Organic solar cells based on graphene derivatives and eutectic alloys vacuum-free deposited as top electrodes

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A B S T R A C T
Here is presented the use of two graphene derivatives in organic solar cells (OSCs) based on PTB7:PC70BM active layer. Reduced graphene oxide (rGO) was used as hole transport layer (HTL). Also, solution-processable functionalized graphene (SPFG) was incorporated as a third component in the active layer. Furthermore, the top electrode was either Field’s metal (FM): Bi/In/Sn or BS: Bi/Sn, eutectic alloys that melt at 62 and 138 °C, respectively; they are vacuum-free deposited by drop coating under normal atmospheric conditions. For OSCs with rGO as HTL, thin films were prepared by reiterative spin-deposition and thermal reduction of GO after each deposition. The best results were achieved for 6-rGO with a PCE = 5.50%, similar to that reached in control devices, i.e., PEDOT:PSS as HTL. On the other hand, ternary active layers were prepared by blending SPFG, at different weight ratios: 0, 2, 4, and 6 wt. %, with PTB7:PC70BM. An increment in PCE (6.73%) for OSCs with 4 wt. % of SPFG was found, which is 22% larger than that of the reference devices. Finally, PCEs of 5.52% and 5.31% were reached in OSCs fabricated and tested under normal room conditions with FM and BS, respectively.

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1. Introduction

Organic solar cells (OSCs) have excellent advantages such as low-cost manufacture, flexibility, lightweight, and semi-transparency in the visible region [1–6]. Nowadays, the power conversion efficiency (PCE) has exceeded 13% for both single-junction and multi-junction OSCs [7–11]. The active layer of bulk-heterojunction (BHJ) OSCs is mainly comprised of an electron-donor (D) conjugated polymer and an electron-acceptor (A) fullerene derivative in which the bi-continuous network is controlled by solvent systems, weight D/A ratio, and vapor/thermal treatments in order to improve the fundamental processes in the active layer [12–15]. In the last years, the design and synthesis of electron-donors with improved properties have been widely reported by several research groups [16–22], meanwhile, the studies of electron-acceptors have been explored to a lesser extent [23–25]. Therefore, the synthesis and use of new electron-acceptor materials should be deeper explored for OSCs.

Carbon-based semiconductors such as carbon nanotubes and graphene have received much attention for energy generation and storage applications [26–29]. Particularly, graphene is a good candidate for optoelectronic applications due to its high electrical conductivity (1.5 × 10^6 S/m) and transparency, as well as high carrier mobility (2 × 10^5 cm^2/V s) [30,31]. Regarding interfacial layers in OSCs, graphene oxide (GO) is compatible due to its energy level alignment and chemical stability, especially as hole transport layer (HTL) [32,33]. However, the conductivity of this graphene derivative is quite low (i.e. 6.8 × 10^8 S/m) due to defects and functional groups, such as epoxy and hydroxyl, on the basal planes and carboxylic acid groups at the edges [34–36]. Thus, an additional reduction process is required for increasing its conductivity, which is an important feature for fast charge carrier transport [37–39].
Graphene derivatives have been used as both hole and electron transport layers (HTL and ETL) in OSCs [37,40]. For instance, in OSCs based on P3HT:PCBM, GO has been deposited onto ITO glass substrates and thermally treated at 150 °C for 10 min for its use as HTL and, compared with PEDOT:PSS; PCEs of 3.25 and 3.15% were respectively reached in a direct configuration: ITO/HTL/P3HT:PCBM/LiF/Al [40]. Very recently, Sun et al. [41] compared PEDOT:PSS, GO and GO doped with a reducing agent CuCl₂ (GO:CuCl₂) as HTL in direct configuration: ITO/HTL/PTB7-Th:[70]PCBM/Al. The average PCE reached with GO:CuCl₂ as HTL was 7.68%, which was higher than that of the devices with untreated GO: PCE = 7.10% and comparable with PEDOT:PSS-based devices: PCE = 7.69% [41]. On the other hand, GO also has been used as HTL in combination with other materials as bilayers to improve the extraction of holes [42,43], for instance, GO and oxygen deficient molybdenum oxide (MoO₃-x)/GO:MoO₃-x bilayer, showed a PV performance comparable to that of PEDOT:PSS for OSCs in direct configuration: PCE = 8.05% for GO/MoO₃-x as HTL and 7.87% for PEDOT:PSS with PTbBDT:[70]PCBM as active layer [42]. Also, a GO/PEDOT:PSS bilayer was investigated as HTL in perovskite solar cells (PeSCs) with the configuration ITO/HTL/perovskite/fullerene/LiF/Ag [43]. In this latter study, both the insulating properties of GO and the non-uniform coating of the ITO with GO were diminished by a deposit of PEDOT:PSS over GO. PeSCs with a GO/PEDOT:PSS bilayer as HTL exhibited a higher PCE = 9.7% than that of devices fabricated with the conventional PEDOT:PSS: PCE = 8.2% [43]. Recently, Cheng et al. [44] synthesized a fluorene-functionalized reduced GO (F-rGO), and it was used as HTL in OSCs based on PTB7-Th:[70]PCBM as active layer: ITO/HTL/PTB7-Th:[70]PCBM/PFN/Al. Devices with F-rGO showed better PCE (8.6%) in comparison to that of the devices with GO or PEDOT:PSS (7.8 and 7.9%, respectively), it was mainly due to a higher conductivity and work function of the F-rGO [44].

