Covalently functionalized SWCNTs as tailored p-type dopants for perovskite solar cells

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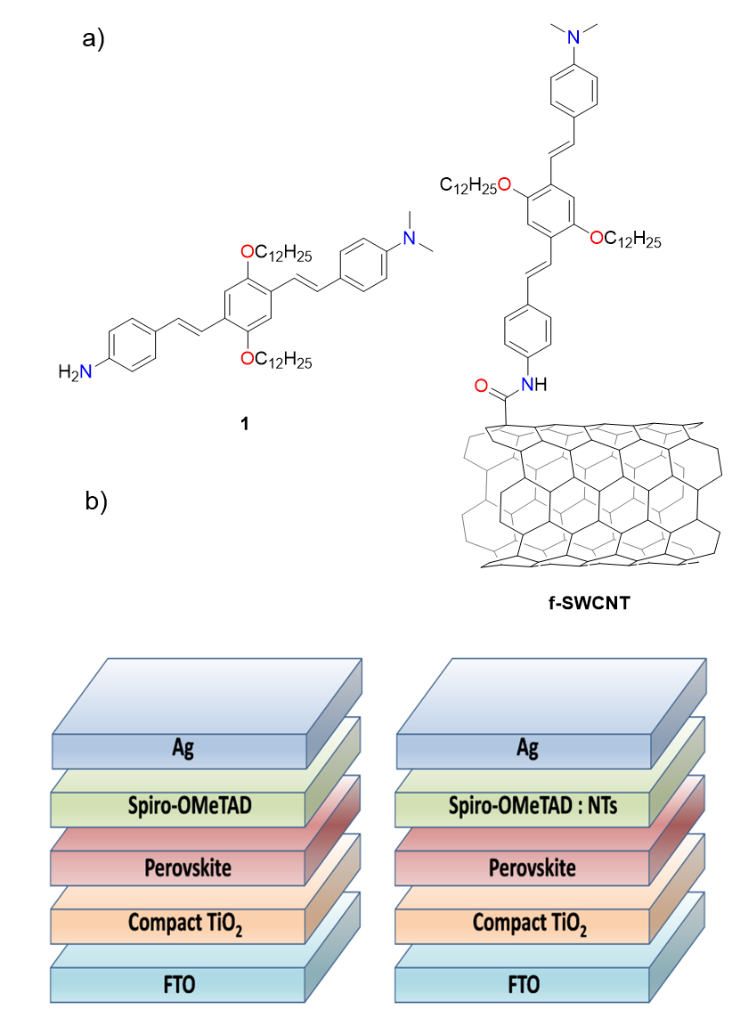
**ABSTRACT:** The covalent functionalization of (7, 6)-enriched single-walled carbon nanotubes (SWCNTs) with oligophenylenevinylene (OPV) moieties terminating with a dimethylamino group is proposed as an efficient way to enhance the affinity of CNTs with Spiro-MeOTAD in perovskite-based solar cells. The evidence of SWCNTs functionalization and the degree of OPV substitution on SWCNTs are established from TGA, XPS, TEM and Raman techniques. Our tailored doping materials display photovoltaic performances in line with conventional Li-doped spiro-MeOTAD system, showing at the same time a significantly improved chemical stability of the perovskite component over time. Furthermore, the comparison of the photovoltaic performances with those obtained with non-functionalized SWCNTs clearly suggest that the presence of the organic appends ensures highly reproducible PV performances. Our results demonstrate the suitability of this material as a valid doping agent for spiro-MeOTAD, representing a viable alternative to the conventional Li-salt.

**KEYWORDS**: *photovoltaics, perovskite solar cells, SWCNTs, covalent functionalization, p-type doping, hole-transport materials, chemical stability.*

