

1 **Fully Solution Processed n-i-p-like Perovskite Solar Cells with Planar Junction: How the**
2 **Charge Extracting Layer Determines the Open Circuit Voltage**

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58 Solution-processable hybrid perovskite semiconductors have risen to the forefront of
59 photovoltaics research, offering the potential to combine low-cost fabrication with high power
60 conversion efficiency.^[1] The first architectures made use of nanocrystalline TiO₂ deposited on
61 the transparent electrode, both in the form of mesoporous and compact films, as selective
62 contact for electrons alike the so-called Grätzel solar cells.^[2-4] Such a structure is generally
63 indicated in the field as *direct architecture* as electrons are collected at the front transparent
64 electrode and holes at the metal contact (often gold). Further development has been driven by
65 empirical optimization strategies and testing of a variety of architectures. One of these
66 promising architectures uses fully organic selective contacts. This choice brings, first of all,
67 the advantage of low temperature processing; additionally, a beneficial effect in terms of
68 electrical stabilization of the device with organic electron extraction layers in a flat junction
69 configuration, with respect to the use of TiO₂, has been repeatedly observed.^[5-7] So far,
70 architectures with fully organic selective contacts are either limited to the so-called *inverted*
71 *architecture*, as a consequence of difficulties in the solution processing of multi-layers, or
72 they have to rely on vacuum deposition methods.^[6-8] Solution-processed, flat junctions, multi-
73 layered direct architectures, which would open the path towards large-area, low-temperature
74 processing of high-efficiency direct cells, have been poorly explored, and their power
75 conversion efficiencies are still limited.^[9-11] Intuitively, the development and optimization of
76 different architectures need a full engineering of different interfaces. This is especially critical
77 for metal halide perovskites that, unlike more widely studied inorganic semiconductors, have
78 fluctuating ionic structures where tilting, distortions and polarizability of the lattice strongly
79 affect their optoelectronic properties. This makes the reliability of perovskite-based devices

80 strongly dependent on the control of the microstructure of the active material and of its
81 response to external stimuli, such as chemical interactions upon interface formation,^[12]
82 electric field,^[13,14] light^[15] and environmental agents.^[16,17]

83 It is also worth noting that, while perovskite solar cells have made spectacular progress in
84 terms of solar-to-electrical current conversion efficiency in very short time, such advances are
85 mainly based on an empirical approach, which has led to a myriad of architectures, whose
86 advantages and limitations cannot be attributed yet to a fundamental property of the active
87 material or to the design and processing of the device.

88 Herein we present the fabrication of a fully solution processed direct perovskite solar cell with
89 planar junction, reaching power conversion efficiencies (PCEs) close to 19% and an open
90 circuit voltage (V_{oc}) larger than 1.1 V. Such a result is achieved by using as a selective contact
91 for electrons a fullerene derivative, the [6,6]-phenyl-C61-butyric styryl dendron ester
92 (PCBSD), functionalized with a dendron containing two styryl groups as thermal cross-linkers.
93 In situ crosslinking of PCBSD by thermal treatment forms a robust, adhesive, and solvent-
94 resistant thin electron accepting layer, on top of which a high quality perovskite film
95 processed from solution can be grown. We show that the choice of the electron extracting
96 layer (EEL) is of utmost importance to maximize the solar cell V_{oc} as interface engineering
97 accounts not only for the energy level alignment between the EELs and the perovskite, but
98 also for the quality of the microstructure of the perovskite bulk film that is driven by the
99 substrate surface. We further demonstrate that in this device architecture, at V_{oc} conditions the
100 high carrier density is sustained not only by the charge extracting contacts but also by the
101 semiconducting active layer, thus rationalizing the optimal opto-electronic performance of the
102 proposed devices as a beneficial effect of the engineering of the solution processed
103 EEL/perovskite interface in terms of micro-structure and reduced carrier recombination/
104 charge extraction improvement.