On the other hand, the use of graphene derivatives as electron-acceptors in OSCs active layers has been reported for binary or ternary blends in order to improve the charge carrier transport [45–48]. Generally, the synthesis of such graphene derivatives involves two steps: oxidation/exfoliation of graphite powder (GO), and further functionalization in oxygenated groups at the edges of GO [45]. For binary OSCs, a graphene derivative has been used as electron-acceptor blended with poly[N,N′-heptadecanoyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) [46]. Synthesis of the electron-acceptor consisted in a photochemical reaction between acylated graphene oxide (GO-COCI) and ethylene-dinitrobenzoyl (EDNB) by laser irradiation at 248 nm (LGO-EDNB). The best PCE = 2.71% was reached for OSCs based on PCDTBT:LGO-EDNB with 20 wt. % of LGO-EDNB in a direct configuration: ITO/PEDOT:PSS:PCDTBT:LGO-EDNB/TiOx/Al [46]. Also, graphene nanoflakes (GNF) functionalized with EDNB molecule has been used as electron-acceptor for ternary OSCs blended with PCDTBT and [70]PCBM [47]. For OSCs based on PCDTBT:GNF-EDNB:[70]PCBM ternary system (0.05% by volume), an enhancement of 18% in PCE (ternary PCE = 6.59%) was achieved compared to PCDTBT:[70]PCBM (binary PCE = 5.59%) due to improved exciton dissociation and charge transport. OSCs based on poly(3-hexylthiophene) (P3HT) and [70]PCBM blend doped systematically with solution-processable functionalized graphene (SPFG) at different weight ratios have also been reported in which for 10 wt. % of SPFG content in ternary system (P3HT:[70]PCBM:SPFG), an increment of 5% in PCE (ternary PCE = 2.15%) compared to undoped devices (0 wt. % SPFG, PCE = 1.55%) was achieved [45].

Regarding ternary blends with PTB7-Th, very few studies have been reported by using graphene derivatives [48]. In this doped work, a fullerene/graphene derivatives as acceptor 1/acceptor 2 system, a graphene-based porphyrin molecule (GO-TPP) was synthesized for its use in OSCs fabricated under N₂ atmosphere conditions with the configuration ITO/PEDOT:PSS/PTB7:GO-TPP:[70]PCBM/Al. An enhancement of about 16% in PCE (8.58%) was obtained for doped devices with 0.3% of GO-TPP respect to undoped ones (7.39%) [48].

