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

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Solution-processable hybrid perovskite semiconductors have risen to the forefront of photovoltaics research, offering the potential to combine low-cost fabrication with high power conversion efficiency.[1] The first architectures made use of nanocrystalline TiO_2 deposited on the transparent electrode, both in the form of mesoporous and compact films, as selective contact for electrons alike the so-called Grätzel solar cells.[2-4] Such a structure is generally indicated in the field as *direct architecture* as electrons are collected at the front transparent electrode and holes at the metal contact (often gold). Further development has been driven by empirical optimization strategies and testing of a variety of architectures. One of these promising architectures uses fully organic selective contacts. This choice brings, first of all, the advantage of low temperature processing; additionally, a beneficial effect in terms of electrical stabilization of the device with organic electron extraction layers in a flat junction configuration, with respect to the use of TiO_2, has been repeatedly observed.[5-7] So far, architectures with fully organic selective contacts are either limited to the so-called *inverted architecture*, as a consequence of difficulties in the solution processing of multi-layers, or they have to rely on vacuum deposition methods.[6-8] Solution-processed, flat junctions, multi-layered direct architectures, which would open the path towards large-area, low-temperature processing of high-efficiency direct cells, have been poorly explored, and their power conversion efficiencies are still limited.[9-11] Intuitively, the development and optimization of different architectures need a full engineering of different interfaces. This is especially critical for metal halide perovskites that, unlike more widely studied inorganic semiconductors, have fluctuating ionic structures where tilting, distortions and polarizability of the lattice strongly affect their optoelectronic properties. This makes the reliability of perovskite-based devices

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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 1**a).[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 CH_2 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 sp^2 carbon atoms of the vinyl groups into sp^3

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   formamidine (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} cm^2 V^{-1} s^{-1} for surface charge densities in the range 8 x 10^{15} to 3 x 10^{16} m^{-2}

135 (1.3 x 10^{-7} to 5.1 x 10^{-7} 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/TiO$_2$ 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 TiO$_2$ and comparable to the [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (60-PCBM) (see Table

147 S1 in SI). Subsequently a methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$) thin film is directly

148 synthesised from solution on top of FTO/TiO$_2$/C-PCBSD via a two-step procedure (see

149 methods in SI for details). The final thickness of CH$_3$NH$_3$PbI$_3$ depends on the thickness of the

150 PbI$_2$ layer (see SI for the layer optimization). **Figure 2**a shows X-ray diffraction spectra

151 measured before and after the CH$_3$NH$_2$I spin cast on top of PbI$_2$ followed by thermal

152 annealing on top of TiO$_2$ and TiO$_2$/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 TiO$_2$ and TiO$_2$/C-PCBSD, respectively, at different magnifications. The perovskite films

156 show a good coverage on both substrates; however, the film grown on TiO$_2$/C-PCBSD

157   presents much larger grains (> 1 µm) 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 formamidine/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 3**a and 3b we

164   show a cross section of the optimized planar devices employing TiO_2 and TiO_2/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 TiO_2/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

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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 4**a)**.** 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 TiO_2, TiO_2/60-PCBM and TiO_2/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 TiO_2/60-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 exciation

243 densities of 10^{13} - 10^{15} cm^{-3} relevant for the PV operation, in comparison to the films grown

244 directly on TiO$_2$ and TiO$_2$/60-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 TiO$_2$/60-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 5**a) 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 (τ > 200 μs). 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 τ = 10 μs. For a fair comparison with the decays recorded for the organic based

284 perovskite solar cells, we have used in Figure 6 the fastest component of the bi-exponential

285 decay.

286

287 In conclusion, by employing a crosslinking strategy we demonstrate a fully solution processed

288 planar junction solar cell in direct architecture. The device delivers a PCE close to 19% and a

289 V_{oc} larger than 1.1 V. It is electrically stable, i.e. its J-V characteristics do not depend on the

290 polarization history of the device, and accordingly the photocurrent has a virtually

291 instantaneous response to polarization and remains stable over time. Such high reliability of

292 the device is fully attributed to the high quality of the interface between the C-PCBSD EEL

293 and the perovskite layer. We demonstrate that in such device architecture, under 1 sun

294 illumination, the high carrier density achieved in open circuit condition is not sustained by the

295 extracting contact only, but accumulates within the active layer as well. Thus to enhance the

296 V_{oc}, where greater separation of the quasi-Fermi levels is desired, the carrier recombination

297 losses via carrier trapping in the bulk perovskite films has to be minimized. Here, we show

298 that the choice of the EEL layer not only determines the interface energetic, but also the

299 electronic quality of the active layer and, with c-PCBSD we achieve superior characteristics

300 in both these aspects. These results, beyond the technological validity provided by the

301 demonstration of a high efficiency, fully solution processed, flat junction solar cell, which is

302 electrically stable, define an important direction towards an engineered design of highly

303 performing perovskite solar cells.