105 The PCBSD is prepared by optimizing the synthesis route described by Hsieh et al. in order to
106 achieve a final yield of 81% (see Supporting Information (SI) for details).^[18] The crosslinking
107 of PCBSD is a thermal-induced radical polymerization between the terminal vinyl bonds of
108 PCBSD (see **Figure 1a**).^[19,20] In order to optimize the timing of the crosslinking process at
109 160 °C (see Figure S16 of SI for the temperature optimization), its progress is monitored with
110 in-situ infrared (IR) spectroscopy for 45 min. Figure 1b presents the initial and the final
111 spectra. The bands at 987 cm⁻¹ and 908 cm⁻¹, which are assigned to the CH and CH₂ wagging
112 of the vinyl groups in *trans* conformation (see Figure S11 in SI for assignment through DFT
113 calculations), show an absolute reduction in intensity in time during the thermal crosslinking.
114 Their lowering is due to the conversion of the sp² carbon atoms of the vinyl groups into sp³
115 carbon atoms, which occurs during the PCBSD crosslinking.^[21] The band at 908 cm⁻¹ is
116 selected for quantitative analysis and monitoring of the crosslinking time. The peak area of
117 the band at 908 cm⁻¹ is determined every 5 min up to a final reaction time of 45 min. The
118 values, normalized over the peak area at t = 0, show that the reaction follows a 1st order
119 exponential decay and 35% of the carbon atoms of the vinyl groups are converted after a 45-
120 min thermal anneal (Figure 1c). To prove that the achieved crosslinking degree is sufficient
121 enough for the crosslinked PCBSD (C-PCBSD) layer to be solvent resistant, UV-visible
122 spectra of the substrates are measured before and after being rinsed with dimethyl
123 formamide (DMF). The as-cast PCBSD films are almost completely washed-off (Figure 1d),
124 whereas only a weak decrease in the intensity of the bands is shown after crosslinking induced
125 with a 30-min thermal anneal at 160 °C (Figure 1e).

126

127 Before incorporating such EELs in a device structure, we tested its electronic properties. One
128 of the main challenges to face upon crosslinking procedure of an organic semiconductor is a
129 possible degradation of its transport properties.^[22] C-PCBSD has been tested in a field-effect
130 transistor (FET) geometry, which is quite demanding device in terms of electronic properties,

131 as it requires in-plane charge, in this case electrons, transport along tens of microns. Electron
132 percolation pathways can be evidently formed and a neat field-effect modulation of the
133 current can be observed, already in a non-optimized device, exhibiting an electron mobility in
134 the order of $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for surface charge densities in the range 8×10^{15} to $3 \times 10^{16} \text{ m}^{-2}$
135 (1.3×10^{-7} to $5.1 \times 10^{-7} \text{ C cm}^{-2}$) (Figure S1 in SI). This result shows that our C-PCBSD has
136 almost an order of magnitude higher mobility than what previously reported in undoped C-
137 PCBSD based FET devices.^[9] Thus we can safely confirm that the C-PCBSD film can sustain
138 in-plane electron transport over several microns, and it is therefore likely to show good
139 transversal electron transport properties over tens of nanometres of its thickness thus being a
140 potential candidate as a thin EEL.

141

142 To start the solar cell fabrication, a very thin layer of C-PCBSD (less than 10-20nm, see
143 Figure S14 in SI) is deposited onto the FTO/TiO₂ substrates as thicker films eventually lead
144 to an increase of the device series resistance (see Figure S15 in SI) . Its surface work function
145 is measured in air by Kelvin probe and it results more electronegative with respect to that of
146 TiO₂ and comparable to the [6,6]-phenyl-C₆₁-butyric acid methyl ester (60-PCBM) (see Table
147 S1 in SI). Subsequently a methylammonium lead iodide (CH₃NH₃PbI₃) thin film is directly
148 synthesised from solution on top of FTO/TiO₂/C-PCBSD via a two-step procedure (see
149 methods in SI for details). The final thickness of CH₃NH₃PbI₃ depends on the thickness of the
150 PbI₂ layer (see SI for the layer optimization). **Figure 2a** shows X-ray diffraction spectra
151 measured before and after the CH₃NH₂I spin cast on top of PbI₂ followed by thermal
152 annealing on top of TiO₂ and TiO₂/C-PCBSD substrates. In both cases we do not observe any
153 trace of the crystal precursors and the sharp peaks suggest the formation of large perovskite
154 grains. Figure 2b, 2c, 2d, and 2e show the top-view images of the perovskite films grown on
155 TiO₂ and TiO₂/C-PCBSD, respectively, at different magnifications. The perovskite films
156 show a good coverage on both substrates; however, the film grown on TiO₂/C-PCBSD