In this work, two graphene derivatives implemented in air processed OSCs are reported: (a) thermally reduced graphene oxide (rGO) as HTL, and (b) solution-processable functionalized graphene (SPFG) as electron-acceptor for ternary active layers. The BHJ OSCs were based on the low bandgap polymer poly[(4,8-bis[2-ethylhexyl]oxyl)benzo[1,2-b:4,5-b’][dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7, as electron-donor) and the fullerene derivative material [70]PCBM as electron-acceptor. In the first case, different deposit layers of rGO were compared with the common reported PEDOT:PSS as hole transport layer in ITO/HTL/PTB7:[70]PCBM/PFN/FM devices. The best performance was reached in OSCs, tested under normal room conditions, with 6-rGO deposits, having a PCE = 5.50%, nearly the same efficiency achieved with PEDOT:PSS. On the other hand, ternary OSCs showed a PCE = 6.73% for doped active layers with 4 wt. % of SPFG, which is 22% superior to the PCE of undoped devices: 0 wt. % of SPFG, PCE = 5.52%. Finally, here is introduced a eutectic alloy based on bismuth and tin, namely BS, as other alternative top electrode vacuum-free deposited for OSCs and, its PV performance is compared with that of previously reported the OSCs with Field’s metal by our group [45,49–52]. It is worth to mention that, for thermally treated OSCs based on PTB7:[70]PCBM at just 80 °C (and not at 120 °C as in the previously mentioned cases; due to comparison purposes, explained fact on the following sections), and by using our alternative top electrode Field’s metal (FM), we were able to reach a PCE as high as 8.29%.

2. Experimental

2.1. Materials

Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate or PEDOT:PSS (Clevios P A4083), and poly[(9,9-bis’-3’-[N,N-dimethylamino]propyl)-2,7-fluorene]-alt-2,7-(9,9-dioctyfluorene)] or PFN were purchased from Heraeus-Clevios and 1-Material Inc., respectively. Both eutectic alloys FM and BS were obtained from Rotometals, and ITO/Glass substrates with 10 Ω/square were acquired from Delta Technologies. The electron-donor polymer PTB7 and the electron-acceptor [70]PCBM were purchased from 1-Material Inc. Graphene derivatives such as graphene oxide (GO) and solution-processable functionalized graphene (SPFG) were synthesized and characterized as described in our previous work [45]. Fig. 1 shows chemical structures of the used materials in this work.

2.2. OSCs with rGO as hole transport layer

ITO glass substrates were cleaned sequentially with detergent, water, acetone and isopropl alcohol in an ultrasonic bath and, O₂ plasma treatment was used to enhance the wettability of ITO surface. A solution of PEDOT:PSS was filtered and spin-coated onto pre-cleaned ITO glass substrates at 4500 rpm for 30 s, followed by heating at 120 °C in air for 30 min to get a 35-nm thick layers as control samples. On the other hand, a solution of graphene oxide (0.5 mg/ml in ethylene glycol) was spin-coated onto ITO glass substrates at 3000 rpm for 90 s, followed by heating at 220 °C in air to obtain a reduced GO layer (rGO). Different rGO deposits and reduction steps were carried out to cover entirely the ITO surface (18 × 18 cm² substrates). Finally, the ITO/rGO films were kept at 220 °C for 12 h in air. Then, a solution of PTB7:[70]PCBM (1:1.5 w/w, 30 mg/ml in chlorobenzene/18-diiodooctane (97:3 v/v)) was spin-coated on the ITO/HTL substrates at 1900 rpm for 90 s.
under normal room conditions to form a 100-nm thick film. The active layers were thermally treated at 120 °C for 20 min in air to keep same experimental conditions than in the case of ternary active films (see next section). For the electron transport layer, a 5-nm thick film of a polyelectrolyte, PFN, was deposited on the active layer by spin-coating a solution of PFN in methanol (2 mg/7 ml) and a small amount of acetic acid (10 μl), followed by a heating at 80 °C for 10 min in air. Finally, Field's metal (FM) was drop-casted at 90 °C in a hot plate as top electrode on a delimited active area of 0.09 cm². For this section, the direct configuration of OSCs was ITO/HTL/PTB7:[70]PCBM/PFN/FM. Fig. 2(a) shows the configuration of OSCs based on PEDOT:PSS or rGO as HTL.

