can still limit the device performance, due to non-radiative recombination processes at the perovskite/ETM interface, and difficulties in smooth film formation, often resulting in a non-uniform layer morphology.^[19–21] Several strategies of improving the PCBM film quality with different additives and dopants added to the fullerene solution were reported.^[22,23] Particularly, insulating polymers, such as polystyrene (PS), poly(ethylene oxide) (PEO), or poly(methyl methacrylate) (PMMA), when blended with PCBM at small weight percentage, lead to smoother morphologies and enhanced solar cell performance.^[24–27] The caveat of this approach is limited carrier transport and extraction properties due to non-conductive character of the added polymer, which could result in another type of losses. Therefore, a more effective approach is highly desirable, where solution-processed, smooth and inexpensive fullerene coating of high optoelectronic properties could be fabricated.

To solve these issues, in this work, we are reporting a fullerene derivative, [6,6]-Phenyl-C61 butyric acid n-hexyl ester (PCBC6), employed as an effective electron transport material in perovskite solar cells of p-i-n configuration. PCBC6 exhibits higher solubility in non-polar solvents due to the presence of a long alkyl chain group, which results in a more uniform and smoother film formation. Interfacial characteristics of perovskite solar cells employing different

fullerene ETMs (PCBC6, PCBM and C₆₀) were analyzed and compared. Devices with PCBC6 exhibit improved power conversion efficiency, reaching 18.4% on flexible substrates, with an active area of 1 cm². This is exceeding the current state-of-the-art large area (above 1 cm²) flexible PSC performance. To the best of our knowledge the highest PCE reported up to date for this type of devices is 20.01% (0.09 cm² active area) and 17.04% (1.08 cm² active area).^[28,29] We found that the incorporation of PCBC6 leads to the reduction of non-radiative recombination losses at the interface with perovskite, as evidenced by transient photovoltage decay measurements and determination of quasi-Fermi level splitting of perovskite layer brought in contact with different ETMs. Reduced interfacial losses result in open-circuit voltage (V_{oc}) improvement for the PCBC6 devices. Significantly, the newly developed material and processing method allow us to demonstrate scalable processing of flexible PSCs, reaching 17% with an ink-jet printed PCBC6. The overall concept paves the way for industrial upscaling of this technology.

2. Results and Discussion

Planar heterojunction thin-film solar cell architectures require an intimate contact between charge selective layer and a photo-absorber. In order to investigate the layer formation ability of different fullerene derivatives (PCBC6 and PCBM), we prepared chlorobenzene solutions and employed spin-coating as a deposition technique to fabricate thin films on the surface of a metal halide perovskite material. We investigated the morphologies of obtained layers with the atomic force microscopy (AFM) imaging and derived the root-mean-square (RMS) roughness of the studied films. PCBC6 sample shows the smoothest surface (RMS = 8 nm), significantly lower than the perovskite itself (RMS = 18.7 nm). Furthermore, the roughness of the PCBM sample processed in the same manner is considerably higher (RMS = 30.8 nm). The 3D surface topography images and

cross-section focused ion beam scanning electron microscopy (FIB-SEM) images are shown in **Figure 1**. It is evident that the PCBC6 displays more conformal and uniform coverage over the perovskite surface than the PCBM sample. For the comparison, we also include images of the C₆₀ layer thermally evaporated on top of perovskite surface. The roughness of this sample (RMS = 17.7 nm) is comparable to the bare perovskite, and cross-section FIB-SEM image depicts very uniform fullerene's coating, with complete coverage of perovskite surface. This is characteristic for a physical vapor deposition (PVD) process, and such layer morphology should be beneficial for the device performance.

(Insert Figure 1 here)

The PCBC6 ability to form smoother, more uniform layers could be a result of a higher tendency to form a more ordered and stable films, and more optimal precipitation dynamics during the spin-coating process. We compared the solubility of the two fullerene derivatives in a host solvent. The PCBM concentration of 50 mg ml⁻¹, both in chlorobenzene and 1,2-dichlorobenzene, resulted in an oversaturated solution (literature values for PCBM solubility: 40 mg ml⁻¹ in chlorobenzene and 35 mg ml⁻¹ in dichlorobenzene),^[30] whereas PCBC6 exhibited solubility higher than 115 mg ml⁻¹ in chlorobenzene. The pictures of both solutions are shown in **Figure S1**, Supporting Information. PCBC6 differs from the PCBM by a longer alkyl chain in the ester group. The structures of both molecules are shown in **Figure 2**. The hexyl group present in the PCBC6 results in a large increase of a solubilization ability in non-polar solvents.^[31] Additionally, it might increase the quality of the films in terms of stability, crystallinity and homogeneous growth.

To gain insight into the packing properties of PCBM and PCBC6, we carried out first principles DFT simulation to evaluate the intermolecular interaction characteristics of the two materials. We modeled the solid state bulk phase of PCBM and PCBC6 molecules, employing periodic boundary

conditions based on a 4-molecule unit cell (see **Figure 2**). As a starting point in both cases, we considered a structure that is available for PCBM from X-ray diffraction (XRD) data, and we performed relaxation of cell parameters and atomic positions.^[32] As we can see in **Table S2**, Supporting Information, the calculated cell parameters of PCBM are in excellent agreement with the experimental measurements confirming the reliability of the method. To evaluate the thermodynamic tendency of forming compact and homogenous film, we calculated aggregation energy between molecules in the bulk by considering total energy of the system with respect to the energy of a single molecule, following the equation:

$$\Delta E = \frac{E_{total} - 4E_{single-molecule}}{4} \quad (1)$$

where E_{total} is the total energy of the simulated system (consisting of 4 PCBM or PCBC6 molecules) and $E_{single-molecule}$ is the energy of the PCBM or PCBC6 molecule simulated in the same theoretical conditions.

