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Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemSusChem 10.1002/cssc.201700180

Link to VoR: http://dx.doi.org/10.1002/cssc.201700180



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Modified fullerenes for Efficient Electron Transport Layer-Free Perovskite:Fullerene Blend-Based Solar Cells

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Abstract: A variety of novel chemically modified fullerenes, showing different electron accepting capabilities, has been synthesized and used to prepare electron transport layer(ETL)-free solar cells based on perovskite:fullerene blends. In particular, isoxazolino[60] fullerenes are proven to be a good candidate for processing blend films with CH₃NH₃PbI₃ and obtaining enhanced power conversion efficiency (PCE) ETL-free perovskite solar cells, improving state-ofthe-art PCE (i.e. 14.3%) for this simplified device architecture. Beneficial impact for pyrazolino and methano[60]fullerene derivatives versus pristine [60]fullerene is also shown. Furthermore, a clear correlation between the LUMO energy level of the fullerene component and the open circuit voltage of the solar cells is found. Apart from the new knowledge on innovative fullerene derivatives for perovskite solar cells, the universality and versatility of perovskite:fullerene blend films to obtain efficient ETL-free perovskite solar cells is demonstrated.

Introduction

In order to face important issues such as global warming, pollution and environmental degradation, the search for clean and sustainable energy sources is nowadays a priority for humankind. In this regard, photovoltaics are amongst the most promising alternatives to address these environmental issues.^[1] In particular, perovskite-based solar cells have recently surpassed the all-organic photovoltaics^[2] and dye sensitized solar cells^[3] in terms of power conversion efficiency.

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Perovskite-based solar cells (PSCs) have revolutionized the photovoltaic field, showing a tremendous leap in power conversion efficiency in the last years.^[4] Within the field of regular PSCs, the big majority of the research work has been devoted to the preparation of perovskite (i.e. including those based on advanced composition engineering with multiple anions and/or cations)^[5] films with improved microstructural properties^[6] and innovative organic hole transporting materials (HTMs),^[7] to afford highly efficient PSCs (Figure 1A).

Titanium dioxide is often the material of choice as electron transporting material (ETM) in regular PSCs. The titanium dioxide used in these solar cells needs generally a sintering process, which requires treatment at high temperatures. This thermal treatment implies a drawback in energy cost for a future commercialization of these devices. Moreover, the use of titanium dioxide influences the rigid morphology of the cell, limiting its use on curved surfaces.^[8] Thus, the replacement of TiO₂ as ETM by organic materials is a very important subject for the suitable development and future commercialization of PSCs. In this regard, some of us have recently described the "Fullerene Saturated Approach" as an innovative strategy to prepare efficient PSCs, while avoiding energy cost processing issues, associated to the use of TiO₂ as ETM.^[9] Nevertheless, the development of novel electron transporting materials (ETMs) able to replace the TiO_2 is just restricted to a few examples, such as azaacenes,^[10] pristine fullerenes (Figure 1B),^[11] mesostructures fullerene architectures^[12] and cross-linkable fullerenes.[13]

Inspired by the outstanding effects of the "Fullerene Saturated Approach", we have recently reported a strategy to prepare electron transport layer-free solar cells based on perovskite-[70]fullerene blends (Figure 1C).^[14] This robust solution-processing protocol for the deposition of pinhole-free methylammonium lead triiodide-[70]fullerene blend films on fluorine-doped tin oxide (FTO) simplifies the solar cell fabrication process (i.e. no ETL deposition step) and provide efficient devices with enhanced stability. Interestingly, significant photostability improvement has also been recently reported for inverted architecture perovskite solar cells based on perovskite:PCBM films.^[15] Indeed, the latter were also proven to improve the fill factor and suppress the hysteresis.^[16] However, there is rather limited knowledge on the interactions between the fullerene (or derivatives) and the perovskite.^[17] Therefore, there is need for further research evaluating the use of different chemically modified fullerene derivatives in perovskite-based blend films and effects on the solar cell performance. Apart from its simplicity, ETL-free device architecture has been chosen due to the absence of interfaces between the perovskite crystals and other electron acceptor materials that might cause some

interference in the analysis of the fullerene (or derivatives) influences on the solar cell performance. However, in order to prove the versatility and scope of this processing methodology to prepare efficient electron transport layer-free solar cells, it is necessary to fabricate solar devices based on blends of perovskite with different chemically modified fullerene derivatives.