2.3. OSCs with SPFG as third component in the active layer

Ternary OSCs were fabricated with SPFG as a third component. PTB7:[70]PCBM:SPFG ternary solutions were prepared by blending the first solution of PTB7:[70]PCBM (1:1.5 w/w, 30 mg/ml in chlorobenzene/1,8-diiodooctane) with different volume loadings of the second SPFG solution (3 mg/ml, in chlorobenzene), and stirred together during 12 h. The amount of SPFG in the PTB7:[70]PCBM mixture was determined respect to the [70]PCBM content in weight percent (wt. %). In summary, for 0, 2, 4 and 6 wt. % of SPFG the current concentration was 0.0, 0.375, 0.75 and 1.125 mg/ml, respectively. PTB7:[70]PCBM:SPFG solutions were then spin-coated (100-nm thickness) on the ITO/PEDOT:PSS(35 nm) substrates at 1900 rpm for 90 s under normal room conditions. All deposited active layers were thermally treated at 120 °C for 20 min in air, such thermal treatment is performed to eliminate the oxygenated functional groups located in the planar base of the graphene derivative (epoxy and hydroxyl groups) that were left during the functionalization and to restore the optoelectronic properties of the graphene derivative as described in our previous work [45]. PFN and FM were deposited as mentioned in the previous section (active area = 0.09 cm²). Fig. 2(b) shows the configuration of ternary OSCs fabricated in this section: ITO/PEDOT:PSS/PTB7:[70]PCBM:SPFG/PFN/FM.

2.4. OSCs with eutectic alloys, FM and BS, as top electrodes

OSCs with the direct configuration ITO/PEDOT:PSS/PTB7:[70]PCBM/PFN/Top electrode, fabricated as described previously, were used to compare the eutectic alloys Field’s metal (FM: Bi = 32.5%, In = 51%, and Sn = 16.5% by wt., m.p. 62 °C) and Bismuth/Tin (BS: Bi = 58%, and Sn = 42% by wt., m.p. 138 °C), as top electrodes (see Fig. 2(c)). In the case of BS, it was first heated at 180 °C on a hot plate and then drop-coated onto ITO/PEDOT:PSS/PTB7:[70]PCBM/PFN previously heated at 90 °C in another hot plate (active area = 0.09 cm²).

PV performance of all the fabricated OSCs was measured with a solar simulator (Oriel Sol3A class AAA) and a source meter (Keithley series 2450) under AM 1.5 illumination. Thickness and morphology films were determined using an atomic force microscope (AFM, easyscan2 from Nanosurf), operating in contact mode. The silicon cantilever was 450 μm long with a force constant of 0.2 N/m. EQE spectra were obtained under short-circuit conditions by using a monochromator (Princeton Instruments Acton Series SP2500), a xenon lamp (Oriel Instruments model 66902) as light source, a power meter (Thorlabs PM100) with a measurement range from 400 to 1100 nm, and a source meter (Keithley 2400).
3. Results and discussion

3.1. Reduced graphene oxide as HTL

First, it was confirmed the film formation of GO onto ITO glass substrates. The general procedure to deposit a thin layer of GO consisted in spin-cast a solution of GO in ethylene glycol (0.5 mg/ml). Because GO is an insulator, an additional step is required to recover the semiconductor character of graphene. Thus, a thermal treatment at 220 °C in air was carried out in order to remove the residual ethylene glycol as well as oxygen functional groups of GO obtaining thermally reduced GO films (rGO). Fig. 3 shows scanning electron microscopy (SEM) images of (a) bare ITO, (b) ITO/1-rGO (i.e. 1 deposit), (c) ITO/4-rGO, (d) ITO/6-rGO, (e) ITO/8-rGO, (f) ITO/10-rGO, and (g) ITO/PEDOT:PSS surfaces, they found that GO film onto the ITO surface shows a larger variation in sheet resistance measurements than those for ITO/PEDOT:PSS surfaces, they found that GO film onto the ITO surface shows a larger variation in sheet resistance measurements than those for ITO/PEDOT:PSS surfaces due to the non-uniform covering of GO film. As it can be noticed, the PEDOT:PSS film covers completely and uniformly the granular structure of ITO for the control HTL used in this work (see Fig. 3(g)).