**INTRODUCTION**

Organometal halide perovskites by virtue of exceptional optical and other physical properties are becoming prominent materials for several optoelectronic applications.1 Facile processing enables low-cost manufacturing and makes them attractive for lasing, light-emitting and, particularly, photovoltaic (PV) applications,2 with the latter having reached record efficiencies as high as 22.1%.3,4 Various PV device structures have been explored,5–11 differing for the morphological and structural properties of the perovskite material, which ultimately affect the PV performances.9,12–15 The conventional perovskite solar cell architecture has a sandwich-like design comprising a layer of hybrid halide perovskite, typically CH3NH3PbI3, acting as light absorbing material between a semiconducting oxide and organic hole transporting material (HTM). The former, typically titanium dioxide (TiO2), is deposited onto a conductive glass (fluorine-doped tin oxide, FTO) and acts as electron transporting layer, while the HTM extracts the generated holes from the active CH3NH3PbI3 layer. The device is completed with the evaporation of a metal anode atop of the HTM.5 Among all the HTMs, Spiro-MeOTAD (2,2′,7,7′-Tetrakis(N,N-di-p-methoxyphenylamine)-9,9′-spirobifluorene) has been largely explored, leading to the best PV performances.16,17 However, this popular HTM exhibits low charge mobility and needs to be doped for being integrated in solar cells.18

The most common way to improve the hole mobility of Spiro-MeOTAD entails the partial oxidation by LiTFSI16,18,19 (lithium bis(trifluoromethanesulfonyl)imide) which promotes an oxidative reaction in the presence of O2.20,21 However, this oxidation process is not easily controllable and the concentration variability of oxidized Spiro-MeOTAD is one of the major sources of instability and irreproducibility of the performance of the resulting devices.22 In order to overcome this limitation, alternative doping agents have been tried.23–27 Recently, due to their remarkable charge mobility28–30 properties and unique dual charge carrier ability,31–37 multi walled and single walled carbon nanotubes (MWCNTs and SWCNTs) have been integrated in perovskite solar cells as stand-alone hole transporting materials or as p-type dopants in P3HT, (Poly(3-hexylthiophene-2,5-diyl)) and Spiro-MeOTAD.38–44 As a further evolution of NTs as dopants for HTM, in this work we propose the chemical functionalization of enriched semiconducting (7,6)-SWCNTs as a versatile approach to enhance their physical and chemical affinity with the hosting matrix. Herein, we present the synthesis of a new class of functionalized SWCNTs (**f-SWCNT**), their photophysical properties in solution and their use as doping agents for spiro-MeOTAD in a flat perovskite solar cell geometry based on CH3NH3PbI3. Our design concept encompasses the use of an oligophenylenevinylene (OPV) bearing alkoxy groups in the central ring and amine residues at the extremities (Figure 1a).



**Figure 1**.(a) Molecule **1** used for this study and OPV-decorated semiconducting SWCNTs enriched in (7, 6) chirality (**f-SWCNT**).(b) Sketch of photovoltaic devices.

These were chosen to improve the compatibility with spiro-MeOTAD relative to non-functionalized nanotubes (**Ox-SWCNTs**) and to enhance the affinity of the HTM mixture with the perovskite active layer at the interface, thanks to the presence of the polar amine moiety. To improve the electronic and structural properties of the materials, the SWCNTs are enriched in the chiral semiconducting (7,6) form and do not contain metallic tubes (see Supporting Information). This choice enhances the intrinsic quality of the doping material and favors the reproducibility of the observed electronic properties in solution and in the working devices. Our results show that the OPV functionalization prompts a better dispersion of SWCNTs within the HTM and affords highly reproducible PV activity. The validity of our approach for spiro-MeOTAD doping is validated by the fact that photoconversion efficiency achieved by SWCNT covalently functionalized with OPV as dopants is comparable with that of the standard doping and it overcomes the hygroscopicity of the Li-salt that dramatically affects the device lifetimes. The PV cell structure is schematized in Figure 1b.

**RESULTS AND DISCUSSION**

**Synthesis**.The synthesis of trimeric OPV **1** is outlined in Schemes S1 and S2 (Supporting Information) and it commenced with the preparation of phosphonate **4** following a protocol reported in the literature45 (Scheme S1, Supporting Information). OPV **5**46 was synthesized through a Horner–Emmons–Wittig (HEW) coupling reaction47,48 of suitably *para* functionalized benzaldehyde (*p*-nitrobenzaldehyde) with diethylphosphonate **4** in the presence of *t*-BuONa in DMF in 63% yield. A selective mono-reduction reaction of the dinitro compound **5** in the presence of a NaS2 aq. sol. gave amino-nitro derivative **6** in 80 % yield. The mono-reduction reaction was achieved following a reported procedure used for the preparation of similar π-extended conjugated chromophores.49 The nitro-amino intermediate **6** was thus selectively protected by treatment with (CHO)*n* and NaBH3CN, in AcOH.50 Final reduction of the nitro group of compound **7** with SnCl251yielded desired amine **1** in 59 % yield (Scheme S2, Supporting Information). The trans-trans configuration of the double bonds in **1** was confirmed *via* 1H-NMR spectroscopy (see Supporting Information). The presence of the dodecyloxy groups confers to compound **1** a good solubility in most of the common organic solvents. Target amine **1** was reacted with benzoyl chloride in the presence of Et3N in acetone to prepare reference amido-compound **8** (Scheme S3, Supporting Information). All the synthesized compounds were characterized by 1H- and 13C-NMR spectroscopy, IR and HRMS (Figures S1−S10, Supporting Information).

