Perovskite solar cells based on polyaniline derivatives as hole transport materials

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Abstract
Perovskite solar cells (PSC) have been extensively studied over the past few years in both academia and industry. Despite their appeal as a low cost and ease processing PV-technology, PSC still rely on materials that are expensive, turning the large-scale production more challenging. In this work, polyaniline (PAni) and its derivative poly(o-methoxyaniline) are employed as hole transport material (HTM) in PSC, replacing the most explored HTM, spiro-OMeTAD. These very well established conducting polymers are doped with 4-dodecylbenzenesulfonic acid (DBSA) to enhance their conductivity. The correlation between the performance of the solar cells using doped and undoped conducting polymers and different metallic contacts are also evaluated. The best power conversion efficiency was 10.05% using doped PAni-DBSA with Au as contact, which is similar to the performance exhibited by our standard device using Spiro-OMeTAD as HTM.

1. Introduction
Perovskite is the name given to a crystallographic structure with ABX₃ composition, where ‘A’ represents a monovalent cation, ‘B’ a divalent cation and ‘X’ an anion. Solar cells based on hybrid organic–inorganic perovskite containing in the A site, organic cations such as methylammonium (CH₃NH₃⁺), formamidinium (HC(NH₂)₂)⁺, Pb₂⁺ and Sn²⁺ in the B site and a mixture of halides (I⁻, Br⁻) present power conversion efficiencies (PCE) higher than 22% [1, 2]. Although the high PCE attained by this technology is close to the theoretical limit for one absorber semiconductor, many fundamental questions are still open. Besides, from practical point of view, this technology needs more reliable thermal and photostability studies. Stability investigation, for example, has been tracking by different approaches such as modification with a layer of hydrophobic material [3], mixture of 2D + 3D perovskites [4, 5] and more recently, by addition of small inorganic cations such as Cs⁺ and Rb⁺ in bromide-iodide perovskites [6].

Perovskite solar cells (PSC) have the appeal of being manufactured using mild conditions (i.e. dispensing the need of high vacuum and/or extreme temperatures). Nevertheless, despite being addressed as a low cost solar cell, the most studied devices still employ materials that are expensive for large-scale production, such as gold (contact) and/or hole and electron transport layers. One of the most expensive material used in hybrid organic–inorganic perovskite cells is the 2,2′,7,7′-tetrakis[N,N-di(4-methoxyphenyl)amino]–9,9′-spirobifluorene, known as Spiro-OMeTAD, a hole transport material (HTM), with prices that can reach USD 300 g⁻¹. The high cost of Spiro-OMeTAD arises from its complex molecular structure, which requires multiple reaction steps until the final product is obtained and purified [7]. Spiro-OMeTAD has also the downside of its intrinsic low conductivity, which is overcome by doping with lithium salts. The doping process oxidizes Spiro-OMeTAD when exposed to air. Unfortunately, lithium salts are hygroscopic, and this property accelerates the decomposition of the perovskite film [8]. Recently, Correa-Baena have pointed out that the recombination at the interface perovskite-HTM caused by dopants is an important issue to be minimized in order to go beyond the 100 mV loss in the open-circuit voltage (V_{oc}) in these devices [9].

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These factors illustrate how the research for other materials to be applied as HTM is crucial. Finding alternatives to Spiro-OMeTAD and at the same time keep the high PCE and the environmental friendly appeal is a key issue to turn this technology very successful in a near future.

Polyaniline (PAni) is one of the most studied intrinsically conducting polymer and the only one produced in large-scale. This polymer has been applied in many different niches, such as coating to protect against corrosion [10], supercapacitors [11], sensors [12], electrochromic devices [12] and many others [13]. The interest in PAni arises from the fact that this material is environmental friendly, chemically stable and it has a low cost due to its easy synthesis, which occurs mainly by two different routes: electrochemical or chemical oxidative polymerization [14]. While the former allows a better control of the initiation and termination of the polymerization process and results in a purer material, the latter allows more material to be obtained, which can lower the final cost.