In order to cover the entire ITO surface with rGO thin films, different deposit/reduction steps were carried out in this work named as n-rGO, where n = 4, 6, 8 and 10 denotes the number of deposit/reduction steps. The film formation for different rGO deposits is presented in Fig. 3. As shown, for 4-rGO films it is still slightly noticeable the granular regions of ITO surface (un-covered zones) that are diminished with 6 to 10-rGO deposits. The roughness, thickness, and transmittance of the HTLs play an important role in the OSCs performance. In our case, when n-rGO films were used as HTLs, variation in roughness for the different deposits (4–10) of rGO films is barely perceptible. The 6-rGO thin film shows a complete coverage of its surface and for this reason it was selected as HTL for OSCs. The root mean square (RMS) roughness of those 6-rGO thin films was 3.7 nm evaluated by atomic force microscopy (AFM), this value is comparable to the RMS roughness of PEDOT:PSS thin films: 2.4 nm, see Fig. 4.

PV performance of rGO films as HTL in OSCs based on the mixture PTB7:[70]PCBM as active layer, was compared with that one of the commonly PEDOT:PSS and without the use of any HTL (bare ITO). In this work, due to the given thermal annealing to the active layers (120 °C for all our devices, which was for comparison purposes in the reported different experiments), it was observed a drop in $J_{oc}$ value with respect to OSCs where the active layer, based on PTB7:[70]PCBM, is usually not thermally treated [12,37,48], it is well known that PTB7 polymer is no thermally stable. For thermally treated devices at just 80 °C, and by using the mentioned alternative top electrode Field’s metal (FM), we reached a PCE as high as 8.29%; see Fig. 5.

Fig. 6(a) shows the J-V curves for OSCs with the configuration ITO/HTL/PTB7:[70]PCBM/PFN/FM, the PV parameters are presented in Table 1 (three sets of OSCs devices for each HTL were fabricated and tested, results followed the same trend). As expected, devices without HTL (bare ITO) show an S-shape curve and lower PV values: $J_{sc} = 7.45$ mA/cm², $V_{oc} = 0.60$ V, FF = 28.73% and PCE = 1.28% than those for 6-rGO and PEDOT:PSS as HTLs; this behavior is due to the accumulation/recombination of free charges at the interface between ITO and the active layer [53,54]. Devices with PEDOT:PSS (control) shows a PCE of 5.52% with $J_{sc}$ of 14.17 mA/cm², $V_{oc}$ of 0.76 V, and FF of 51.31%. With 6-rGO films a very comparable PV performance is reached: $J_{sc} = 13.43$ mA/cm², $V_{oc} = 0.70$ V, and a

![Fig. 4. AFM surface images (15 x 15 μm) of (a) bare ITO, (b) ITO/6-rGO, and (c) ITO/PEDOT:PSS. (A colour version of this figure can be viewed online.)](image)

![Fig. 5. J-V curve of OSC with the active layer thermally treated at just 80 °C and FM as top electrode. OSCs were fabricated and tested under room atmosphere conditions. (A colour version of this figure can be viewed online.)](image)
conditions [39]. The work function of rGO also has been reported around 4.9 eV for other authors [33,42,55], the energy level diagram of the studied OSCs in this section is presented in Fig. 6(b).

Regarding previous results with rGO as HTL, Kim et al. [33] implemented microwave-assisted reduced graphene oxide (MR-GO) as HTL in OSCs in a direct configuration: ITO/MR-GO/P3HT:[60] PCBM/Al; PEDOT:PSS was used for comparison in control devices. They determined the work function of ITO, PEDOT:PSS and MR-GO by ultraviolet photoelectron spectroscopy (UPS) as 4.76, 5.11 and 5.01 eV, respectively. Their results show that the work function of MR-GO aligns better than that of PEDOT:PSS with the HOMO level of the P3HT for hole extraction towards the ITO anode, obtaining PCEs of 2.95 and 3.57% for PEDOT:PSS and MR-GO as HTLs, respectively. On the other hand, Cheng et al. [44] used a fluorinated reduced graphene oxide (F-rGO) as HTL in OSCs based on PTB7-Th: [70]PCBM as active layer (ITO/HTL/PTB7-Th: [70]PCBM/PFN/Al). PCE values, when GO or PEDOT:PSS were used as HTLs, were 7.8 and 7.9%, respectively, and for F-rGO PCE was 8.6%. In our case, the use of 6-rGO as HTL in PTB7-based OSCs, by a reiterative deposition/reduction method, shows a similar PCE ~ 5.50% compared with PEDOT:PSS, which suggest a good electronic alignment between ITO/6-rGO and PTB7 HOMO level for hole extraction. On the other hand, Lee et al. [43] investigated the bilayer GO/PEDOT:PSS as HTL for perovskite solar cells (PeSC). In the case of PeSC with the conventional PEDOT:PSS as HTL showed an adequate PCE of 8.23%, while for GO as HTL a reduced performance, PCE of 6.42%, was achieved mainly due to the non-uniform formation of GO film onto the ITO/Glass substrate. In contrast, a superior PCE ~ 9.74% was achieved by using the GO/PEDOT-PSS bilayer as HTL. However, in this mentioned work PEDOT:PSS is still used.