We found that aggregation is preferentially favored for PCBC6, which gains additional 0.32 eV when compared to PCBM (see **Table S2**). Stronger intermolecular interactions found for PCBC6 are related to its structure, where long alkyl chains are interacting through dispersion forces, as shown in **Figure 2c-d**. Specifically, as reported in **Table S2**, these interactions completely drive the aggregation of our systems, and imply preferred packing of PCBC6 with respect to PCBM (ΔE of -2.35 and -2.76 eV for PCBM and PCBC6, respectively). If only the electronic contributions were considered, it would give the opposite result (ΔE of 0.12 and 0.21 eV for PCBM and PCBC6, respectively). The higher aggregation tendency calculated for PCBC6 with respect to PCBM we associate with a tendency to form more uniform, smoother and more stable film, due to the stronger intermolecular dispersion interactions that optimize, as it was proposed by Benetto et al.^[33]

(Insert Figure 2 here)

Having established a rational interpretation of the different film morphologies for the investigated molecules, we move to analyze the electronic properties of both ETMs. The role of an ETM in perovskite solar cells is to extract photogenerated electrons and reflect holes. The electrons subsequently need to be efficiently transported to the electrode contact. The position of ETM's energy levels provides insights on the efficiency of electron extraction process. Therefore, we evaluated the projected density of states for both, PCBM and PCBC6 optimized bulk phase, as shown in **Figure 2e**. After the alignment of energetic levels to the lowest energy band, we can clearly see that the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of bulk PCBC6 are slightly lower than those of PCBM. In both cases, the distribution of states is nearly the same in the innermost levels of valence band, however, those of PCBM are slightly shifted to the higher energies. Conversely, for the isolated molecules we found almost no differences in the HOMO/LUMO energies between PCBM and PCBC6, as shown in **Table S3**, Supporting Information. This suggests that the modification of the electronic properties are not due to different chemical structures of both ETMs, but can be rather ascribed to the geometrical distortion induced by the molecular packing. Therefore, PCBC6 is well suited to selectively extract electrons from the perovskite layer from energetic point of view. In order to investigate the PCBC6 charge carrier transport properties, we performed electrical conductivity measurements. We prepared in-plane samples of fullerene layers processed on the PEN/ITO substrates, where a 100 μm wide trench in the ITO layer was scribed with a laser. We extracted conductivity values from current-voltage curves (shown in **Figure S3**, Supporting Information). The PCBC6 conductivity of $6.58 \times 10^{-5} \text{ S cm}^{-1}$ is at the same range as the value obtained for PCBM, $4.68 \times 10^{-5} \text{ S cm}^{-1}$. This is consistent with the PCBM conductivities reported in literature.^[34]

2.1. Photovoltaics Devices

After demonstrating the basic feasibility of PCBC6 to be used as an ETM in perovskite solar cells, we constructed planar heterojunction devices of the p-i-n configuration, using different fullerenes as the n-type layers. We applied the following solar cell structure: PET/IZO/PTAA/perovskite/ETM (varied)/BCP/Ag. All the photovoltaic devices reported in this work, we fabricated on flexible substrates (PET foil), with 1 cm² device area. We chose to work with the polymer foils due to broad and attractive commercial prospects of flexible photovoltaics, and particularly flexible perovskite PV. We employed a perovskite layer of the mixed cation and mixed halide composition, Cs_{0.04}(MA_{0.17}FA_{0.83})_{0.96}Pb(I_{0.83}Br_{0.17})₃, which we fabricated with a solvent engineering strategy, modifying a method reported before.^[35] All the solution-based depositions were carried out by the spin-coating process inside the nitrogen-filled glovebox. In the Supporting Information, **Figure S4**, we demonstrate the scheme of the device architecture with corresponding energy levels for each layer in the stack. Additionally, we show the cross-section FIB-SEM image of the solar cell, documenting all the materials in the device, and their thicknesses. For the reference, we fabricated perovskite solar cells with the two commonly used ETMs, evaporated fullerene C₆₀, and spin coated PCBM layer (processed from a dichlorobenzene solution). We present the current density-voltage curves (J-V) and stabilized power output (SPO) of the most efficient devices employing different ETMs in **Figure 3**. The external quantum efficiency (EQE) spectra and integrated current density values for each solar cell type are shown in **Figure S5**, Supporting Information. All the studied devices displayed minimal hysteresis effects. We present J-V curves in both scan directions for the representative cells in **Figure S6**, Supporting Information. In **Table 1** we report average values of the photovoltaic parameters extracted from

the J-V curves, based on measurements of 31 independent cells, the parameters for the champion devices are given in brackets. The graphical representation of the statistics is shown in **Figure 3a**. The new fullerene derivative delivered the J-V-measured power conversion efficiency (PCE) of 18.4%. We observe that the stabilized power output (SPO) efficiency, measured at close to maximum power point, is lower, reaching 16.6%. For the reference device, employing solution-processed PCBM, we measured the PCE of 13.9%, and 13.3% SPO. The cell with the evaporated C₆₀ yielded the PCE of 18.5%, and 18.3% SPO. Lower SPO value for the PCBC6 sample could be a result of pertaining areas with thinner PCBC6, or even non-complete coverage where rougher perovskite surface structures occur (see **Figure 1e**). The optimized PCBC6 thickness, which resulted in the highest J_{SC}, is relatively low, and local drop of charge selectivity and increased recombination can reflect in higher hysteresis and reduced SPO value.^[36,37] In comparison, C₆₀ layer is very thin, but highly conformal and uniform, with no thickness variations (see **Figure 1g**), as it was deposited by thermal evaporation process. Therefore, the SPO value shows a good match with the J-V-derived efficiency for this device.