Many properties associated to PAni have their origin on its structure-oxidation state relation. PAni exists in one of three different forms: pernigralnine (fully oxidized, \( y = 0 \)), leucoemeraldine (fully reduced, \( y = 1 \)) and emeraldine (half oxidized, \( y = 0.5 \)) (figure 1). The latter oxidation state is the most conductive due to the extended \( \pi \) conjugation backbone. PAni properties can be further enhanced by doping during synthesis or by post processing procedures. P-type doping occurs mainly by mixing the polymer with acids, leading to the formation of a positive charge (polarons) along the backbone, preferentially located at imine sites (\( –N=\)). Depending on dopant used, the synthesis can result in an intractable material. This intractability arises from the attractive Coulombic forces between the anion (represented by \( A^- \) in figure 1) and the charged polymer. To solve this problem, organic acids such as dodecylbenzenesulfonlic acid (DBSA), camphor sulfonic acid, p-toluene sulfonic acid are commonly employed as dopants. The organic chain of these acids can interact with the solvent, resulting in a material that is doped and can be solution processed.

Despite the exceptional properties associated to PAni, and its derivatives, their application in PSC as HTM is scarce. Our group has already reported the use of PAni and its derivatives in solid-state dye sensitized solar cells (ss-DSSC) [15, 16]. Xiao et al [17] reported the use of PAni obtained through electropolymerization as HTM in PSCs. The device achieved a PCE of 7.3%. Ameen et al [18] also reported the use of PAni in PSC. PAni nanoparticles were obtained through chemical polymerization and the solar cell exhibited PCE of 6.3% mostly because of the poor fill factor (FF). More recently, Lee et al [19] employed PAni with PEDOT:PSS as HTM in a PSC with inverted architecture ITO/PAni:PSS/CH\(_3\)NH\(_3\)PbI\(_3\)/PCBM/Au, achieving a PCE of 11.1%.

In this present work, we evaluated the performance of PSC in standard configuration (n-i-p) using PAni and its derivative poly(o-methoxy)aniline (PoMA) as HTM. 4-dodecylbenzenesulfonic acid was used as dopant in order to further improve the solubility and film processing. The influence of the dopant as well the type of the metal contact were also investigated and correlated to the overall performance of the devices.

2. Materials and methods

2.1 Synthesis of PAni and PoMA materials

All chemicals were purchased from Sigma-Aldrich. PAni and poly(o-methoxyaniline) doped with 4-dodecylbenzenesulfonic acid were synthesized by oxidative polymerization of the respective monomer based on the method described by Gazotti et al [20]. Firstly, a water/ethanol solution 70/30 (v/v) containing 1.0 M HCl and sodium dodecylbenzenesulfonate was prepared. This solution was left stirring for 24 h at ambient temperature to prepare the acid by hydrolysis of the sodium salt. After 24 h, the solution was used to carry out the polymerization. Ammonium persulphate (0.375 M) was diluted in 40.0 ml of this solution (solution A). In another 100.0 ml of the same solution, aniline previously distilled was diluted (0.1 M) (solution B). CoSO\(_4\) was
used as catalyst. Solution B was kept in an ice bath with a magnetic stirrer while the solution A containing ammonium persulphate was added dropwise. After addition, the resultant solution was kept at 0 °C for 6 h to proceed with the polymerization. By the end of polymerization, the resulting solution was vacuum filtered through a Durapore membrane 0.22 μm. The precipitate was washed with ethanol until filtrate was completely colorless. The resulting dark green solid was left to dry at ambient temperature overnight and then transferred to a vacuum oven at 50 °C for 6 h to be completely dry. The final solid was grounded and stored in a closed recipient.

For preparation of PoMA doped with DBSA the same procedure was used with the exception of the monomer, in this case o-methoxyaniline.

To obtain the polymers in their undoped form, firstly another synthesis of PANi and PoMA doped with HCl was carried out. The polymerization solution was comprised of 1 M HCl and 3 M NaCl, following the procedure described above. After, PANi and PoMA doped with HCl powders were suspended in a solution of 10% (v/v) NH₄OH and left stirring during 24 h to completely remove the dopant from the polymers. After this step the materials were vacuum filtered and then washed with de-ionized water until filtrate reached pH 7. The drying process was the same for the doped polymers.

2.2 Device fabrication

Devices were prepared on a fluorinated tin oxide glass, (FTO Glass, Hartford 20 Ω/sq). These substrates were partially etched with zinc powder and HCl 2.0 M. The substrates were cleaned with detergent followed by bath ultrasound with water, acetone and isopropyl alcohol. Prior to use, the substrates were treated with UV-ozone for 30 min.

The blocking layer was made using a solution 0.15 M of titanium di-isopropoxide-bis(acetylacetonate) (75% wt in isopropanol) in 1-butanol. This solution was spin coated onto the substrate at 2000 rpm for 20 s, followed by a heat treatment at 125 °C for 5 min. For the mesoporous layer it was used a 150 mg ml⁻¹ 18-NRT paste (Dyesol) in ethanol. The deposition occurred at 5000 rpm for 30 s, followed by a annealing at 150 °C and 500 °C for 30 min each.