### 3.2. SPFG as third component in the active layer

The addition of SPFG into the PTB7: [70]PCBM active layer of OSCs was carried out as an attempt to improve their PV performance. To evaluate this issue, PV parameters of the fabricated OSCs with different amounts of SPFG were compared. Five sets of OSCs devices were fabricated and tested for each SPFG contents, results followed the same trend. As mentioned previously, for comparison purposes and discussion in all sections of this work, all active layers were thermally treated at 120 °C; in this section, it was to enhance the properties of the used SPFG as described in our previous work [45]. Under this high thermal treatment, PTB7 is not very stable and PCE decreases with respect to that reached when OSCs are annealed just at 80 °C (see Fig. 5). Fig. 7(a) shows the J-V plots of OSCs with 0, 2, 4 and 6 wt. % of SPFG as the third component in ternary active layers, an increment in JSC on devices with 4 wt. % was observed compared to control devices (0 wt. % of SPFG). Fig. 7(b) shows the PV parameters JSC, VOC, FF, and PCE as a function of SPFG content into active layers. For OSCs with 0 wt. % of SPFG (control) a PCE of 5.52% was reached. By contrast, the PCE of PTB7: [70] PCBM:SPFG ternary OSCs with 4 wt. % of SPFG was 6.73%; this behavior was mainly due to the increment of JSC by 3 mA/cm². In order to provide additional information about the contribution of the SPFG into the PTB7: [70]PCBM:SPFG active layer, external quantum efficiency (EQE) measurements were performed for devices with 0 and 4 wt. % of SPFG content. Because SPFG has almost no absorption in the Vis/NIR region [45], it is expected that SPFG amounts into the active layers do not contribute to the light harvesting. However, as shown in Fig. 7(c), the EQE spectrum for the device comprised of PTB7: [70]PCBM:SPFG (4 wt. % of SPFG) ternary active layer is clearly higher in comparison with that of PEDOT: PSS as HTL device (0 wt. % of SPFG). It can be attributed to a better charge transport and collection for the OSC device with 4 wt. % of SPFG. JSC values calculated from the EQE spectra for the devices based on

### Table 1

<table>
<thead>
<tr>
<th>HTL</th>
<th>JSC (mA/cm²)</th>
<th>VOC (V)</th>
<th>FF</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS</td>
<td>-14.17</td>
<td>0.76</td>
<td>51.31</td>
<td>5.52 (5.30)</td>
</tr>
<tr>
<td>6-rGO</td>
<td>-13.43</td>
<td>0.70</td>
<td>58.46</td>
<td>5.50 (5.28)</td>
</tr>
<tr>
<td>None</td>
<td>-7.45</td>
<td>0.60</td>
<td>28.73</td>
<td>1.28 (-----)</td>
</tr>
</tbody>
</table>
binary and ternary active layers were 13.87 and 16.25 mA/cm², respectively, which are in a good agreement with those obtained from the J-V curves: 14.17 mA/cm² (binary) and 17.27 mA/cm² (ternary with 4 wt. % of SPFG). Table 2 summarizes the PV parameters for the different contents of SPFG in the active layer.