Figure 1. Different types of regular architecture perovskite solar cells discussed in the text.

In this report, perovskite-based blend films with a variety of new fullerene derivatives endowed with different organic addends and with tailored electronic properties are studied. The fullerene-based materials include two novel pyrazolino[60]fullerene derivatives (**PI-1** and **PI-2**),^[18] two new isoxazolino[60]fullerene derivatives (**IS-1** and **IS-2**)^[19] and two methano[60]fullerene derivatives (**DPM-6**^[20] and **PC**₆₁**BM**), all of them shown in Figure 2.

It is important to underline here that pyrazolino[60]fullerenes and isoxazolino[60]fullerenes have never been previously used in PSCs. Therefore, to the best of our knowledge, this study represents the first attemp of their use in PSCs. In the case of methano[60]fullerenes, the most employed fullerene derivative in PSCs is by far **PC**₆₁**BM** ([6,6]-phenyl-C₆₁-butyric acid methyl ester).^[21] However, the related **DPM-6** endowed with two aryl groups in the cyclopropane ring remains unexplored in regular or inverted PSCs. Therefore, additionally to the unambiguous proof of universality and versatility of perovskite:fullerene blend films to obtain efficient ETL-free perovskite solar cells, new knowledge about innovative fullerenes in the PSC field is provided.

Results and Discussion

Synthesis

In this study, we have designed and synthesized new fullerene materials displaying tailored electron accepting properties, to investigate its effect on the performance of electron transport layer-free solar cells based in perovskite-fullerene blends. For this purpose. we have prepared two novel pyrazolino[60]fullerene molecules and two novel isoxazolino[60]fullerene molecules, as well as known methano[60]fullerene derivatives, namely DPM-6 and $PC_{61}BM$.



Figure 2. Fullerene derivatives synthesized in the present study.

Owing to the presence of a heteroatom directly connected to the fullerene cage, pyrazolino[60]fullerenes and isoxazolino[60]fullerenes display better electron accepting properties than methano[60]fullerenes.[22] Moreover, the presence of highly electron withdrawing fluorine atoms on the phenyl rings of pyrazolino[60]fullerenes and isoxazolino[60]fullerenes also contribute to the enhancement of these electron accepting properties.^[23] The novel precursor materials 1-4, were prepared in excellent yields by reaction of 3,5-bis(trifluoromethyl)benzaldehyde or pentafluorobenzaldehyde with hydroxylamine to afford oximes 1 and 2, and with pentafluorophenylhydrazine to afford hydrazones 4 and 3. The innovative fullerene materials were obtained by in situ cycloaddition of the corresponding precursors (1-4) with NBS in the presence of trimethylamine and [60]fullerene, to afford isoxazolino[60]fullerenes IS-1 and IS-2 and pyrazolino[60]fullerenes PI-1 and PI-2 in good yields (Scheme 1).^[22b] Methano[60]fullerene DPM-6 was prepared according to a protocol described by our group.^[24] PC₆₁BM was synthesized following an already reported protocol.^[25] All the novel precursors and fullerene derivatives were fully characterized by means of ¹H NMR, ¹³C NMR, ¹⁹F NMR, UV-Vis spectroscopy, MALDI-MS and Cyclic Voltammetry (See Supporting Information).

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Scheme 1. Reagents and conditions used for the preparation of precursors 1–4 and fullerene materials IS-1, IS-2, PI-1 and PI-2.