The preparation of OPV functionalized material **f-SWCNT** was accomplished by covalent attachment of the trimeric OPV **1** onto the surface of previously oxidized SWCNTs (7,6) by amidation reaction (Scheme 1). **Ox-SWCNT** were obtained by reaction of high purity pristine CoMoCat p-SWCNTs (7,6) with a 3:1 aq. solution of 3M H2SO4 : 3M HNO3 at 80 °C for 2 h, following a modified protocol described in the literature.52–55 The resulting oxidized material was treated with SOCl2 to give a SWCNT-acid chloride intermediate53,56 that was allowed to react with aminostyryl-N,N-dimethylaniline **1** in the presence of Et3N in DMF, to give aminostyryl-N,N-dimethylaniline decorated SWCNTs enriched in (7,6) chirality (**f-SWCNT**). The OPV-SWCNT hybrid was characterized by UV-Vis-NIR spectroscopy, photoluminescence spectroscopy for chirality determination, thermogravimetric analysis (TGA), Raman spectroscopy, [X-ray photoelectron spectroscopy](https://en.wikipedia.org/wiki/X-ray_photoelectron_spectroscopy) (XPS) and transmission electron microscopy (TEM).



**Scheme 1**.Preparation of OPV-decorated SWCNTs (7,6) (**f-SWCNT**).

**Characterization of the OPV functionalized SWCNT**. The comparison of the TGA profiles of pristine and functionalized SWCNTs gave a first evidence of the sidewall functionalization of nanotubes (Figure S11, Supporting Information). The weight loss plots relative to **p–SWCNTs** and **Ox–SWCNTs** display the pyrolytic step of oxygenated functionalities in the range between 100 and ≈ 500 °C, with a weight loss of 4.5 % for **Ox-SWCNTs** with respect to **p-SWCNTs** (calculated at 500 °C). A mass content of 1000 µmol of –COOH per g of nanotube is estimated. An additional 5.0 % weight loss is observed for **f-SWCNTs**, resulting in one OPV moiety approximately every 914 carbon atoms, corresponding to 71 µmol of OPV per g of nanotube (see Supporting Information for calculating the functionalization degree).57 Raman spectroscopy was used to confirm the SWCNTs functionalization (Figure S12 Supporting Information). The relative increase of the intensity of the D band is commonly used as a fingerprint to confirm the SWCNTs functionalization, as it reflects the rehybridization of the carbon atoms involved in the functionalization, suggesting the considerable alteration of the sp2 carbon network.58 The Raman spectrum of the **Ox-SWCNT** sample (λexc=532 nm) reveals an increased D band around 1330 cm-1 (ID/IG = 0.21) in comparison to that of pristine SWCNTs, where the intensity of the defect band is very low (ID/IG = 0.086). The amidation reaction used for linking **1** onto the **Ox-SWCNTs** surface does not significantly modify the intensity of the D band (Figure S12, Supporting Information), where the ID/IG ratio for **f-SWCNT** is 0.22.

X-ray photoelectron spectroscopy (XPS) was performed to assess the surface composition of SWCNTs before and after functionalization. XPS studies show an increase of O content in the oxidized sample (9.27 at% for O 1s at 532.7 eV meaning a 2.52 at% with respect to *p*-SWCNTs). Compositional data obtained from the XPS analysis of SWCNTs are reported in Table 1 (Figures S13-S14, Supporting Information). As expected, the presence of dimethylamino derivative groups on the SWCNTs surface leads to the appearance of a N signature in the XPS spectrum of samples containing **f-SWCNT** (1.83 at % for N1s at 400.1 eV), supporting the idea for which the OPV **1** is linked to the SWCNT surface. This is in full agreement with the TGA results for **f-SWCNT** that show a weight-loss profile very similar to that of the OPV alone. Surprisingly, a small presence of N was also detected in the **Ox-SWCNTs** (0.54 at % for N1s at 400 eV), which can be attributed to the sulfo-nitric oxidation treatment.