157 presents much larger grains ($> 1 \mu\text{m}$) and a lower roughness. The static contact angle of water
158 on C-PCBSD is more than twice larger with respect to the case of TiO_2 (shown in Figure S2),
159 indicating a more hydrophobic surface. Thus we conclude that the different morphology is the
160 result of a lower wettability of the C-PCBSD surface to dimethyl formamide/ PbI_2 solution
161 with respect to the TiO_2 surface, which drives the formation of crystallite with larger aspect
162 ratio.^[6] To complete the devices, we deposited spiro-MeOTAD by spin coating as hole-
163 extracting layer (HEL) followed by gold via thermal evaporation. In **Figure 3a** and **3b** we
164 show a cross section of the optimized planar devices employing TiO_2 and $\text{TiO}_2/\text{C-PCBSD}$ as
165 EELs. Please note that such layers are extremely thin, of the order a few tens of nanometres,
166 nearly conformal to the rough FTO substrate, while the perovskite layers have a different
167 optimized thicknesses, approximately 400 nm and 320 nm respectively. Figure 3c and 3d
168 show the current density versus voltage (J - V) characteristics measured in air under air mass
169 1.5 global (AM 1.5G) conditions. To check for the possible hysteresis phenomena, which are
170 known to strongly influence the device testing, especially for the planar junctions reported so
171 far in the literatures^[12,23,24] we show the J - V curves as a function of scan rate, in forward and
172 reverse scan directions. **Table 1** summarizes the main figures of merit of the tested samples,
173 i.e., short-circuit current density (J_{sc}), V_{oc} , fill factor (FF) and PCE. As expected, the device
174 based on bare TiO_2 as EEL has a characteristic that depends on the polarization record of the
175 device (Figure 3c), and the photocurrent, upon polarization, has a transient time of a few
176 seconds (Figure 3e). The figures of merit of such a device correspondingly depend on the
177 testing conditions and are reported in Table 1. On the other hand, the $\text{TiO}_2/\text{C-PCBSD}$
178 interface electrically stabilizes the device. Not only the J - V characteristics have very limited
179 dependence on scan directions and rates (Figure 3d), but also the photocurrent has no
180 transient time upon polarization (Figure 3f). Such a stable device delivers a PCE as high as
181 18.7%, with a J_{sc} of approximately 21 mA cm^{-2} , V_{oc} over 1.1 V and FF close to 80%. The

182 reliability of such numbers is confirmed by a statistical study made over 61 devices, which
183 can be found in Figure S3 and S4 in SI.