Methylammonium iodide (MAI) was prepared by a reaction of equimolar hydriodic acid (HI, 57% in water) and methyamine (40% in water). The reaction mixture was stirred for 2 h in an ice bath and afterwards the solvent was evaporated. The resulting solid was dissolved in ethanol and recrystallized with diethyl ether, filtrated and dried in a vacuum oven at 50 °C for 12 h. To prepare the active layer, a perovskite precursor solution containing PbI₂ and MAI with the concentration 1.3 M is prepared in DMF/NMP 7:1 (v/v) as a solvent. The deposition occurs in two steps, the first step at 1000 rpm for 15 s and the second step at 4000 rpm for 24 s. In the second step, 300 μl of diethyl ether was dropped onto the sample to act as anti-solvent and complete the crystallization. After the deposition, the substrate containing the perovskite layer was placed on top of a hot plate at 100 °C for 10 min.

The standard device using Spiro-OMeTAD as HTM was prepared using the following composition, for 1 ml of chlorobenzene: 80.0 mg of Spiro-OMeTAD, 32.0 μl of 4-tert-butlypyridine, 18.0 μl of a LiTSFI solution (170 mg ml⁻¹ in acetonitrile) and 32.6 μl of a H₂SO₄ solution in ethanol (0.2 M).

For PANi and PoMA applied as HTM, a solution of 100 mg ml⁻¹ of the polymer was prepared in m-cresol. For both materials the deposition parameters are 4000 rpm for 1 min, however, more material was needed for PANi deposition during the first 30 s of the process to ensure the complete coverage of the substrate (figure 2). After the deposition, the substrates were placed onto a hot plate at 70 °C to evaporate the residual solvent. 70 nm layer of gold or silver as top contacts of the device was deposited by thermal deposition in nitrogen filled glove box. The active area of the solar cells was 0.15 cm².

2.3 Characterization

IR spectra of the polymer were taken with an Agilent Cary 630 spectrometer; samples were mixed with KBr and transformed into pellets by applying a pressure of 7 MPa. UV—vis spectra of the polymer solutions in m-cresol were taken in an Agilent Cary 60 UV—vis spectrophotometer. X ray diffraction was performed in a XRD-7000 Shimadzu diffractometer with Cu-Kα (1.541 Å) with a scan speed of 2.0° min⁻¹. Hall effect were measured in a Ecopia HMS-3000 instrument using a 0.55 T magnet. Cyclic Voltammetry was carried in an Autolab Potentiostat using a three compartment cell with Ag/AgCl in ethanol saturated LiCl as the reference electrode. Tetrabutylammonium hexafluorophosphate (0.1 M) in acetonitrile was used as electrolyte and ferrocene was used as standard. The samples were deposited over a bare FTO. The voltage sweep was carried at speed of 20 mV s⁻¹. After the measurements, the onset potentials were converted to NHE values and used to calculate the energy levels of the bands. SEM-FEG images were obtained in a FEI Inspect F50 with a beam acceleration of 10 kV and work distance around 9 mm.
Solar cells were characterized using a Sciencetech class AAA calibrated with a reference silicon solar cell with KG5 filter in AM 1.5 G to 100 mW cm$^{-2}$. The J–V curves were carried out using a Keithley 2400 sourcemeter, in forward (from 0 to 1.0 V) and reverse (from 1.0 to 0 V) scan. The delay time used was 0.50 s with step of 25 mV resulting in a scan rate of 50 mV s$^{-1}$. The mean photovoltaic values were obtained by at least six different devices.

The electrochemical impedance plots were taken in an Autolab potentiostat under a frequency range of 1 kHz–0.1 Hz under illumination at 0 bias voltage.

### 3. Results and discussion

After the synthesis, the materials were firstly characterized to verify the correct oxidation state and the success of doping with DBSA. The IR spectra obtained for the conducting polymers PAni and PoMA (figure S1 in the supplementary information is available online: stacks.iop.org/JPENERGY/1/015004/mmedia), showed the absorption bands of the benzenoid and quinoid rings. From these IR absorptions, the oxidation state was estimated and it is displayed in table 1. Both PAni and PoMA are found in the emeraldine state, although PoMA samples were slightly more oxidized because of the electron donating characteristic of the methoxy group [21].