Optical and Electrochemical Properties

The optical properties of the fullerene derivative materials prepared in this study were investigated by means of UV-Vis spectroscopy. As it can be seen in Figure 3, the fullerene materials display an intense absorption in the UV region, while the visible region remains almost transparent. All the fullerene derivatives display the characteristic absorption peak at ~ 430 nm, which is a typical feature of 1,2–dihydrofullerenes, due to the saturation of a double bound on the [60]fullerene cage.^[26]



Figure 3. UV-Vis absorption spectra of the fullerene derivatives synthesized in the present study, measured in dichloromethane $(1 \times 10^{-5} \text{ M})$. The inset shows the cyclic voltammograms of selected fullerene materials (DPM-6, IS-2 and PI-2), illustrating its different electron accepting capabilities by showing their first reduction wave. UV-Vis spectra of the different fullerenes in DMF are shown in Figure S35.

The electrochemical properties of IS-1, IS-2, PI-1, PI-2, DPM-6 and PC₆₁BM were determined by means of cyclic voltammetry in o–DCB/MeCN (4:1) at room temperature and using a three-electrode cell equipped with a glassy carbon working electrode, a Pt wire counter electrode and a Ag/AgNO₃ reference electrode. DPM-6 and PC₆₁BM showed a lower electron accepting ability than pyrazolino[60]fullerenes and isoxazolino[60]fullerenes, with a first reduction wave centered at -0.430 V and -0.450 V, respectively. Isoxazolino[60]fullerenes IS-1 and IS-2 showed first reduction waves centered at -0.347 V and -0.352 V, respectively.

The best electron accepting properties were shown by **PI-1** and **PI-2**, exhibiting first reduction waves centered at -0.322 V and -0.316 V, respectively (Figure 3 inset). **PI-1** and **PI-2** showed first reduction waves shifted 30 mV compared with its isoxazolino[60]fullerenes analogous (**IS-2** and **IS-1**), due to the presence of the electron withdrawing pentafluorophenyl ring directly connected to the sp^3 N atom of the pyrazoline heterocycle (Table 1). The origin of the different electron capabilities of these materials stem from the presence of a nitrogen or oxygen atom directly connected to the fullerene cage in pyrazolino[60]fullerenes and isoxazolino[60]fullerenes, respectively.^[22a]

Table 1. Reduction potentials (CV) and energy levels of the LUMO for fullerene materials IS-1, IS-2, PI-1, PI-2, DPM-6, $PC_{61}BM$ and C_{60} .

Fulle	erene Derivative	E ^{1/2} red ^[a]	٤LUMO (eV) ^[b]
	IS-1	-0.347	-4.055
	IS-2	-0.352	-4.048
7	PI-1	-0.322	-4.078
	PI-2	-0.316	-4.084
	DPM-6	-0.430	-3.970
	PC ₆₁ BM	-0.450	-3.950
	C ₆₀	-0.349	-4.050

[a] V vs. Ag=AgNO₃. Cyclic voltammograms for compounds **IS-1**, **IS-2**, **PI-1**, **PI-2**, **DPM-6** and **PC**₆₁**BM** were recorded at a scan rate of 100 mV s⁻¹. GCE as working electrode. Reduction potentials were measured in *o*-DCB/MeCN (4:1) solution (Bu₄NPF₆ 0.1 M as supporting electrolyte) at room temperature. All potentials are reported with reference to an internal standard of the ferrocene/ferrocenium couple (Fc/Fc+ = 0.00 V). [b] The energetic level of the LUMO for each fullerene material has been estimated using the following equation $E_{LUMO} = -[E^{1/2}_{red} + 4.4] eV$.