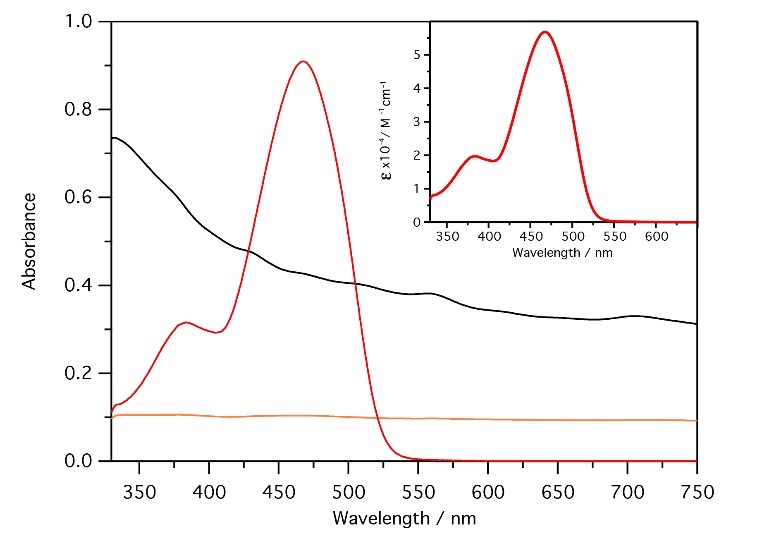
**Table 1**. Compositional data obtained from the XPS analysis of the SWCNTs derivatives.

|  |  |  |  |
| --- | --- | --- | --- |
| Sample | C at% | N at% | O at% |
| **p-SWCNT (7,6)** | 92.82±0.24 | - | 6.74 ±0.27 |
| **Ox-SWCNT (7,6)** | 89.31±0.71 | 0.54±0.12 | 9.26±0.47 |
| **f-SWCNT** | 86.73±0.45 | 1.83±0.22 | 8.00±0.42 |

Finally, visualization of **p-**, **Ox-** and **f-SWCNTs** was achieved by means of TEM analyses providing the most direct evidence that the soluble samples contain carbon nanotubes. The TEM images of a carbon-coated copper grid after the deposition of few drops of a 0.1 mg/mL dispersion of **p-, Ox-** and **f-SWCNTs** as well as of **1** in DMF are reported in the Supporting Information (Figures S15-S16, Supporting Information).

**Spectroscopic characterization of SWCNTs enriched in (7,6)**.UV-Vis-NIR absorption and luminescence spectroscopy is the most powerful tool to identify the variety of semiconducting species occurring in samples of single walled carbon nanotubes, which are classified according to their (n,m) indices. In particular, photoluminescence mapping (PLM) provides emission spectra recorded as a function of the excitation wavelength and the resulting three-dimensional plot exhibits a distribution of spots representing the signals of specific (n,m) species.59 Accordingly, our SWCNTs sample was investigated by recording the absorption spectra and the photoluminescence maps, so as to verify the enrichment in the (7,6) species (see Supporting Information). According to the literature,60 SWCNTs (7,6) have two characteristic absorption features at 648 nm and 1120 nm, corresponding to the transitions E22 and E11 respectively. The experimental absorption spectrum (Figure S17, Supporting Information) clearly exhibits the peak at about 650 nm, while the weaker NIR transition is less evident, due to the overlapping with other species absorbing in the same region.45 The PLM of the SWCNT sample (Figure S18, Supporting Information) shows some emission features with different intensity, the highest being found at λexc = 650 nm and λem = 1120 nm, which is unambiguously assigned to SWCNTs (7,6). In fact, the excitation wavelength corresponds to the E22 transition while the emission maximum is centred at about 1120 nm, which corresponds to the lowest energy transition E11.59 The situation is completely different for SWCNTs which have undergone chemical treatment. Upon oxidation, the electronic features of SWCNTs (7,6) are substantially altered due to a rehybridization of the carbon atoms from sp2 to sp3, leading to a loss of conjugation. Accordingly, the sample of oxidized-SWCNTs (7,6), dispersed in DMF, does not exhibit any luminescence.