The incorporation of the third component SPFG as electron-acceptor in the active layer could improve (at the appropriate content) the PV performance of OSCs by three physical processes: (a) formation of charge-carriers pathways, (b) electron-cascade formation in the energy levels of the active materials (Donor/Acceptor 1/Acceptor 2), and (c) balanced hole and electron mobilities in the active layer [48,56]. Cheng et al. [56] also reported the addition of small amounts of a fullerene derivative (Indene-C60 bisadduct, ICBA) into the active layers based on PTB7:[70]PCBM. They found that, for an addition of 15 wt. % of ICBA, a better phase separation (measured by AFM in phase contrast) is presented at the D/A interfaces, which represents an improvement in the dissociation of the excitons into free charges and the formation of pathways to reach the corresponding electrodes. Ternary blend devices with 15 wt. % of ICBA content exhibited an average PCE of 8.13%, whereas 7.23% for the PTB7:[70]PCBM binary blend. Also, hole and electron mobilities balance was carried out for active layers with 15 wt. % of ICBA measured by space charge limited current (SCLC) method, which consists in the fabrication and characterization of “hole-only” and “electron-only” diodes: ITO/PEDOT:PSS/PTB7:ICBA:[70]PCBM/Au and Al/PTB7:ICBA:[70]PCBM/Al, respectively [56]. Stylianakis et al. [48] determined a favorable energy alignment between the energy levels of the donor/acceptor facilitating the electron-cascade effect by the addition of a graphene-based porphyrin molecule, as second electron-acceptor in the active layer based on PTB7:[70]PCBM, where an improved PCE = 8.81% was achieved while for the reference devices PCE was 7.60%. On the other hand, Bonaccorso et al. [47] investigated the use of graphene nanoflakes functionalized with ethylene dinitrobenzoyl (GNF-EDNB) as electron-cascade acceptor material in PCDTBT:[70]PCBM-based OSCs. The calculated HOMO and LUMO levels of GNF-EDNB
were –5.7 and –3.9 eV, respectively; they are properly located between the HOMO and the LUMO levels of the used [70]PCBM and PCDTBT as principal components of the active layers. This favorable energy alignment enabled GNF-EDNB as an electron-cascade material, which after an optimized added content (0.05% v.), reached a superior PCE = 6.41% compared to that obtained in control devices: PCE = 5.59%.

In this work, for 2 wt. % of SPFG there is no significant change in the PV parameters and at the same time, according to AFM images (see Fig. 8), RMS roughness of the active layer remains around 4.1 nm (Fig. 8(b)) similar to that with 0 wt. % of SPFG (5 nm). According to these results, it is suggested a better transport/collection of charges due to the formation of charge-carrier pathways in the active layer with 4 wt. % of SPFG (RMS roughness = 11.3 nm (Fig. 8(c)), where a maximum PCE of 6.73% was reached by, mainly, an increment in $J_{sc}$ (17.27 mA/cm²). On the other hand, for devices with 6 wt. % of SPFG, the RMS roughness is increased up to 15.5 nm and the active films show SPFG aggregates (see Fig. 8(d)), which could create traps for charge carriers. Because of these aggregates, FF and $J_{sc}$ parameters are affected (see Fig. 7(b)) for devices with 6 wt. % of SPFG since free charges cannot be efficiently extracted.

Finally, it was also implemented simultaneously the use of both graphene derivatives, 6-rGO as HTL and SPFG as the third component in the active layer (4 wt. %), in OSC devices with the structure: ITO/6-rGO/PTB7:[70]PCBM/SPFG(4 wt. %)/PFN/FM. According to the achieved results in the previous sections, we expected here OSCs performance equal or higher than that for devices without any graphene derivative (i.e. PCE up to 5.52% of control devices). Fig. 9 shows the PV performance of a group of three devices fabricated under the configuration described above where a maximum PCE of 5.66% was reached. To the best of our knowledge, it is the first time that OSCs have been manufactured with graphene derivatives in the HTL as well as in the active layer at the same time, and efficiencies are comparable with those in which common materials are used; these results could contribute to the goal of having all-graphene based OSCs. It is important to mention that further studies are needed to optimize the PV performance of these graphene-based devices.