The UV–vis spectra of doped samples are very similar, displaying three absorption bands, while the undoped polymers showed only two (figure S2 in the supplementary information). The difference in the number of absorption bands in UV–vis spectra of the doped and undoped samples is related to the absence of dopant in the latter, which leads to the disappearance of the band of the polaron–π$^*$ transition. The UV–vis and FTIR analysis confirmed the preparation of both polymers in undoped and doped emeraldine state, the most conductive one. The Tauc-plots for the doped PAni and PoMA polymers are shown in figure S3 (supplementary information); the band gap energy obtained for these materials are 2.5 and 2.6 eV, respectively.

Cyclic voltammetry was carried in the polymer films to determine their energy levels. The HOMO level of the polymeric materials can be obtained through the following equation [22]:

$$E_{\text{HOMO}} = - (E_{\text{onset,oxvs NHE}} + 4.75) \text{ eV}.$$  

LUMO energy can be obtained using $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{gap}}$. Using the values obtained by the Tauc-plot and cyclic voltammetry, it was possible to obtain the energy levels for PAni and PoMA materials and correlate them with energy levels of the CH$_3$NH$_3$PbI$_3$, TiO$_2$ mesoporous layers and metallic contacts [23–25]. As shown in the figure 3, the energy of the HOMO of the PAni is aligned with valence band of the perovskite, however the PoMA presented a higher energy mismatch in relation to perovskite. The energy levels revealed that the perovskite can transfer the holes to both polymers.

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### Table 1. Oxidation state and calculated band gap energy of the doped conducting polymers.

| Sample      | Oxidation state | Band gap (eV) |
|-------------|-----------------|---------------|
| PAni-DBSA   | 0.50            | 2.5           |
| Undoped PAni| 0.50            | —             |
| PoMA-DBSA   | 0.49            | 2.6           |
| Undoped PoMA| 0.48            | —             |
The conductivity of the polymeric HTM materials was measured by Hall effect. For the DBSA-doped PANi, the conductivity was $2.48 \text{ S cm}^{-1}$ while the DBSA-doped PoMA exhibited a lower value, $8.06 \times 10^{-3} \text{ S cm}^{-1}$. Other interesting parameters can be extracted from the Hall effect are the mobility and the concentration of the charge carriers. For PANi, the mobility and concentration of the charge carriers were $3.71 \times 10^{-2} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and $4.16 \times 10^{20} \text{ cm}^{-3}$, respectively; while for PoMA the values were $2.47 \times 10^{-1} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and $2.04 \times 10^{17} \text{ cm}^{-3}$. Although the mobility of the charge carriers was one order of magnitude higher for PoMA, the carrier concentration is much lower than PANi. As the conductivity is calculated by $\sigma = n\mu e$, where $n$ is the concentration of carriers, $\mu$ their mobility and $e$ the elementary charge, carrier concentration of charge carriers played the major role, explaining the high conductivity achieved by PANi. It was not possible to determinate the mobility of both undoped samples as the conductivity of these materials is below the limit of the experimental setup. The values of the emeraldine base PANi in the literature can be low as $10^{-10} \text{ S cm}^{-1}$ [26].

To verify the performance of the polymers in PSC, devices in the n-i-p configuration were prepared. The x-ray diffraction pattern of FTO/TiO$_2$/Perovskite (figure S5, supplementary information) displayed very sharp and intensive peaks due to the high crystallinity of this material. The diffraction peaks at $2\theta = 14.1^\circ$, $28.4^\circ$ and $31.9^\circ$ can be assigned to the crystallographic planes (110), (220) and (310), respectively [27].

SEM-FEG images of the TiO$_2$/perovskite substrate prior and after deposition of the conducting polymers layers as HTM were obtained. The perovskite layer is comprised of grains between 100 to 450 nm in size (figure 4). In the images obtained at different magnifications (figure S6) it is possible to observe that the perovskite grains have completely covered the TiO$_2$ mesoscopic layer.

The PoMA layer onto the top of perovskite film appeared as a smooth and thick continuous layer while the PANi layer is visually thinner, as can be seen by the polymer layer resembling the shape of the perovskite grains underneath. Ameen et al [18] have also observed the same pattern and their AFM images confirmed that the high roughness associated to the PANi layer was due to the perovskite layer underneath. The cross section of the FTO/TiO$_2$/Perovskite/PANi (figure S8, supplementary information) showed that the thickness of the polymeric layer is within the range of 50–160 nm whereas the thickness of the perovskite layer is about 560 nm and the mesoporous TiO$_2$ layer, 180 nm. For the PoMA layer deposited through the same procedure as PANi, the resulting layer is much thicker, reaching up to 670 nm (figure S8 in the supplementary information).

