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 in the field of emerging photovoltaic technologies. The possibility of fabricating perovskite solar cells (PSCs) on lightweight, flexible substrates, with facile processing methods, provides very attractive commercial possibilities. Nevertheless, efficiency values for flexible devices reported in the literature typically fall short in comparison to rigid, glass-based architectures. Here, a solution-processable fullerene derivative, [6,6]-phenyl-C61 butyric acid n-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 phenyl-C61-butyric acid methyl ester 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 nonradiative recombination at the perovskite/electron transporting material interface. Solution-processed PCBC6 films are 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 (PCE) 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 lightweight 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 toward 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. Detrimental defects tend to form at both of these interfaces.
with the perovskite layer, which leads to an increase of nonradia-
tive recombination losses and deterioration of a solar cell
performance.\[8\] Suitable chemical functionalization of perov-
skite’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 degra-
dation 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 (C_{60}) and
various fullerene derivatives were widely applied in efficient
p-i-n devices due to their demonstrated effective electron extrac-
tion from the perovskite layer. Additionally, these organic mate-
rials 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 sur-
face of perovskite layer.\[16\] Solution-processed fullerenes confor-
mally 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 nonradiative recombination
processes at the perovskite/ETM interface, and difficulties in
smooth film formation, often resulting in a nonuniform 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),
or poly(methyl methacrylate), 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 nonconductive character of the added polymer, which
could result in another type of losses. Therefore, a more effec-
tive approach is highly desirable, where solution-processed,
smooth, and inexpensive fullerene coating of high optoelec-
tronic 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 nonpolar solvents due to the presence of a
long alkyl chain group, which results in a more uniform and
smoother film formation. Interfacial characteristics of perov-
skite solar cells employing different fullerene ETMs (PCBC6,
PCBM, and C_{60}) 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 nonradiative recombination losses at the in-
terface with perovskite, as evidenced by transient photovoltage
(TPV) decay measurements and determination of quasi-Fermi
level splitting of perovskite layer brought in contact with dif-
ferent ETMs. Reduced interfacial losses result in open-circuit
voltage (V_{OC}) improvement for the PCBC6 devices. Signifi-
cantly, 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 con-
cept 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 mor-
phologies 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
smallest 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 consid-
erably 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 evi-
dent 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 C_{60} layer
thermally evaporated on top of perovskite surface. The rough-
ness of this sample (RMS = 127 nm) is comparable to the bare
perovskite, and cross-section FIB-SEM image depicts very uni-
form fullerene’s coating, with complete coverage of perovskite
surface. This is characteristic for a physical vapor deposition
process, and such layer morphology should be beneficial for the
device performance.

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 (lit-
erature values for PCBM solubility: 40 mg mL⁻¹ in chlorobenze-
ne 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 in the
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 nonpolar solvents.\textsuperscript{[31]} Additionally, it might increase the quality of the films in terms of stability, crystallinity, and homogenous growth.

To gain insight into the packing properties of PCBM and PCBC6, we carried out first principles density functional theory (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 data, and we performed relaxation of cell parameters and atomic positions.\textsuperscript{[32]} As we can see in Table S2 in the 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

Figure 1. a–d) AFM 3D surface topography images (scanning range: 25 × 25 µm\textsuperscript{2}) of a perovskite layer and perovskite coated with PCBC6, PCBM, or C\textsubscript{60} films. e–g) Cross-section FIB-SEM images of a perovskite layer coated with PCBM, PCBC6 or C\textsubscript{60} film.
by considering total energy of the system with respect to the energy of a single molecule, following the equation:

\[ \Delta E = -4E_{\text{single-molecule}} \]

where \( E_{\text{total}} \) is the total energy of the simulated system (consisting of four PCBM or PCBC6 molecules) and \( E_{\text{single-molecule}} \) 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, Supporting Information). 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 in the Supporting Information, these interactions completely drive the aggregation of our systems and imply preferred packing of PCBC6 with respect to PCBM (\( \Delta E \) 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 (\( \Delta E \) 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 its growth, as it was proposed by Benetto et al.[33]

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 in the 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 polyethylene naphthalate (PEN)/indium tin oxide (ITO) substrates, where a 100 mm 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 \( 6.58 \times 10^{-5} \) S cm\(^{-1} \) is at the same range as the value obtained for PCBM, \( 4.68 \times 10^{-5} \) 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 fulleranes as the n-type layers. We applied the following solar cell structure: Polyethylene terephthalate (PET)/indium doped zinc oxide (IZO)/poly[bis(4-phenyl)(2,4,6-trimethylphenyl) amine] (PTAA)/perovskite/ETM (varied)/bathocuproine (BCP)/Ag. All the photovoltaic devices reported in this work, we fabricated on flexible substrates (PET foil), with 1 cm\(^2\) 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, \( \text{Cs}_{0.04}(\text{MA}_{0.17}\text{FA}_{0.83})_{0.96}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_{3} \), 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 Figure S4 in the Supporting Information, 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 \( \text{C}_{60} \), 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 in the 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 in the 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 PCE of 18.4\%. We observe that the 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 \( \text{C}_{60} \) 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 noncomplete coverage where rougher perovskite surface structures occur (see Figure 1e).