### 3.3. FM and BS eutectic alloys as top electrodes for OSCs

As commented previously, the most usual configuration to fabricate OSCs is: ITO/PEDOT:PSS/Active layer/ETL/Al or Ag with PCE in the range of 5–9% (for those cells based on PTB7). Here, two eutectic alloys, Field’s metal (FM: Bi = 32.5%, In = 51%, and Sn = 16.5% by wt., m.p. 62 °C) and bismuth/tin (BS: Bi = 58%, and Sn = 42% by wt., m.p. 138 °C), were tested as top electrodes in OSCs based on PTB7:[70]PCBM as active layer. These eutectic alloys, FM and BS, are easy and fast of depositing by heating them (90 and 180 °C, respectively) under normal atmosphere conditions. In our group, we have previously reported the use of FM in the fabrication of OSCs [45,49–52] including OSC modules of 9 cm² [51]. Although FM as top electrode shows acceptable thermal stability to the real solar irradiation heating, it is desirable that such eutectic alloys be more robust to temperatures that will be reached during solar exposure. With this fact in mind, FM and BS were used as top electrodes and compared the fabrication and PV performance of OSCs under the configuration: ITO/PEDOT:PSS/PTB7:[70]PCBM/PFN/Top electrode. Fig. 10 shows the J–V curves of OSCs fabricated with FM and BS (where, once again, the active layer was thermally annealed at 120 °C for comparison with the other sections) and, Table 3 summarizes the PV parameters. The reached PV performance with BS is very similar to that observed with FM, $J_{sc}$ of 14.49 and 14.17 mA/cm² were obtained in OSCs with BS and FM, respectively. PCE value with BS was 5.31% and 5.52% by using FM as top electrode (control). However, FM shows better adhesion and greater mechanical stability than BS because its cooling process is slower due to the lower melting temperature.

Fig. 11 shows SEM images and energy dispersive X-ray spectroscopy (EDS) for both FM (a, c) and BS (b, d), respectively. As it can be observed, there exist defined domains of Bi/In/Sn for FM, and Bi/ Sn for BS. Currently, it is not very well determined the work

### Table 2

<table>
<thead>
<tr>
<th>SPFG content (wt. %)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
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<tr>
<td>0</td>
<td>–14.17 0.76</td>
<td>51.31</td>
<td>5.52 (5.30)</td>
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<tr>
<td>2</td>
<td>–14.74 0.77</td>
<td>48.64</td>
<td>5.52 (5.28)</td>
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</tr>
<tr>
<td>4</td>
<td>–17.27 0.77</td>
<td>50.58</td>
<td>6.73 (6.45)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>–13.70 0.77</td>
<td>44.18</td>
<td>4.66 (4.32)</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 9. J–V curves of OSCs with 6-rGO as HTL and, simultaneously, 4 wt. % of SPFG as the third component in ternary active layer based on the PTB7:[70]PCBM blend. (A colour version of this figure can be viewed online.)

Fig. 10. J–V curves of ITO/PEDOT:PSS/PTB7:[70]PCBM/PFN/Top electrode OSCs fabricated with FM or BS eutectic alloys as top electrodes. (A colour version of this figure can be viewed online.)
Two graphene derivatives were synthesized and used in OSCs based on the PTB7/[70]:PCBM blend; for both cases, as top electrode was used the non-conventional Field’s metal, which was vacuum free deposited. First, rGO was deposited homogeneously onto ITO glass substrates by iterative spin-cast and thermal reduction processes and, used as HTL (6-rGO). The PCE of 5.50% reached with 6-rGO as HTL was as high as that for control devices based on PEDOT:PSS. These results suggest a good electronic alignment of 6-rGO films between ITO and the active layer (i.e. PTB7 HOMO level). The other graphene derivative, SPFG, was introduced as a third component in the active layer of ternary OSCs. By varying the amount of SPFG (0, 2, 4, 6 wt. %), it was found that the optimal doping level was 4 wt. %. The enhancement in PCE for a ternary system was 22% (PCE = 6.73%) regarding the control device (0 wt. % of SPFG: PCE = 5.52%), it is because the addition of SPFG leads additional charge-carrier pathways. This fact is mainly manifested in the increase of Jsc by 3 mA/cm². When 6-rGO as HTL and SPFG as the third component in ternary active films were simultaneously implemented in OSCs, a PCE of 5.66% was reached by using also FM as the top electrode. Finally, it was also showed the use of the eutectic alloy BS with a melting point of 138 °C, as another non-conventional top electrode. PCEs of OSCs based on FM and BS top electrodes were 5.52% and 5.31%, respectively. These results suggest and motivate that, the use of low-temperature melting point eutectic alloys should continue being explored as low cost alternative top electrodes instead of high-purity metals, which are evaporated under high vacuum in sophisticated and costly chambers.

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References