**Photophysical Properties of OPV-SWCNTs Derivatives**. The electronic absorption spectra of **1** and **f-SWCNT** in DMF are reported in Figure 2 (molar extinction coefficients were assessed only for **1**). The reference **1** exhibits two absorption maxima at 467 nm (*ε* = 57000 M-1 cm-1) and 381 nm (*ε* = 20000 M-1 cm-1). The absorption spectrum of **f-SWCNT** is featureless and it is not possible to single out the UV–Vis absorption bands of the reference OPV molecule, due to an overwhelming absorption of **Ox-SWCNTs** in the same spectral region. In addition, the absence of marked features of SWCNTs is ascribable to the oxidative functionalization, because the electronic structure of SWCNTs is increasingly modified by enhancing the presence of the defects onto the carbon scaffold.53 Only at a low extent of covalent derivatization the E11 and E22 transitions can still be discerned.53,61,62



**Figure 2**. Absorption spectra of **1** (red), **f-SWCNT** (orange), **Ox-SWCNT** (black) in DMF. Inset: molar extinction coefficients of **1** in DMF.

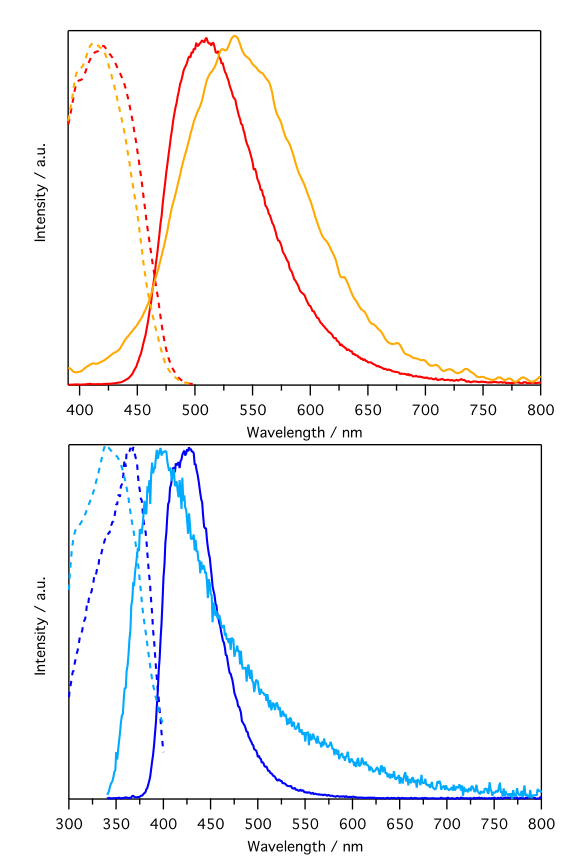
In order to verify the presence of photoinduced processes between the carbon nanotube and the OPV-type moieties, luminescence studies were made for **f-SWCNT** (in DMF), in comparison with the related reference compound **1**. Spectra are displayed in Figure 3 and key photophysical data are collected in Table 2. It has to be emphasized that, typically, photophysical studies of samples containing SWCNTs are affected by high uncertainty. In particular, it is not possible to determine absorbance values and, accordingly, to make quantitative luminescence assessments. This is due to: (i) the nanometric nature of the SWCNTs causing extensive light scattering and (ii) poor solubility in any medium and tendency to self-aggregate. However, **f-SWCNT** form stable and optically transparent dispersions in DMF, allowing comparative studies with the reference compound and quantitative luminescence assessments.

The reference compound **1** exhibits a relatively strong fluorescence band in the green region, with quantum yield (*Φ*FL) of about 38%. Such emission is also detectable in the functionalized carbon nanomaterial, but it is strongly quenched in intensity (Table 2), indicating substantial electronic interactions between the nanotubes and the anchored organic conjugated moieties. This finding is in line with previous reports by *Langa* and co-workers, who reported strong chromophoric interactions of nanohorns and carbon nanotubes with oligo(thienylenevinylenes) moieties.63–65 The fluorescence decay profiles of **1** and **f-SWCNT** are fitted monoexponentially, yielding singlet lifetimes of 1.3 and 1.5 ns, respectively. The latter value suggests the presence of very small amounts of free **1** in the **f-SWCNT** sample. No shorter lifetimes were detected for **f-SWCNT** with the single photon counting spectrometer, which has a time resolution of 40 ps. Therefore, intercomponent photoinduced processes (energy or electron transfer) must take place at earlier times. Attempts to determine the quenched OPV lifetimes of **f-SWCNT** at shorter time scales with a streak camera apparatus (1 ps resolution) did not afford significant results, as the OPV moieties undergo photodegradation upon intensive irradiation with a Ti:Sa ultrafast laser.