The possible reason for the differences observed in film coverage may be related to differences at molecular level. The difference between PANi and PoMA relies on the presence of the o-methoxy (–OCH$_3$) group. This group found in PoMA induces a steric effect which reduces the interaction between polymers chains. As polymer–polymer interaction is weakened, it is easier for the solvent to solvate the material, increasing the polymer–solvent interaction which results in a final material that has higher solubility [21, 28]. This increased solubility seems to be beneficial in film’s processing, as the resulting film is more homogeneous, with less aggregates. In fact, using the same deposition parameters, 4000 RPM for 60 s, we could not obtain a complete coverage of the perovskite layer in the case of PANi solution (figure S8, supplementary information). This is not desired and may cause short-circuits and increase charge recombination. To guarantee that the perovskite layer is covered, more PANi solution was dropped during the spinning process. The complete deposition steps of the polymeric layers are depicted in figure 2.

Both DBSA-doped PANi and PoMA conducting polymers were tested as HTM in PSC. For comparison, a standard device was also assembled with the following configuration: FTO/TiO$_2$/Perovskite/Spiro-OMeTAD/Au. Initially, the devices with PANi and PoMA were tested using silver as a metallic top contact.

Devices with PoMA achieved the maximum efficiency of 5.59% in reverse scan while the device with PANi achieved 3.34% (figure S10 and table S2 in the supplementary information). Devices using the undoped
polymers were also assembled and the PCE was lower than the doped ones, 1.29% and 3.20% for PAni and PoMA, respectively (figure S12 and table S3 in the supplementary information). $J_{sc}$ is the photovoltaic parameter that is most affected, being approximately halved in comparison to devices with doped polymers. The lower efficiency reflects the low conductivity of the undoped form [26]. In fact, the use of Spiro-OMeTAD as HTM showed the importance of the conductivity of the HTM layer on both $J_{sc}$ and the FF parameters and that this can be increased by doping [29].

It is reported that silver can diffuse through the HTM leading to AgI formation [39], decreasing the performance of the devices, then, gold was used as top contact. In figure 5 is shown the JV curves and table 2 displays the photovoltaic parameters of the devices using DBSA-doped PAni and PoMA as HTM and gold as metallic contact. All devices presented hysteresis when comparing the forward and reverse scans and this can be associated to an increase in the capacitance at the interface perovskite/polymer caused by the presence of ionic

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**Figure 4.** SEM-FEG images of the perovskite layer (A) and PAni (B) and PoMA (C) films onto the top of perovskite layer.
dopants in the HTM. These ions can migrate under the effect of an external electrical field and accumulate at the interface, modifying the energy levels and creating an energy barrier to the injection of electronic carriers [30].

For PANi-DBSA based devices, the change to gold as top electrode improved all photovoltaic parameters and a maximum PCE of 10.1% was obtained in the reverse scan. From the best of our knowledge this efficiency value is the record for this type of polymeric HTM using the standard configuration (n-i-p).

The maximum theoretical $V_{oc}$ that can be obtained with PANi using the hybrid perovskite CH$_3$NH$_3$PbI$_3$ is around 0.9 V (table supplementary info, table S4), which is in accordance with previous results in the literature [18, 31]. In this case, PSC using Spiro has an advantage as it can reach a higher value of $V_{oc}$ [23], leading to higher PCE values, and also with less (or almost no) hysteresis.

In order to have a better understanding of the results with Au and Ag as top metallic electrodes, electrochemical impedance spectroscopy (EIS) of the devices made with the doped form of both polymers were carried out. As the devices only differ by the HTM, it is possible to relate this difference to the performance exhibited by them.