Electron Transport Layer-Free Solar Cells

To evaluate the synthesized fullerene derivatives in ETL-free PSCs, perovskite:fullerene derivative films were prepared by the recently described protocol.^[14] Briefly, the perovskite solution was prepared by dissolving 7.71 mmol of CH₃NH₂ and 2.57 mmol of PbCl₂ (molar ratio 3:1) in 3 mL of DMF and stirring overnight. Prior to deposition, each fullerene derivative (IS-1, IS-2, PI-2, DPM-6 and PC61BM) was added to the perovskite solution to prepare the solar cells. It is noted that PI-1 was not used in this photovoltaic study due to its lack of solubility in DMF. However, the solubility of the other fullerene derivatives was around 0.3 mg/mL (i.e. significantly higher than that of pristine [60]fullerene: 0.1 mg/mL). The blend films resulting from the use of the five different fullerene derivatives were used to fabricate solar cells the following configuration in glass/FTO/CH₃NH₃Pbl₃:fullerene derivative/spiro-OMeTAD/Au (detailed information can be found in the experimental section). The top-view SEM micrographs of perovskite:fullerene blends did not show major differences other than the elimination of a big amount of pinholes (as occurred in perovskite:C₇₀ blend films^[14]). (Figure S43). However, some effect of the fullerene derivative on the blend film roughness cannot be fully ruled out Solar cells based on perovskite films with pristine fullerene ((i.e. glass/FTO/CH₃NH₃PbI₃:C₆₀/spiro-OMeTAD/Au) and without fullerene (i.e. glass/FTO/CH₃NH₃PbI₃/spiro-OMeTAD/Au) were also prepared for comparison purposes. Figure 5 shows the J-V curves, under AM1.5G simulated sunlight, of the best devices.



Figure 5. J–V characteristics, under AM1.5G simulated sunlight, of the best PCE ETL–free solar cells based on CH_3NH_3Pbl_3:fullerene blends.

The photovoltaic parameters extracted from the *J-V* curves are summarized in Table 2. It is noted that, additionally to the best values, the mean ones (i.e. extracted from the full series, see statistical analysis in Figures S36-39) are also included in the table. As it can be seen, the power conversion efficiency (PCE) of the solar cells prepared with blend films including fullerene or derivatives is significantly higher than the reference device (i.e. with perovskite film with no fullerene). Furthermore, the performance of solar cells based on blend films with fullerene derivatives is better than the analogue with pristine fullerene. This finding suggests that all here studied chemical modifications have a beneficial impact on the fullerene for their use in perovskite:fullerene blend films for photovoltaic applications.

Table 2.	Photovoltaic	parameters	for the	best	PCE	solar	cell	(average
values of	a series of de	vices, see st	atistical	analy	sis in I	Figure	s S3(5-39).

Fullerene Derivative	J _{sc} (mA cm ⁻²)	Voc (mV)	FF (%)	PCE (%)
IS-1	16.7 (17.2)	1030 (1013)	68.7 (67.2)	11.8 (11.7)
IS-2	16.1 (15.9)	1062 (1046)	73.8 (72.3)	12.7 (12.0)
PI-2	16.5 (16.0)	1022 (1002)	69.4 (68.7)	11.7 (11.0)
DPM-6	16.1 (16.1)	1043 (1012)	69.2 (66.1)	11.6 (10.8)
PC ₆₁ BM	14.5 (14.6)	1064 (1050)	72.2 (71.2)	11.2 (10.9)
Fullerene- free	17.0 (15.2)	1040 (950)	69.6 (61.2)	10.5 (9.0)

It is worth to note that the main improvement versus devices with pristine fullerene was detected for the J_{sc} . This may be due to the better solubility in DMF exhibited by the fullerene derivatives, making possible to prepare processing solutions with fullerene/PbCl₂ ratios of 1:7200 (i.e. close to those claimed as the best from recent studies with [70]fullerene).^[14] However, further comparative analysis of the photovoltaic parameters indicates that in general the open circuit voltage (Voc) increases in the following order: pyrazolino[60]fullerenes isoxazolino[60]fullerenes < methano[60]fullerenes, following a similar trend to that observed for the [£]LUMO energy estimated by electrochemistry (Table 1). This experimental observation suggests, additionally to the increase of fullerene solubility, the chemical functionalization may play a significant role in the solar cell performance. In particular, it seems that the use of less electron accepting fullerenes within these blends results in an increase in the V_{oc} . Although further device characterization is required in order to determine the involved mechanisms, this finding may provide some useful practical guidelines for selecting fullerene derivatives for their use in PSCs. Another relevant aspect to bear in mind is the functionalization of the fullerenes. More in particular, the isoxazolino moiety might represent a binding site for a better interaction with perovskite.