**Table 2**. Luminescence band maxima, fluorescence quantum yields and excited state lifetimes of **1** and **f-SWCNTs** (in DMF).

|  |  |  |  |
| --- | --- | --- | --- |
| Sample | *λmax* (nm) | *Φ* (%) | *τ* (ns) |
| **1** | 510 | 38.5 | 1.37 |
| **f-SWCNT** | 530 | (a) | 1.51 |

(a)*Φ*FL of the hybrid material could not be determined as the light partitioning among the OPV and CNT moieties is not known. However, the quenching of the luminescence intensity of solution of **f-SWCNTs** *vs* **1** is above 99%. The excitation wavelengths used in these experiments correspond to the absorption maxima of **1** (467 nm).



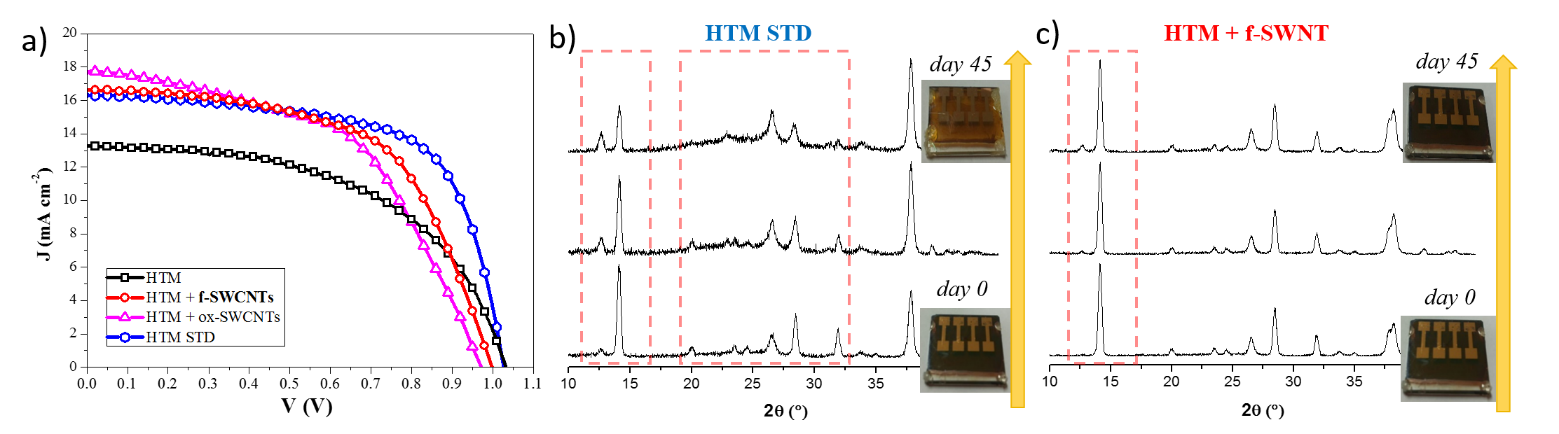
**Figure 3**. Excitation spectra at λem = 520 nm (dashed line) and emission spectra at λex = 350 nm (full line) of **1** (red) and **f-SWCNT** (orange) in DMF.

**SWCNTs-doping of spiro-OMeTAD in CH3NH3PbI3-based solar cell. Ox-SWCNTs** and functionalized **f-SWCNT** dispersions in chlorobenzene (CB) have been used to prepare solutions of Spiro-MeOTAD to be employed as hole transporter in perovskite solar cells with a planar architecture FTO/TiO2/perovskite/spiro-MeOTAD/Ag (sketch in Figure 1b). **SWCNTs** doped deviceshave been compared with undoped (HTM) and conventionally-doped devices with LiTFSI (HTM STD), having comparable spiro-MeOTAD thickness (~ 90 nm). Characteristic curves of best performing devices are shown in Figure 4, while the corresponding PV parameters with the statistical distribution of PCE are reported in Table 3.