It is evident that the cells with the solution-processed PCBC6 deliver higher V_{OC} than the C₆₀ and PCBM-based devices. This observation points at the reduction of the non-radiative losses in this cell type. It can either originate from the more effective perovskite surface passivation by the fullerene moiety of PCBC6 molecules, or from suppressed recombination rates across the perovskite/ETM interface (without changing defect density on the perovskite side). The reduction of the perovskite trap state density by the fullerene-halide complex formation was reported before.^[38] To investigate this hypothesis, we performed space charge limited current (SCLC) measurements of electron only devices. From the J-V curves, we extracted defect densities of perovskite devices with different ETMs processed on top (the curves are shown in **Figure S7**,

Supporting Information). We estimated the smallest value of $1.01 \times 10^{16} \text{ cm}^{-3}$ for PCBC6, which compares to $1.91 \times 10^{16} \text{ cm}^{-3}$ and $1.40 \times 10^{16} \text{ cm}^{-3}$ derived for C_{60} and PCBM, respectively. This is consistent with the reports of stronger perovskite passivation effect imposed by solution-processed fullerene molecules, which can possibly penetrate deeper into the film structure through the grain boundaries.^[16] We note that these defect density values should be rather used for a comparative analysis, rather than precise quantitative determination of trap state population. It was recently reported that due to perovskite's ionic nature, the precise onset voltage where a device changes its operation mode can largely depend on the experimental conditions (voltage scan rate, scan direction, temperature).^[39] Nevertheless, considering that the perovskite fabrication process and SCLC measuring protocol in all three analyzed cases was exactly the same, observed differences we assign to surface phenomena caused by perovskite's interaction with different fullerene molecules. Surface passivation effects should have significant impact on non-radiative recombination processes occurring at that interface. We are providing further analysis of these processes with spectroscopic and electrical characterizations in the following sections.

Referring to the photovoltaic data compared in **Table 1**, we also point out higher short-circuit current-densities obtained for the C_{60} cells. The evaporated C_{60} layer is conformal and more uniform, with lower thickness variations across the sample than the solution-processed fullerene derivatives (PCBM, PCBC6), which are more affected by the perovskite surface roughness. This could influence the carrier extraction ability. The cells with the PCBM layer significantly lag behind the other two types. This is expected considering the poor layer formation of the PCBM film, as we showed with the AFM and FIB-SEM imaging. Highly non-uniform morphology results in a poor quality of the interface with the perovskite film. Thus, the efficacy of carrier extraction and carrier transport through the PCBM layer can be affected.

Furthermore, we point out a good reproducibility of the solar cell results, showing relatively low standard deviation of the performance parameters for the PCBC6 and C₆₀ cell types. We highlight that our devices had larger active areas than typically reported in literature, and they were processed on a PET foil. It is significantly more challenging from the reproducibility and layer formation point of view.

(Insert Table 1 here)

(Insert Figure 3 here)

2.2. Inkjet printed PCBC6 Devices

In order to show the scalability of the PCBC6 processing, we employed an ink-jet printing technique for the fullerene deposition and applied it to the flexible perovskite solar cells of the same architecture as described above. We used PixDro LP50 printer, equipped with the Konica Minolta printhead. The printing settings we optimized with the resolution of 360 dots per inch (dpi). To deposit a fullerene layer with the ink-jet process, we adjusted an ink composition to obtain optimal drying profile and appropriate rheological properties (viscosity, surface tension) of the solution. The best drop formation and most uniform film quality of a desired thickness we obtained for the PCBC6 solution in chlorobenzene, with a small addition of octane. Cross-section and 3D surface topography images of the printed layers we are showing in **Figure S8**, Supporting Information.

Perovskite solar cells (flexible substrate, 1 cm² active area) with the optimized ink-jet printed ETM showed a very good photovoltaic performance, surpassing 17% PCE for the best device. We are showing the J-V curves (both scan directions) and steady-state measurement in **Figure 4**. We can observe negligible hysteresis in these cells, with a small difference between J-V and SPO-derived

PCE values. Optimized ink-jet printed PCBC6 layers are thicker than spin-coated films, which results in a complete coverage of all the perovskite roughness (see **Figure S8c**), and therefore hysteretic effects are minimized. The statistics of photovoltaic parameters of 8 devices using printed PCBC6 are shown in **Figure S8a**.

(Insert Figure 4 here)

In the next step, within the range of studied fullerenes, we compare their ability to extract photogenerated electrons from the perovskite film, and the amount of interfacial non-radiative recombination occurring at that contact.