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306 **Supporting Information**
307 Supporting Information is available online from the Wiley Online Library or from the author.
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395   Figures Captions

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397   **Figure 1.** (a) Polymerization of PCBSD in solid state at 160 °C. (b) FT-IR spectra of as-cast
398   PCBSD film (dash line) and after 45 min at 160 °C (solid line). (c) The 1st order exponential
399   decay of polymerization reaction determined by normalized peak area of the band at 908 cm^{-1}.
400   The absorption spectra of as-cast PCBSD (c) and C-PCBSD (d) before (solid) and after (dash)
401   being rinsed with DMF.

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404   **Figure 2.** (a) XRD patterns of PbI_2 on glass/FTO/TiO_2 and glass/FTO/TiO_2/C-PCBSD before
405   and after the transformation. SEM top-view of $CH_3NH_3PbI_3$ grown on TiO_2 (b, c) and
406   TiO_2/C-PCBSD (d, e).

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409   **Figure 3.** SEM cross section of complete photovoltaic devices:
410   glass/FTO/TiO_2/$CH_3NH_3PbI_3$/spiro-OMeTAD/Au (a) and glass/FTO/TiO_2/C-PCBSD/
411    $CH_3NH_3PbI_3$/spiro-OMeTAD/Au (b). *J-V* curves for photovoltaic devices
412   FTO/TiO_2/$CH_3NH_3PbI_3$/spiro-OMeTAD/Au (c) and FTO/TiO_2/C-PCBSD/
413    $CH_3NH_3PbI_3$/spiro-OMeTAD/Au (d) measured with different scan rates (V s^{-1}) and different
414   scan directions under AM 1.5G white light illumination with an intensity of approximately
415   100 mW cm^{-2}. Stabilized current density and power output measured close to the maximum
416   power point for TiO_2 (e) and TiO_2/C-PCBSD (f) devices with the corresponding *J-V* curves
417   shown in (c) and (d), respectively.

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420   **Figure 4.** (a) Sketch of the sample geometry for photocurrent measurement. (b) Photocurrent
421   as a function of excitation density of four perovskite layers deposited via evaporation
422   (eMAPbI$_3$) or spincoating (sMAPbI$_3$) on different electron extracting layers. The scattered
423   points represent the measured data, the lines are fits according to $y = c(ax + b\sqrt{x})$. The grey
424   lines show the two extreme cases of the fit model (b = 0 and a = 0, respectively) as a guide to
425   the eyes.

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430   **Figure 5.** Capacitance after subtraction of the geometrical capacitance (a) and the charge
431   density (b) of TiO_2, TiO_2/60-PCBM, and TiO_2/C-PCBSD photovoltaic devices.

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434   **Figure 6.** Recombination lifetime versus charge density deduced from TPV measurements of
435   TiO_2, TiO_2/60-PCBM, and TiO_2/C-PCBSD photovoltaic devices.

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438   **Table 1.** Summary of the best device performance for perovskite solar cells with TiO_2 and
439   TiO_2/C-PCBSD as EELs with the structure of FTO/EEL/$CH_3NH_3PbI_3$/spiro-OMeTAD/Au.

Device	Scan direction	Scan rate (V s^{-1})	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)

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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Fully solution processed direct perovskite solar cells with planar junction are realized by incorporating a crosslinked [6,6]-phenyl-C61-butyric styryl dendron ester layer as electron extracting layer. They deliver power conversion efficiencies close to 19% and an open circuit voltage exceeding 1.1 V with negligible hysteresis. A perovskite film with superb optoelectronic qualities is grown, which reduces carrier recombination losses and hence increases V_{oc}.

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Fully Solution Processed Direct Perovskite Solar Cells with Planar Junction: How the Charge Extracting Layer Determines the Open Circuit Voltage