**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 (\( J_{sc \text{Best}} \)) [mA cm\(^{-2} \)] | \( FF \) avg ± SD (\( FF_{\text{Best}} \)) [%] | \( V_{oc} \) avg ± SD (\( V_{oc \text{Best}} \)) [V] | PCE avg ± SD (PCE\(_{\text{Best}} \)) [%] |
|--------|---------------------------------|---------------------------------|---------------------------------|----------------------------------|
| 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)          |
| \( \text{C}_{60} \) | 22.48 ± 0.56 (23.42)          | 73.30 ± 2.03 (75.82)            | 1.03 ± 0.02 (1.043)            | 17.03 ± 0.68 (18.53)          |

**Figure 3.** a) Statistics of the photovoltaic performance parameters measured for the perovskite solar cells with different ETMs: evaporated \( \text{C}_{60} \) (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, and c) stabilized power output measurement of the same devices.
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. In comparison, C$_{60}$ 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 C$_{60}$ and PCBM-based devices. This observation points at the reduction of the nonradiative 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. 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 $1.01 \times 10^{16}$ cm$^{-3}$ for PCBC6, which compares to $1.91 \times 10^{16}$ and $1.40 \times 10^{16}$ 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. 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, and temperature). Nevertheless, considering that the perovskite fabrication process and SCLC measuring protocol in all three analyzed cases were 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 nonradiative 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 and 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 nonuniform 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 C$_{60}$ 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.

### 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 and 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 in the Supporting Information.

Perovskite solar cells (flexible substrate, 1 cm$^2$ 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 result in a complete coverage of all the perovskite roughness (see Figure S8c, Supporting Information), and therefore hysteretic effects are minimized. The statistics of photovoltaic parameters of 15 devices using printed PCBC6 are shown in Figure S8a and Table S5 in the Supporting Information.

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 nonradiative recombination occurring at that contact.

### 2.3. Interface Study

#### 2.3.1. Quasi-Fermi Level Splitting

Determination of a 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. The PLQY is generally influenced by all the different nonradiative recombination channels and rate constants of each of these processes in respect to a radiative recombination rate. 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, and perovskite/C$_{60}$).
We are showing the measured photoluminescence (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 nonradiative recombination at the perovskite/ETM interface. The layer stack with the PCBC6 shows higher PL signal compared to other ETMs.

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 Equation (2).

\[
\text{QFLS} = \text{QFLS}_{\text{rad}} + kT \ln(\text{PLQY})
\]

where QFLS\(_{\text{rad}}\) is the quasi-Fermi-level splitting in the radiative limit, \(k\) is the Boltzmann constant, and \(T\) is the temperature.

In the Table 2 and Figure 5a, we provide the summary of PLQY values, together with the calculated QFLS, for the four cases described above. For the comparison, we also provide the average \(V_{\text{OC}}\) 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 C\(_{60}\) samples are 1.126, 1.093, and 1.089 eV, respectively. The samples containing PCBC6 as the n-type layer exhibit the highest device \(V_{\text{OC}}\) 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 (\(V_{\text{OC}}\) was also recorded) and short-circuit. We are showing the graphs in Figure 5b,c. The summary of \(V_{\text{OC}}\) values and integrated PL intensities are listed in Table 3.

We observe a clear trend, with the PCBC6-based device delivering the highest \(V_{\text{OC}}\), 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
In order to further corroborate the analysis of the perovskite interface with the selected n-type materials, we performed TPC and 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 light emitting diode (LED) excitation light source. We applied ten 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.

The analysis of the TPC/TPV measurements of PSCs with the different ETMs. 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 light emitting diode (LED) excitation light source. We applied ten 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.

### Table 2. Summary of the PLOY and QFLS values determined from the spectroscopic measurements and \(V_{OC}\) values of respective solar cells obtained from the electrical measurements.

| Materials  | Measurement in open circuit | Measurement in short circuit |
|------------|-----------------------------|-----------------------------|
| PS         | PL intensity [cps] | \(J_{sc}\) [mA cm\(^{-2}\)] | PL quenching [(\(V_{OC}-J_{sc}\))/\(V_{OC}\)] |
| PS/PC6     | 1.02 \times 10^3  | 2.88 \times 10^{-1}  | 2.47 \times 10^{-1}  |
| PS/PCBM    | 1.126  | 1.093  | 1.089  |
| PS/C\(60\) | 1.159  | 1.07   | 1.01   | 1.03   |

**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.
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 cm²), employing C60doped (MA0.37FA0.63)PbI0.83Br0.17 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 characterization 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 nonradiative recombination losses, as compared to C60 and PCBM cell types. This is consistent with higher open-circuit voltages recorded for PCBC6 samples. The caveat of PCBC6 material in perovskite solar cells of p-i-n configuration. Flexfullerene-derivative, PCBC6, as an efficient electron transport layer (ETL) for perovskite solar cells. This work shows that PCBC6 can be used as an efficient electron transport layer with promising potential for applications in perovskite solar cells.