2.3. Interface Study

2.3.1. Quasi-Fermi Level Splitting

Determination of a quasi-Fermi level splitting (QFLS) in the photoactive layer was recently demonstrated as an effective way to assess the recombination losses at the perovskite interface with different charge selective materials. The QFLS can be derived from the photoluminescence quantum yield (PLQY) measurements.^[40,41] The PLQY is generally influenced by all the different non-radiative recombination channels and rate constants of each of these processes in respect to a radiative recombination rate.^[42] To probe the loss processes at the n-type contact, we measured the PLQY of perovskite films deposited directly on a glass substrate, and coated with different ETMs (bare perovskite, perovskite/PCBC6, perovskite/PCBM, perovskite/C₆₀).

We are showing the measured PL spectra in **Figure 5a**. We can observe that the bare perovskite layer shows the highest PL intensity. Addition of the n-type layer partially quenches the signal, primarily due to increased non-radiative recombination at the perovskite/ETM interface.^[43] The layer stack with the PCBC6 shows higher PL signal compared to other ETMs.

(Insert Figure 5 here)

We extracted PLQY values from the PL spectra measured at low light intensity (excitation wavelength: 405 nm, intensity: 5 mW cm⁻²), using the embedded software tool of the spectrofluorometer, more details are provided in the experimental section. Then, we calculated the QFLS of the perovskite stacks following the Equation 2.^[44]

$$QFLS = QFLS_{rad} + kT \cdot \ln(PLQY) \quad (2)$$

where, $QFLS_{rad}$ is the quasi-Fermi-level splitting in the radiative limit, k the Boltzmann constant and T the temperature.

(Insert Table 2 here)

In the **Table 2** and **Figure 5a**, we provide the summary of PLQY values, together with the calculated QFLS, for the 4 cases described above. For the comparison, we also provide the average V_{OC} values determined from the J-V measurements of the respective photovoltaic devices. The bare perovskite layer shows the highest PL signal with the PLQY of 0.0366% (measured at 0.05 sun), which corresponds to the QFLS value of 1.159 eV. The QFLS obtained for the PCBC6, PCBM and C₆₀ samples are 1.126 eV, 1.093 eV and 1.089 eV, respectively. The samples containing PCBC6 as the n-type layer exhibit the highest device V_{OC} , and the highest QFLS. This suggests that the voltage improvements recorded for the PCBC6 cells are strongly related to the reduced interface recombination at the n-type contact.

2.3.2. Photoluminescence Study

We extended the framework of the interface study by measuring the PL spectra of the complete perovskite solar cells with different ETMs (excitation wavelength: 532 nm, intensity: 100 mW cm^{-2}), at two different working conditions: open-circuit (V_{OC} was also recorded) and short-circuit. We are showing the graphs in **Figure 5b-c**. The summary of V_{OC} values and integrated PL intensities are listed in **Table 3**.

(Insert Table 3 here)

We observe a clear trend, with the PCBC6-based device delivering the highest V_{OC} , followed by the C_{60} cell type with 60 mV drop, and the PCBM sample with 130 mV drop in voltage in respect to the PCBC6 cell. This is consistent with the photovoltaic performance results presented in **Figure 3**. The integrated PL intensity follows the same order, being the highest for the PCBC6 and smallest for the PCBM cell type. When we switch the solar cell working point from the open-circuit to short-circuit condition, photogenerated charge carriers are being extracted. Thus, the PL quenching monitored at this condition can be used as a measure of the carrier extraction ability for each device type. Both C_{60} and PCBC6-based devices show high PL quenching which indicates their high charge carrier extraction efficacy. We should point out that the spin-coated PCBC6 film is likely to display larger inhomogeneity and thickness variations than evaporated C_{60} layers. This could contribute to the fact that the C_{60} -based cell type also displayed the highest average short-circuit current density, as shown in **Figure 3a**. Higher inhomogeneity of the PCBC6 cell could lead to a slower rate of the charge transfer across the perovskite interface in the regions where PCBC6 layer is too thick. This could explain larger differences in the PCE values derived from the J-V and SPO measurements, which we pointed out above. It was reported before that interfacial extraction barriers in a perovskite solar cell could contribute to the hysteresis effect and reduced steady-state power output.^[45] The direct link between optical and electrical measurements

provided here strongly suggests that the PCBC6-based device displays reduced non-radiative recombination at the n-type interface, possibly due to perovskite surface passivation effect.

2.3.3. Transient Photovoltage and Transient Photocurrent Study

In order to further corroborate the analysis of the perovskite interface with the selected n-type materials, we performed transient photocurrent (TPC) and transient photovoltage (TPV) measurements. The TPC measurement was performed in a high perturbation regime, which means that the cell went from dark to a specific illumination set by the LED excitation light source. We applied 10 different light intensities, ranging from 30 to 160 mW cm⁻² (the details are provided in **Table S1**, Supporting Information). The cell was kept in the short-circuit condition during the entire measurement. The decay of current density was monitored over time after switching off the light. We integrated the current density time decay to obtain the extracted charge density. **Figure 6a** shows the charge density values derived at different perturbation light intensities. We can observe that the cell with C₆₀ layer exhibits slightly improved carrier extraction efficacy in comparison to the PCBC6 and PCBM types, especially at lower light intensities. This is consistent with the spectroscopic data discussed above. It could originate from the deeper LUMO level of the C₆₀ molecule when compared to the PCBM/PCBC6.^[45] The TPV measurement was performed in a small perturbation regime. The cell was kept at open-circuit, with a specific background illumination applied from the LED light source. Then, a small overcurrent was sent to the LED to create a voltage perturbation (20 mV), which decay was subsequently monitored. **Figure 6b** displays the extracted recombination lifetimes derived from fitting voltage decay curves for different light intensities. The PCBC6 cell type exhibits the longest lifetimes (slower recombination) throughout the majority of used light intensity range. The C₆₀ device shows the fastest recombination, especially at the lower light intensity. Again, the transient decay results agree very well with the photoluminescence studies presented above.