184 It is worthy to notice that flat junction solar cells, especially those with direct architecture,
185 hardly achieve a V_{oc} of 1 V.^[3,25,26] However here we show a V_{oc} that is consistently higher
186 than 1.1 V (see statistics in Figure S3). In this regard, these devices even outperform those
187 made with 60-PCBM (Figure S5 in SI), despite the two EELs presenting very similar energy
188 levels, which will likely align in the same way once interfaced with the perovskite
189 semiconductor given the same nature of the material. Recently, it has been shown that the
190 structural order of the 60-PCBM layer has a significant impact on the enhancement in V_{oc} due
191 to a concomitant reduction of the energy disorder, as deduced from the significant decrease in
192 the DOS of the organic semiconductor.^[27] However, here, while the 60-PCBM clearly shows
193 a sharp X-ray diffraction peak at 20.5° as a signature of order and crystallinity, there is hardly
194 any diffraction peak in C-PCBSD (see Figure S6 in SI), thus excluding any direct role of the
195 electron extracting layer morphology. Note that, for a fair comparison, we grew the perovskite
196 film by thermally evaporating PbI_2 followed by MAI deposition by spin coating from 2-
197 propanol, a procedure that some of us have recently developed^[7] to preserve the soluble 60-
198 PCBM layer and we noticed, also in this case, a tendency of forming larger crystallites over
199 the C-PCBSD (see Figure S7 in SI). Overall, beyond the interfacial energetics, the
200 recombination dynamics will contribute to the definition of V_{oc} of solar cells. Since the
201 perovskite film is grown on top of the EEL, the latter's choice will determine its micro-
202 structure, which may influence the degree of defect states and the carrier recombination losses
203 within the perovskite film.^[28] In the following we will try to disentangle all these effects by
204 combining excitation density dependent steady state photocurrent measurements and photo-
205 induced transient techniques.

206

207 To understand the effect of the fabrication route and the substrate on the quality of the thin
208 perovskite film, we performed photo-current measurements within a photo-conductor device
209 configuration.^[29] Briefly, planar symmetric gold contacts separated by 1 mm are evaporated
210 on top of the film and continuous wavelength (cw)-laser induced carriers are extracted by
211 applying a bias voltage of 10 V across them (**Figure 4a**). Note that the electric fields within
212 this configuration are smaller by a factor of 100 in comparison to the usual electric fields
213 within the solar cell architecture. In Figure 4b we show the photocurrent plotted as a function
214 of the photo-excitation density. All measured films are approximately 300 nm thick and
215 grown on a thin layer of TiO₂, TiO₂/60-PCBM and TiO₂/C-PCBSD on glass; this guarantees
216 to have a thin film micro-structure comparable to the one present in the device while
217 observing mainly bulk processes upon top layer illumination. Since perovskite cannot be
218 solution processed on top of TiO₂/60-PCBM we also compare two thin films grown on C-
219 PCBSD, one solution processed and the other grown through thermal evaporation.

220

221 While all the films show a monotonic growth of photocurrent with the excitation density, they
222 exhibit distinct intensity trends. As a guide for the eyes, we draw hypothetical linear ($\sim I$) and
223 sublinear ($\sim\sqrt{I}$) intensity dependent photocurrent in dotted lines. The photocurrent trends in
224 all the films follow sublinear behaviour at low excitation densities and reach a linear trend at
225 higher densities. Such a behaviour can be explained within a trap-limited Shockley-Read-Hall
226 (SRH) like recombination scenario, where at low-excitation densities, electrons (holes) are
227 most likely trapped within defects and thus do not contribute to the photocurrent. In such case
228 the photocurrent has a sole contribution from hole (electrons) population, which can be shown
229 to scale as \sqrt{I} under steady state conditions,^[35] subsequently giving rise to the sublinear
230 behaviour of the photocurrent. As the excitation density is increased, there is a substantial
231 contribution from the untrapped electron (hole) current. Nevertheless, given that the effective
232 defect density is around 10^{16} cm⁻³, the carrier dynamics at the investigated densities still lie

233 within the trap-limited regime,^[36,37] where the electron (hole) population can be shown to
234 scale linearly with intensity within the SRH formalism.

235

236 Since the photocurrent is proportional to the number of free charge carriers and therefore
237 composed of electron and hole current density, $j = j_e + j_p$, we expect that the general light
238 intensity dependence in the simplest approximation can be described with a linear and square
239 root contribution. The ratio between this sublinear and linear component is therefore an
240 indication for the degree of trap-limited behaviour of the perovskite films, with greater linear
241 component suggesting lower degree of carrier trapping. The photocurrent extracted from films
242 grown on C-PCBSD in Figure 4b follows a behaviour closer to the linear limit at excitation
243 densities of $10^{13} - 10^{15} \text{ cm}^{-3}$ relevant for the PV operation, in comparison to the films grown
244 directly on TiO_2 and $\text{TiO}_2/60\text{-PCBM}$, indicating a lower density of traps. We have already
245 highlighted above that the wettability of PbI_2 dissolved in DMF on C-PCBSD is quite poor
246 with respect to TiO_2 , which leads to the formation of larger and flatter grains and hence a
247 lower density of defects. Interestingly, the intensity dependence of the photocurrent in
248 evaporated MAPbI_3 on TiO_2 and $\text{TiO}_2/60\text{-PCBM}$ follows exactly the same behaviour, proving
249 similar film growth conditions on both bottom layers. Thus, the choice of the EEL on the
250 bottom strongly influences the opto-electronic property of the perovskite films and thus must
251 be take into account in the device optimization.