As the best PCE was obtained for devices based on CH₃NH₃Pbl₃:**IS-2** blend films, a further optimization protocol was applied on the deposition of these films by using *o*-xylene as a co-solvent.^[14] As a result, solar cells with improved photovoltaic performance were obtained (Figure 6a shows a micrography of the cross section of the device). In particular, champion devices

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showing a J_{SC} = 17.3 mA cm⁻², V_{OC} = 1077 mV, FF = 78% and an overall PCE of 14.3% (Figure 6b). Good agreement between the measured J_{sc} and value estimated from the eQE spectrum (Figure S44), is noted. It is worth to mention that 14.3 % PCE results in an improvement versus the recently reported on perovskite:[70]fullerene blend-based solar cells, meaning, to the best of our knowledge, the highest PCE value achieved for ETLfree perovskite solar cells up to date.^[27] In addition, this formulation leads to highly reproducible devices, with rather narrow PCE dispersion as it can be seen in Figure 6c.



Figure 6. a) Cross-section micrograph obtained by FE-SEM means and b) J-V curve and PV parameters for champion perovskite:IS-2 device; c) distribution of champion device PCE values, pointing out its reproducibility.

As discussed in the introduction, the beneficial impact of using perovskite:fullerene blend films on the solar cell stability has been recently claimed.^[14,15] Therefore, the effect of the different fullerene derivatives on the photostability of the unencapsulated perovskite solar cells was also investigated. Figure 7 shows the evolution of PCE versus time under continuous AM1.5G simulated sunlight for solar cells based on blend films including the best-performing fullerene from each derivative family (i.e. IS-2, PI-2 and DPM-6). As can be seen in Figure 6, there are no clear differences, concluding that all fullerenes have similar beneficial impact on the photostability of the device. This finding suggests fullerene core (i.e. irrespectively of the chemical modification) as the main cause of the stability enhancement. Indeed, all perovskite:fullerene derivative blend films exhibited similar water contact angle (Table S1), pointing out similar behaviour versus moisture which may be one of the main degrading agents for PSCs. In addition, it is noted that FF is the most relevant parameter concerning photostability as V_{oc} and J_{sc} did almost not vary with exposure time (Figure S40-42).



Figure 7. Evolution of PCE (normalized values) versus time under AM1.5 simulated sunlight for non-encapsulated solar cells containing the best working fullerene for each type.

Therefore, the present results point out isoxazolino[60]derivatives as very good fullerene candidates to be used in the perovskite solar cells, placing them in an advantageous position versus the very well-known PC₆₁BM. This finding anticipates significant potential and may open wide avenues for isoxazolino[60]derivatives, which up to our best knowledge have not been previously proposed and/or evaluated for photovoltaic applications. Although the relatively lower photovoltaic performance detected for devices based on perovskite: PI-2 blend film, the pyrazolino[60] fullerenes may also have some opportunities in perovskite solar cells. The scenario seems indeed to be quite different to their application in organic solar cells, for which the highest reported PCE using this kind of 1%.[28] derivative is Concerning fullerene the methano[60]fullerene bisadducts, it is concluded that DPM-6 seems to be a competitive alternative to the well-known PC61BM also to be used in PSCs, as previously demonstrated for organic solar cells.[29]