(Insert Figure 6 here)

3. Conclusions

In summary, we have demonstrated a solution-processible fullerene-derivative, PCBC6, as an efficient electron transport material in perovskite solar cells of p-i-n configuration. Flexible devices of relatively large active areas (1 cm^2), employing $\text{Cs}_{0.04}(\text{MA}_{0.17}\text{FA}_{0.83})_{0.96}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ perovskite composition reached PCE values of up to 18.4% with the PCBC6 n-type layer. This is nearly 30% higher than the best performance obtained for the cells employing PCBM layer. By applying different imaging techniques, we have shown that this difference in large part can be assigned to significantly improved film morphology, thanks to higher solubility of PCBC6, and its stronger intermolecular interactions. Additionally, we have demonstrated facile scalable deposition of PCBC6 layers by applying ink-jet printing technique. The cells with printed PCBC6 films reached efficiencies above 17%. Through various spectroscopic and electrical characterisation methods we have provided detailed analysis of the character of the interface between perovskite and selected n-type layers. Notably, PCBC6-based devices display reduced non-radiative recombination losses, as compared to C_{60} and PCBM cell types. This is consistent with higher open-circuit voltages recorded for PCBC6 samples. The caveat of PCBC6 material seems to be non-ideal electron extraction efficacy, resulting in lower short-circuit current densities when compared to thinner and more uniform C_{60} films (thermally evaporated). It was recently discussed that majority carrier mobility of the organic interlayer in perovskite solar cells can limit the driving force for photocurrent generation in the case of low built-in potential.^[46] Therefore, suitable PCBC6 doping strategy constitutes an interesting outlook for further improvement of this interface.

4. Experimental Section

Materials: Polyethylene terephthalate (PET) substrates coated with indium doped zinc oxide (IZO, sheet resistance of $15 \Omega/\square$) were bought from Eastman Chemical Company, formamidinium iodide (FAI) from Ajay North America, poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) from Osilla, [6,6]-phenyl-C61 butyric acid n-hexyl ester (PCBC6) from Nano-C, and methylammonium bromide (MABr) was synthesized at Saule Technologies following the previously reported method.^[47] All the rest of materials were purchased from Sigma-Aldrich and used as received without further purification.

Device fabrication: Planar heterojunction flexible PSCs were fabricated with the following architecture: PET/IZO/PTAA/Cs_{0.04}(MA_{0.17}FA_{0.83})_{0.96}Pb(I_{0.83}Br_{0.17})₃/PCBC6/BCP/Ag. PET/IZO ($15 \Omega/\square$) substrates were cut ($18 \times 13 \text{ mm}^2$ pieces) and patterned by dipping one side in the HCl solution (15 wt.% in DI water). The etched substrates were then sonicated in DI water and isopropanol. Before layer processing, 30 seconds of oxygen plasma treatment was applied. PTAA solution (2 mg mL⁻¹ in toluene) was spin-coated under ambient conditions at 5000 rpm for 30 seconds, followed by annealing at 100°C for 10 min, resulting in a ~20 nm film. Subsequently, the samples were transferred into a nitrogen-filled glovebox for the perovskite layer deposition. The perovskite precursor solution composed of mixed cations and halides was prepared according to the procedure reported before.^[48] First, stock solutions of PbI₂ and PbBr₂ (1.5 M) in DMF/DMSO mixture (4:1 v/v) were prepared. Then, for FAPbI₃ and MAPbBr₃ solutions, FAI and MABr powders were weighed out into separate vials, followed by addition of PbI₂ (into FAI) and PbBr₂ (into MABr) solutions. Both lead solutions were added in excess, to obtain an over stoichiometric lead content (FAI/MABr : PbI₂/PbBr₂ equals 1.0 : 1.09). The final perovskite precursor solution was prepared by mixing the solutions of FAPbI₃ and MAPbBr₃ in a 5:1 v/v ratio. Then, 40 μL of CsI solution (1.5 M solution in DMSO) was added to 1 mL of the mixture. Perovskite layer (~580 nm thick) was deposited

on top of PTAA with a two-step spin-coating procedure, 1500 rpm for 2 seconds and 5000 rpm for 34 seconds. Anhydrous ethyl acetate (150 μL) was dispensed on the sample at the 11th second before the end of the spinning sequence. Then, the sample was kept at rest for one minute before transferring to the hotplate for the two-step annealing process, 1 minute at 60°C and 60 minutes at 100°C. The electron transporting layers were deposited by spin-coating (PCBC6 or PCBM) or thermal evaporation (C_{60}). PCBC6 solution (20 mg mL^{-1} in chlorobenzene) was spin-coated at 4000 rpm for 30 seconds, and PCBM solution (20 mg mL^{-1} in ortho-dichlorobenzene) was spin-coated at 2000 rpm for 30 seconds. The solution-processed ETMs were annealed for 10 minutes at 60°C. Finally, 8 nm of BCP buffer layer and 100 nm of Ag electrode were deposited on top of devices by thermal evaporation at $\sim 10^{-6}$ mbar, through a shadow mask.