The Nyquist plots from the devices shows two distinct charge transport regimes, with two semicircles (figure 6). The semicircle closest to the origin is associated with the higher frequency spectrum and is attributed predominantly to impedance arising from the electronic transport and charge transfer at interfaces, whereas, at mid-to-high frequencies we only observe the beginning of the other semicircle [32, 33]. The slope of this part of the curve is close to 45°, which suggests processes related to diffusion. The equivalent circuit analysis used here (figure 6) was based on previous findings that connect EIS to the properties of solar cells [32–35]. Apart from the series resistance ($R_s$) accounting for the ohmic contribution of contacts and wires, the first semicircle can be adjusted with a resistive element ($R_1$) and a capacitive element, represented by a constant phase element (CPE), both connected in parallel [33, 36]. As the active layer of perovskite can be considered an infinite dimensions reservoir of electrochemically inactive species, the second frequency regime was adjusted with a Gerischer element. It means that the region from which it is possible to collect charge will be thinner than thickness of the sample. Due the existence of the Gerischer pattern, the transport resistance ($R_{tr}$) and the recombination resistance ($R_{rec}$) cannot be distinguished and only a resultant resistance, the Gerisher resistance ($R_{Ger}$), can be obtained. According to Birquest et al [33], the transport resistance has a major role in the obtained resistance as $R_{Ger} > R_{rec}$ and is given by:

$$R_{Ger} = \frac{1}{\frac{1}{R_{tr}} + \frac{1}{R_{rec}}}$$
where \( L \) is the thickness, \( A \) the area and \( \sigma \) the conductivity.

We found that the \( R_s \) for the devices with different components do not exhibit, as expected, a huge difference between them (table 3). Comparing \( R_s \) values obtained when both polymers are used as HTM (table 3) it is noticeable that the \( R_s \) increased for the PoMA Au sample, this factor is probably related to the energy levels of PoMA/Au. As there is a mismatch between their energy levels, an energy barrier is created, therefore increasing the resistance which leads to the loss of performance observed. The capacitance associated with the charge transfer (CPE, considering it as a pure capacitor, which is a good approximation, as \( n \) values are close to 1) presented different values, depending on the polymer used. Devices made with PoMA had higher capacitance values (table 3) compared with those made with PANi, this shows that there is a greater charge accumulation at the interfaces between the layers of the devices made with the former. This behavior can be associated with the lower conductivity of PoMA in comparison to PANi (table 2).

It can, also, be observed in table 3 that \( R_G \) is lower for Spiro, followed by polymer cells that showed better efficiency in each situation, PANi-DBSA-Au and PoMA-DBSA-Ag, (table S4). In the other two cases, in which the polymers did not show good results, \( R_G \) was higher.

The difference in performance of the devices using silver as metallic contact cannot be explained as straightforward as was the case with gold. Comparing devices made with each polymer it is possible to notice that the \( R_s \) is not so different between them, and PoMA presented a slight lower \( R_s \). Although the capacitance is higher for PoMA, the devices presented an increase of this parameter when Au was changed to Ag, and by similar values (21.7 for PANi and 28.0 for PoMA), and yet only PANi showed a huge decrease in performance.

In this case we propose that the key to the difference in their performance, while changing the metallic contact, lies in the morphology of the HTM. As seen in the SEM-FEG images, the PANi layer is more prone to the occurrence of pinholes which will facilitate the contact between the perovskite and the Ag. It is known that the iodine in perovskite can react with silver, forming AgI, this degradation of the active layer leads to a loss of performance, mostly because of the drop of \( V_{oc} \) [37, 38]. Even if more material was applied during the spinning process this can be a source of the drop of efficiency observed when comparing the results of the cells using PANi and Au (table 2) and Ag (table S2 in supplementary information). This can also explain why PANi showed the highest \( R_G \) of all samples. In fact, this same trend can be seem when comparing the performance of both PoMA and PANi in undoped states, as PANi is more insoluble than its counterpart, due to lower polymer–solvent interaction, the thin film would present more defects, leading the loss of performance, mainly due the \( V_{oc} \) drop, observed in table S3 (supplementary information).
4. Conclusions

In the present work, doped forms of PANi and poly(o-methoxyaniline) were used as HTM in PSC. We found that besides having similar structure these polymers showed different behavior as thin films. While PoMA gave rise to a smooth thick layer, PANi films were thinner and had pinholes on it. We attributed this difference to the o-methoxy group existent in PoMA, which induces a steric effect, lowering the polymer-polymer and increasing the polymer-solvent interaction.

The choice of the metal used as electrode had a significant impact in the performance of the devices. PANi with gold as metallic contact exhibited a PCE of 10%, comparable with the device using Spiro-OMeTAD, while PoMA had the best performance when silver was used, achieving 5.5%. Both polymers showed a huge increase of the PCE compared to their undoped forms.

Besides the advantages that PANi and its derivatives possess such as low cost, easy synthesis and flexibility in device’s architecture, it is noteworthy that these polymer materials are a promising alternative to Spiro-OMeTAD if different materials, with the correct energy alignment and non-reactive to the perovskite, are applied as a final contact.

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