Conclusions

A variety of novel (**IS-1**, **IS-2**, **PI-1**, **PI-2**) and well-known fullerene materials (**DPM-6**, **PC**₆₁**BM**) showing different electron accepting capabilities have been designed and synthesized to study the effect over the photovoltaic performance of electron transport layer-free solar cells based on perovskite:fullerene blends. In particular, 14.3% PCE ETL-free perovskite solar cells, based on CH₃NH₃Pbl₃:isoxazolino[60] derivative blend films, were obtained. The photovoltaic performance improvement, in comparison to devices based on CH₃NH₃Pbl₃:[60]fullerene blend films and [70]fullerene analogues,^[14] points out the beneficial impact of the fullerene chemical modification. Furthermore, an interesting experimental correlation between the open circuit

voltage value of the devices and the LUMO energy level of the fullerene material, which may be very helpful in future materials design for perovskite solar cells, has been found out as well. All in all, the current photovoltaic study, which includes ETL-free perovskite solar cells based on a large variety of perovskite:fullerene derivative blends, allows to confirm the universality of using solution processed perovskite:fullerene blend films as light absorber material for ETL-free solar cells.

It is important to remark that the synthetic costs associated to the fabrication of pyrazolino[60]fullerenes and isoxazolino[60]fullerenes, are similar to those required for PCBM, evidencing the high potential of these fullerene derivatives in this emerging field. This gained knowledge paves the way to the use of new modified fullerenes as well as nonfullerene electron acceptors with a controlled LUMO level.

Experimental Section

Materials

Chemicals and reagents for synthesis were purchased from commercial suppliers and used as received. All solvents were dried according to standard procedures. Air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230-240 Analytical thin layer chromatography (TLC) was performed using aluminum coated Merck Kieselgel 60 F254 plates. The materials used in the photovoltaic study were obtained from commercial suppliers in high purity and used without further purification: glass/FTO (TEC15, Hartford Glass), methylammonium iodide (MAI, DYESOL), PbCl₂ (98%, Sigma–Aldrich), spiro-OMeTAD (99%, Feiming Chemicals Limited), lithium bis(trifluoromethane) sulfonimidate (LiTFSI, 99.9%, Solvionic), *tert*–butylpyridine (96%, Sigma–Aldrich), DMF (extra pure, Scharlab), 2-propanol (synthetic grade, Scharlab), acetone (technical grade, Scharlab), chlorobenzene (99.8%, Sigma–Aldrich) and acetonitrile (UV HPLC grade, Scharlab).

Characterization

NMR spectra were recorded on a Bruker Advance 300 (¹H: 400 MHz; ¹³C: 101 or 75 MHz) and Bruker Advance DRX-500 (¹⁹F: 471 MHz) spectrometers at 298 K using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet. UV-Vis spectra were recorded in a Varian Cary 50 spectrophotometer. Matrix assisted Laser desorption ionization (coupled to a Time-of-Flight analyzer) experiments (MALDI-TOF) were recorded on a MAT 95 thermo spectrometer and a Bruker REFLEX spectrometer respectively. Cyclic voltammograms for compounds were recorded at a scan rate of 100 mV s⁻¹ using an air-tight single-compartment three-electrode cell equipped with a glassy carbon working electrode, Pt wire counter electrode, and Ag/AgNO₃ reference electrode. Reduction potentials were measured in o-DCB/MeCN (4:1) solution (Bu₄NPF₆ 0.1 M as supporting electrolyte) at room temperature. All potentials are reported with reference to an internal standard of the ferrocene/ferrocenium couple (Fc/Fc⁺ = 0.00 V). UV–Visible spectra were recorded in a Varian Cary 50 spectrophotometer in dichloromethane $(1x10^{-5} \text{ M})$