PCBC6 ink preparation and ink-jet printing: PCBC6 was dissolved in chlorobenzene (10 mg mL^{-1}), followed by sonication for 10 minutes. The solution was then diluted with octane (1 ml of octane for 6 ml of PCBC6 solution). The ink was filtered with a 0.22 μm PTFE filter before use. Ink-jet printing was done with a PixDro LP50 printer, equipped with a Konica Minolta printhead (512 nozzles). The printing settings were optimized with the resolution of 360x360 dots per inch (dpi).

Theoretical Methods: The density functional theory (DFT) was employed for all the simulations reported in this paper. To assess the influence of the chemical variations on the energetic levels of PCBM and PCBC6, HOMO and LUMO energy levels of these molecules were calculated in toluene with the Gaussian 09 software, employing B3LYP/6-311++G** level of theory and C-PCM implicit solvation model.^[49,50] Aggregation energies of fullerene-based systems have already been theoretically studied by several research groups adopting different computational approaches.^[51,52] In our case, estimation of this energy for solid state PCBM and PCBC6 were carried out with the CP2K software version 6.1, employing a GGA-PBE functional, DZVP basis

sets and GTH Pseudo Potentials, with a cutoff on the grid of 600 Ry and Grimme VdW correction (DFT-D3) to take into account dispersion interactions.^[53–57]

Current-voltage characterization: Current density–voltage characterization and stabilized power output measurements were performed using a Keithley 2461 source measure unit (SMU) under simulated AM1.5G irradiation (100 mA cm^{-2}) using an AAA-rated solar simulator (Abet Technologies, sun 2000) calibrated against an RR-208-KG5 silicon reference cell (Abet Technologies). The mismatch factor for the studied perovskite solar cells was 0.94, and this value was used to correct the intensity of the solar simulator lamp to provide one sun (for discussion see Supporting Information, Section 1.6 and **Table S4**). Solar cells were masked to 1 cm^2 . J-V measurements were performed in two scan directions, from forward bias to short-circuit and from short-circuit to forward bias. The scanning rate was set to 500 mV s^{-1} . The stabilized power conversion efficiency (SPO) was measured at the maximum power point voltage for a duration of 30 seconds.

External quantum efficiency: The EQE was measured using Bentham PVE300 photovoltaic characterization system and the control software BenWin+.

Scanning electron microscopy: Cross-section images were obtained by employing focus ion beam scanning electron microscope, FIB-SEM (FEI Helios 600), with an accelerating voltage of 2 kV. The samples were prepared by depositing carbon and platinum films on top of a sample.

Atomic force microscopy: The AFM images were obtained using a Park Systems, Model XE7 in non-contact mode and scanning over a range of $25 \text{ }\mu\text{m}$ by $25 \text{ }\mu\text{m}$ at a resolution of 128×128 data points. The surface roughness was measured as the root mean-squared roughness over the scanning area.

Photoluminescence quantum yield (PLQY): or this experiment, perovskite films were processed directly on pre-cleaned plain glass substrates. Subsequently, different electron transporting materials were deposited on top of perovskite layer (following the procedures described in device fabrication section). The measuring setup was based on FS5 Spectrofluorometer (Edinburgh Instruments), equipped with an integrating sphere. An excitation wavelength of 405 nm was used with the intensity of the order of 0.05 sun (5 mW cm^{-2}). This means that the PLQY and QFLS values are lower than those expected at 1 sun.^[58] The PL signal is collected in the spectral range of 720-820 nm. A glass substrate was used as a reference for the glass/perovskite/(ETL) samples.

Photoluminescence of solar cells at open-circuit and short-circuit: Complete flexible perovskite solar cells were used for this experiment. The measurement setup was based on Andor Shamrock 193i Czerny-Turner type spectrometer. The illumination source for PL measurements was a frequency doubled continuous wave Nd-YAG laser from Pegasus laser systems (Pluto, P532.400, $\lambda=532\text{nm}$). The working point of the measured solar cell was set by a LabVIEW controlled Keithley 2400 source meter. To calibrate the excitation intensity, short circuit current of one cell was measured. The laser intensity was adjusted that the cells J_{SC} on the PL setup matched the J_{SC} previously measured on a mismatch corrected solar simulator (AM 1.5G equivalent). For samples having the same architecture and differing only in a transport layer material, the laser power was kept constant, so the measured PL intensities could be compared directly.

Transient photovoltage (TPV) and transient photocurrent (TPC) measurements: The transient photovoltage (TPV) and transient photocurrent (TPC) were measured with a commercial apparatus (Arkeo, Cicci Research s.r.l.) based on a high-speed Waveform Generator that drives a high-speed LED (5000 Kelvin). The device is connected to a transimpedance amplifier and a differential voltage amplifier to monitor short circuit current or open circuit voltage. The measurements are

executed with varied light intensities throughout the measurement, using the white LED. The intensities ranged between 30 mW cm^{-2} and 160 mW cm^{-2} . For each illumination level 200 traces were recorded, both in TPC and TPV experiment.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflicts of interest

The authors declare no conflicts of financial/commercial interest.

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Figures

Figure 1. (a-d) AFM 3D surface topography images (scanning range: $25 \times 25 \mu\text{m}^2$) of a perovskite layer, and perovskite coated with PCBC6, PCBM, or C₆₀ films; (e-g) cross-section FIB-SEM images of a perovskite layer coated with PCBM, PCBC6 or C₆₀ film.