252 We now turn to the measurement of carrier recombination kinetics in working conditions (i.e.
253 under 1 sun light bias), comparing the different devices architecture presented in this work.
254 First, we carried out the measurement of the device capacitances using photo-induced
255 differential charging (PIDC) after subtraction of the geometrical capacitance (**Figure 5a**) as
256 reported before.^[30] Keeping the layers thickness comparable, these measurements allow us to
257 compare the accumulated charge densities in solar cells at different bias. We report such
258 densities in Figure 5b, showing that the solar cell with the C-PCBSD fullerene selective

259 contact is capable to accumulate higher amount of charges. It is worthy to mention that the
260 capacitance increases super linearly for voltages above 0.8 V and it is independent on the
261 thickness of the C-PCBSD layer (see Figures S12 and S13 in the SI). This profile has been
262 also observed in other thin film solar cells alike polymer^[31] and small molecule organic solar
263 cells.^[32,33] While the linear increase of capacitance with the light bias is correlated to the
264 accumulation of carriers at the device contacts,^[34] the super linear behaviour indicates that the
265 contacts are not able to sustain the entire density of charges which accumulate in the bulk of
266 the device as well. This is further supported by the fact that charge density, as well as the
267 charges lifetimes, scale as the thickness of the perovskite active layer (see Figures
268 S16,S17,S18 of the SI). Importantly, this leads to a greater split of the quasi-Fermi levels for
269 holes and electrons leading to a larger V_{oc} - as long as strong recombination losses do not kick
270 in which then points to the importance of the electronic quality of bulk semiconductor layer.
271 We now can compare the carrier recombination kinetics for the solar cells at equal carrier
272 densities (n). As mentioned above the V_{oc} of solar cells will be influenced by the materials
273 energetics (band alignment) and the carrier recombination kinetics. **Figure 6** illustrates the
274 measurements carried out using the same devices as in Figure 5 in identical light irradiation
275 conditions. As can be seen, the solar cells using C-PCBSD as electron selective contact show
276 longer carrier lifetimes and lower recombination losses. For instance at illumination
277 intensities equivalent at 1 sun the 60-PCBM based devices display a total charge density of 20
278 nC cm^{-2} alike the TiO_2 based ones and carrier lifetimes of 0.6 μs and 2 μs , respectively
279 (shown with a vertical line in Figure 6). Nonetheless, considering the same charge density for
280 C-PCBSD perovskite solar cells the carrier lifetime is hundred times slower ($\tau > 200 \mu\text{s}$). In
281 fact, illuminating these solar cells at 1 sun the total charge was of hundreds of nC cm^{-2} and
282 still the carrier recombination lifetime was the slowest between the three devices with a value
283 close to $\tau = 10 \mu\text{s}$. For a fair comparison with the decays recorded for the organic based

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TiO ₂	Reverse scan	0.2	0.80	19.0	74.5	11.4
		0.023	0.85	18.7	73.1	11.6
	Forward scan	0.2	0.73	19.1	64.4	9.0
		0.023	0.73	18.9	64.7	8.9
TiO ₂ /C-PCBSD	Reverse scan	0.2	1.12	21.1	79.0	18.7
		0.023	1.11	21.1	77.8	18.3
	Forward scan	0.2	1.10	21.2	69.4	16.2
		0.023	1.11	21.1	76.1	17.8

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