Device fabrication

Glass/FTO samples were cleaned by the following procedure: the samples were sonicated in distilled water with soap for 5 min, rinsed thoroughly with distilled water, dried and sonicated in acetone and 2-propanol for 15 min in each solvent. The perovskite solution was prepared by dissolving 7.71 mmol of MAI and 2.57 mmol of PbCl₂ (molar ratio 3:1) in 3 mL of DMF and stirring overnight. Prior to deposition, the perovskite solution was saturated with the corresponding fullerene material (i.e. materials IS-1, IS-2, PI-2, DPM-6 and PC₆₁BM.). It is noted that fullerene solubility in the perovskite solution was around 0.3 mg ml⁻¹ for all of them. The resulting solution was spin coated on the substrates following a two-step protocol, which consisted of a first step of 500 rpm for 5 s followed by a second step of 2000 rpm for 45 s. Subsequently, the samples were annealed at 100°C for 2 h to ensure complete perovskite formation. On top of the perovskite layer, the spiro-OMeTAD holeselective contact was deposited from a solution that contained spiro-OMeTAD (108.4 mg) in chlorobenzene (953.43 mL), LiTFSI solution in MeCN (17.17 mL, 520 mg mL⁻¹) and tert-butylpyridine (29.4 mL). The HTL was deposited by spin coating the solution at 3000 rpm for 30 s. The samples were left in a desiccator overnight. Finally, an array of round Au back contacts (~ 0.07 cm²) was deposited by thermal evaporation at more than 5x10⁻⁶ torr with a NANO38 (Kurt J. Lesker) apparatus with a shadow mask.

Device characterization

The *J*–*V* characteristics of the solar cells were measured under a xenon arc lamp simulator equipped with an AM1.5G spectral filter (Sun 2000, ABET Technologies). The intensity was adjusted to provide 1 sun illumination (100 mW cm⁻²) by using a calibrated silicon solar cell. The *J*–*V* characteristics were recorded by scanning the potential from higher than the V_{OC} to zero (i.e., "reverse mode") at approximately 300 mV s⁻¹. Before the measurement, a voltage of approximately 1.2 V was applied to the devices for 1 min. It is noted that unmasked devices were generally used for the J-V characterization. However, only relatively minor differences were detected when mask was used (Fig. S45).Stability measurements were carried out under continuous AM1.5G simulated sunlight, recording the *J*–*V* characteristics (in "reverse mode" and without applying any previous external voltage) every 10 min during the first 60 min and from there every 30 min.

Acknowledgements

We thank Sandra Rodriguez for the excellent technical support. This work was partially supported by the European Research Council (ERC-320441-Chirallcarbon), Basque Government (PC2015-1-03 (16-79)), Comunidad de Madrid (FOTOCARBON Project S2013/MIT-2841), MINECO of Spain (Grant Numbers CTQ-2014-52045-R, MAT2013-47192-C3-2-R and CTQ201570921) and Red Guipuzcoana de Ciencia, Tecnología e Innovación (MSFP). J.P. acknowledge Polymat for PhD research grant. S.C. acknowledges the Basque Government for a PhD research grant. J.L.D. acknowledges Ikerbasque, the Basque Foundation for Science, for an "Ikerbasque Research Fellow" contract, Polymat Foundation and MINECO of Spain for IEDI-2015-00666 grant. J.P. and J.L.D. acknowledge Iberdrola Foundation for financial support.

Keywords: fullerenes • solar cells • perovskite:fullerene blend films • ETL-free

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FULL PAPER

Novel CH₃NH₃PbI₃:fullerene blends based on a variety of fullerene derivatives (i.e. isoxazolino, pyrazolino and methano[60]fullerenes) are demonstrated to fabricate electron transport layer-free solar cells that efficiently (i.e. up to 14.3%) convert sunlight into electricity.

Spiro-OMeTAD Electron Layer Free CH₃NH₃Pbl₃-Fullerene blend Pyrazolino(60)fullerenes Isoxazolino(60)fullerenes Methano(60)fullerenes R. Sandoval-Torrientes, J. Pascual, I. García-Benito, S. Collavini, I. Kosta, R. Tena-Zaera,* N. Martín,* J. L. Delgado*

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Modified fullerenes for Efficient Electron Transport Layer-Free Perovskite:Fullerene Blend-Based Solar Cells