Figure 2. Optimized geometry structure of a bulk (a) PCBM and (b) PCBC6 materials. Overview of the intermolecular interaction between the alkyl chains for (c) PCBM and (d) PCBC6 molecule along with the average distances in Å, (e) Projected density of states of optimized bulk PCBM (in blue) and PCBC6 (in red) phases. The numbers in the inset indicate HOMO and LUMO energy values in eV.

Figure 3. (a) Statistics of the photovoltaic performance parameters measured for the perovskite solar cells with different ETMs: evaporated C₆₀ (black), solution-processed PCBC6 (red) and solution-processed PCBM (blue), (b) current density-voltage characteristics (light and dark) of the best PSCs with different ETMs, (c) stabilized power output measurement of the same devices.

Figure 4. (a) Current density-voltage characteristics of the flexible perovskite solar cell employing ink-jet printed PCBC6 (1 cm^2 active area); (b) steady-state power output measurement of the same device.

Figure 5. (a) The PL spectra of perovskite samples (with and without different n-type layers) deposited on plain glass substrate. Spectral PL measurement of the flexible solar cells with different ETMs, in (b) open circuit and (c) in short circuit.

Figure 6. The analysis of the TPC/TPV measurements of PSCs with the different ETMs, (a) charge density extracted from the photocurrent decay measurements, plotted as a function of a short-circuit current density, which corresponds to varied perturbation light intensities; (b) recombination lifetimes derived from the fitting of photovoltage decay, plotted as a function of an open-circuit voltage at varied background light intensities.

Tables

Table 1. Photovoltaic parameters extracted from the current-voltage characterization measurements of the perovskite solar cells fabricated with different ETMs.

ETM	J_{sc} ^{avg ± SD} (J_{sc} Best) [mA cm ⁻²]	FF ^{avg ± SD} (FF Best) [%]	V_{oc} ^{avg ± SD} (V_{oc} Best) [V]	PCE ^{avg ± SD} (PCE Best) [%]
PCBC6	21.44±0.78 (23.22)	73.98±2.80 (76.14)	1.07±0.02 (1.050)	17.08±0.62 (18.41)
PCBM	17.63± 1.43 (20.59)	60.72±5.83 (72.40)	1.01±0.04 (1.035)	11.05±1.59 (13.93)
C ₆₀	22.48±0.56 (23.42)	73.30±2.03 (75.82)	1.03±0.02 (1.043)	17.03±0.68 (18.53)

Table 2. Summary of the PLQY and QFLS values determined from the spectroscopic measurements, and V_{oc} values of respective solar cells obtained from the electrical measurements.

	PS	PS/PCBC6	PS/PCBM	PS/C₆₀
PLQY [%]	3.66×10^{-2}	1.02×10^{-2}	2.88×10^{-3}	2.47×10^{-3}
QFLS [eV]	1.159	1.126	1.093	1.089
AVERAGE V_{oc} [V]	-	1.07	1.01	1.03

Table 3. V_{oc} , J_{sc} and spectrally integrated PL for the devices (in open-circuit and short-circuit) with C₆₀, PCBC6 and PCBM as ETMs.

Materials	MEASUREMENT IN OPEN CIRCUIT		MEASUREMENT IN SHORT CIRCUIT		
	V_{oc} [V]	PL-intensity [cps]	J_{sc} [mA cm⁻²]	PL-intensity [cps]	PL Quenching [(V_{oc}-J_{sc})/V_{oc}]
PCBC6	1.14	1.5×10^8	17.2	2.8×10^7	0.81
C₆₀	1.08	5.7×10^7	17.3	1.7×10^7	0.70
PCBM	1.01	2.3×10^7	9.5	2.0×10^7	0.13

Table of contents (ToC):**Keyword:** Photovoltaic Devices

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New fullerene derivative as an n-type material for highly efficient, flexible perovskite solar cells of a p-i-n configuration

Solution-processed fullerene derivative, PCBC6, is reported as an effective electron transport material in perovskite solar cells. It allows smooth capping of perovskite surface, resulting in a high power conversion efficiency, reaching 18.4% for large-area, flexible devices. Furthermore, compared to other fullerenes, it shows reduced recombination losses at the interface with perovskite, and facile scalability with ink-jet printing technique.

Supporting Information

New fullerene derivative as an n-type material for highly efficient, flexible perovskite solar cells of a p-i-n configuration

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ADDITIONAL DATA**1.1. Illumination level traces for both TPC and TPV experiment****Table S1.** Light intensity values used in TPC/TPV measurements.

Step Number	Power density [mW cm^{-2}]
1	30.4
2	45.2
3	60.0
4	74.4
5	89.2
6	103.6
7	117.6
8	132.0
9	146.0
10	160.4

1.2. Comparison of highly concentrated inks of PCBM and PCBC6

Figure S1. Photographs of the PCBC6 and PCBM highly concentrated inks prepared by dissolving (57.5 mg of PCBC6 in 500 μ L) of chlorobenzene, and (25 mg of PCBM in 500 μ l of o-dichlorobenzene).

1.3. Density functional theory (DFT) simulations data

Table S2. Lattice parameters a , b and c in Å and α , β , and γ angles in degrees of the investigated systems. The cell volume and the density are also reported in cm^3 and g.cm^{-3} along with the total aggregation energy in eV and its dispersion and electronic separated contributions.