4. Experimental Section

Materials: PET substrates coated with IZO (sheet resistance of 15 Ω/□) were bought from Eastman Chemical Company, formamidinium iodide (FAI) was bought from Ajay North America, PTAA was bought from Osilla, [6,6]-phenyl-C61 butyric acid methyl ester (PCBM) was bought from Nano-C, and methylammonium bromide (MABr) was synthesized at Saule Technologies following the previously reported method. All the rest of the 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/ITO/PTAA/C60doped (MA0.37FA0.63)PbI0.83Br0.17/PCBC6/BCP/Ag. PET/ITO (15 Ω/□) substrates were cut (8 × 13 mm² pieces) and patterned by dipping one side in the HCl solution (15 wt%) in deionized (DI) water. The etched substrates were then sonicated in DI water and isopropanol. Before layer processing, the substrate was kept at rest for 1 min before transferring to the hotplate for the two-step annealing process, 1 min at 60 °C and 60 min at 100 °C. The electron transporting layers were deposited by spin coating (PCBC6 or PCBM) or thermal evaporation (C60). PCBC6 solution (20 mg mL⁻¹ in chlorobenzene) was spin coated at 4000 rpm for 30 s, and PCBM solution (20 mg mL⁻¹ in ortho-dichlorobenzene) was spin coated at 2000 rpm for 30 s. The solution-processed ETMs were annealed for 10 min 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 ~10⁻⁶ mbar, through a shadow mask.

PCBC6 Ink Preparation and Inkjet Printing: PCBC6 was dissolved in chlorobenzene (10 mg mL⁻¹), followed by sonication for 10 min. 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 polytetrafluoroethylene (PTFE) filter before use. Inkjet printing was done with a Pixdor LP50 printer, equipped with a Konica Minolta printhead (512 nozzles). The printing settings were optimized with the resolution of 360 × 360 dpi.

Theoretical Methods: The 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 polarizable conductor solvent model (C-PCM) implicit solvation model. [59] Aggregation energies of fullerene-based systems have already been theoretically studied by several research groups adopting different computational approaches. In the case of estimation of energy for solid state PCBM and PCBC6, we carried out with the CP2K software version 6.1, employing a Generalised Gradient Approximation (GGA)-Perdew-Burke-Ernzerhof (PBE) functional, double-zeta valence polarized (DZVP) basis sets, and Goedecker-Teter-Hutter (GTH) Pseudo Potentials, with a cutoff on the grid of 600 Ry and Grimme D3 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 2400 source-measurement unit under simulated AM 1.5G irradiation (100 mA cm⁻²) using an AAA-rated solar simulator (Abet Technologies, sun 2000) calibrated against an RR-208-KC5 silicon reference cell (Abet Technologies). The mismatch factor for the studied perovskite solar cells was 0.94 and this value was used correct the intensity of the solar simulator lamp to provide 1 sun (for discussion see Section S1.6 and Table S4, Supporting Information). Solar cells were masked to 1 cm², 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 (SPC) was measured at the maximum power point voltage for a duration of 30 s.

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 (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 System, Model XE7 in noncontact mode, and scanning over a range of 25 µm by 25 µm at a resolution of 128 × 128 data points. The surface roughness was measured as the root mean-squared roughness over the scanning area.

PLQY: 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 the Device Fabrication section). The measuring setup was
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 neodymium-doped yttrium aluminium garnet (Nd:YAG) laser from Pegasus laser systems (Pluto, P532.400, \( \lambda = 532 \) 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.

#### Supporting Information

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

#### Acknowledgements

This work was partly funded by the European Union’s Horizon 2020 research and innovation program under the Grant Agreement No. 764047 (Epresso project) and the Foundation of Polish Science (First TEAM/2017-3/30). I.A.C. would like to acknowledge the European Union’s Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie Grant Agreement No. 764787 MAESTRO. F.D.A. and E.R. acknowledge support from the Ministero Istruzione dell’Università e della Ricerca (MIUR) and the University of Perugia through the program “Dipartimenti di Eccellenza 2018–2022” (grant AMIS). The authors would like to acknowledge scientific and technical assistance by Saule Technologies Research and Development Team.

#### Conflict of Interest

The authors declare no conflict of interest.

#### Keywords

electron transport materials, flexible solar cells, fullerene derivative, ink-jet, perovskites
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