	PCBM		PCBC6
	Experimental	Theoretical	Theoretical
a	13.47	13.46	16.93
b	15.10	15.12	15.52
c	19.01	19.21	19.37
α	90.00	89.93	107.04
β	106.90	107.27	101.41
γ	90.00	90.03	106.09
Volume [cm^3]		3.74×10^{-4}	4.45×10^{-4}
ΔE Total		-2.23	-2.55
Aggregation Energy [eV]			
ΔE Dispersion [eV]		-2.35	-2.76
ΔE Electronic [eV]		0.12	0.21

Table S3. The HOMO and LUMO energy levels derived from the DFT calculations for the PCBM, C₆₀ and PCBC6 molecules in toluene. Values with * are the experimental values from reference.^[1]

	PCBC6	PCBM	C ₆₀
HOMO [eV]	-6.04	-6.04 (-6.18)*	-6.34
LUMO [eV]	-3.51	-3.52 (-3.70)*	-3.61

1.4. Conductivity measurements

Figure S3. (a) Current-voltage (J-V) characteristics of PCBC6 and PCBM thin films, (b) Scheme of a sample structure used for this measurement. The ETL conductivity was measured between the two ITO stripes, which were formed by laser ablating a 100 μm wide trench. The length of each electrode finger is 5 mm.

1.5. Visualization of a device structure

Figure S4. (a) Schematic illustration of a perovskite device structure of p-i-n configuration, (b) diagram of energy levels of the perovskite solar cell architecture used in this study, (c) FIB-SEM cross-section image of a flexible perovskite solar cell with PCBC6 layer as an ETM.

1.6. Mismatch factor calculation

The mismatch factor corrects the error originating from the difference in spectral responsivity of the test cell and the reference device, and the mismatch in spectral irradiance of the used light source and the reference spectrum (AM1.5G). It can be expressed by **Equation 1.**^[2]

$$M = \frac{\int_{\lambda_1}^{\lambda_2} E_{Ref}(\lambda) S_R(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} E_{Ref}(\lambda) S_T(\lambda) d\lambda} \frac{\int_{\lambda_1}^{\lambda_2} E_S(\lambda) S_T(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} E_S(\lambda) S_R(\lambda) d\lambda} \quad (1)$$

where $E_{Ref}(\lambda)$ is the reference spectral irradiance, $E_S(\lambda)$ is the light source spectral irradiance, $S_R(\lambda)$ is the spectral responsivity of the reference cell, $S_T(\lambda)$ is the spectral responsivity of the test cell, λ_1 and λ_2 define the spectral range where the reference and test cells respond.

The spectrum of the solar simulator lamp, the AM1.5G spectrum, and EQE spectra of studied perovskite solar cells and silicon reference diode is shown in **Figure S5**.

Figure S5. (a) Spectrum of solar simulator lamp and AM1.5G is shown, that is used for the mismatch factor correction, (b) measured external quantum efficiency (EQE) and corresponding integrated current density of cells with various ETMs. EQE of KG5 silicon reference cell is shown (green). The measured spectra are in the range from 287 nm to 900 nm.

Table S4. Calculated mismatch factor for different ETMs.

Material	Mismatch Factor (M)
PCBC6	0.939
PCBM	0.940
C ₆₀	0.941

We applied the mismatch factor to correct the intensity of the solar simulator lamp and provide one sun illumination. For that, we corrected measured current density values according to the **Equation 2.**

$$J_{sc_{corrected}} = \frac{J_{sc_{measured}}}{M} \quad (2)$$

1.7. J-V curves of the best performing devices for each ETM type (reverse and forward scan directions)

Figure S6. J-V characteristics of the best performing devices with different n-type layers (C₆₀, PCBC6 and PCBM). Two scan directions are shown, from short-circuit to forward bias (forward), and from forward bias to short-circuit (reverse).

1.8. Space charge limited current measurements

SCLC measurements were performed on electron-only devices of the following structure: PET-IZO/SnO₂/perovskite/ETM (PCBM or PCBC6)/BCP/Ag. **Figure S7** shows J-V curves obtained during the measurement (carried out in dark). Two regions can be distinguished in the plots: ohmic region at low voltage bias ($I \propto V$, red solid line) and the trap-filling limited region at intermediate voltage bias (blue solid line) ($I \propto V^n$, where $n > 2$).^[3] Upon applying the forward bias, the trap sites present in the photoactive layer get filled up with the injected carriers and the current values rapidly

increase (trap-filling region). The inflection point, where the device operation mode changes to the trap-filled limit can be derived from the Mott Gurney law (**Equation 3**).^[4]

$$V_{TFL} = \frac{eN_t d^2}{2\epsilon\epsilon_0} \quad (3)$$

where e is elementary charge, ϵ is perovskite's dielectric constant, ϵ_0 is vacuum permittivity, N_t is trap state density in the semiconductor's layer, and d refers to film thickness. Therefore, by defining the onset voltage point (V_{TFL}) the trap state density in the photoactive layer can be estimated. Values derived for each sample were displayed on the graph.

Figure S7. Space charge limited current (SCLC) measurements of electron-only devices employing different ETMs processed on top of perovskite layer. For each curve estimate trap state density in the perovskite film was marked.

1.9. Perovskite solar cells with ink-jet printed PCBC6

Figure S8. (a) Statistics of photovoltaic performance parameters derived from J-V curves of flexible PSCs employing evaporated C₆₀, or ink-jet printed PCBC6 as n-type layers, (b) AFM 3D surface topography images (scanning range: 25 × 25 μm²) of an inkjet printed PCBC6 film; (c) cross-section FIB-SEM images of a perovskite layer with inkjet printed PCBC6 film.

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