**Table 3**. PV parameters for the best performing devices (average PCE in brackets, calculated on a statistical sample of minimum 11 cells).

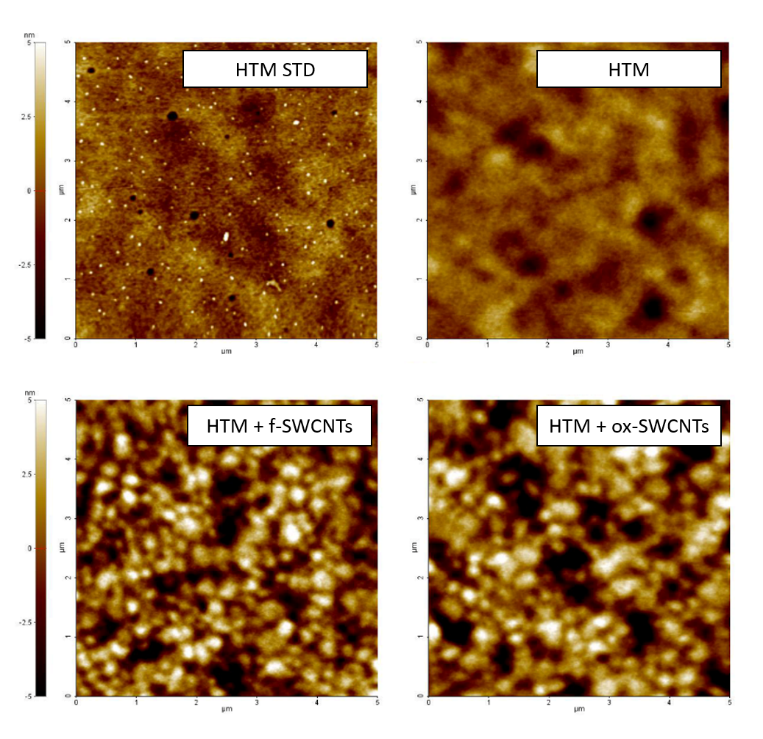
|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | PCE (%) | FF | *V*oc  (V) | *J*sc  (mA cm-2) |
| HTM | 7.1 (6.5±0.6) | 0.53 | 1.02 | 13.2 |
| HTM + **f-SWCNT** | 9.6 (7.9±1.0) | 0.58 | 1.00 | 16.6 |
| HTM + **Ox-SWCNTs** | 9.0 (6.4±2.1) | 0.52 | 0.97 | 17.7 |
| HTM STD | 10.9 (9.8±1.1) | 0.65 | 1.03 | 16.4 |

A comparison between the performance obtained with the undoped HTM and both the SWCNT-doped materials highlights that the carbon doping significantly enhances the short-circuit current (16.6 and 17.7 mA/cm2 for **f-SWCNT** and **Ox-SWCNTs**, respectively, versus 13.2 mA/cm2 for HTM), resulting in a generally improved PCE with respect to the undoped system, likely due to a better charge extraction at the electrode thanks to the presence of the carbon nanotubes framework. A maximum PCE of 9.6% was achieved for **f-SWCNT**, with respect to 7.1% with the undoped spiro-MeOTAD. In order to unravel the role of the organic functionalization, we compared **f-SWCNT** with the non-functionalized **Ox-SWCNT**, both as doping agents of HTM. Devices including **Ox-SWCNTs** show lower performances, in average, and an extremely scattered PCE (6.4±2.1) with respect to the functionalized ones (7.9±1.0), which is attributed to a non-homogenous distribution of the nanotubes within the film. Furthermore, an improved FF (0.58) of **f-SWCNTs**, higher than both HTM (0.53) and **Ox-SWCNTs** (0.52), suggests and improved charge transport within the spiro-MeOTAD layer (standard deviations calculated for FF are reported in Table S1, Supporting Information). We calculate the series resistance (Rs) (Table S1) for the pristine spiro-MeOTAD and the differently doped HTM, and found that Rs reaches the lowest value for the standard doping with LiTFSI. However, the series resistance significantly decreases also for the SWCNTs doping with respect to the pristine spiro-OMeTAD, indicating an improvement of the overall charge transport properties of the doped HTM. Additionally, all the devices embedding doped HTM show similarly reduced hysteresis with respect to the undoped spiro-MeOTAD (Table S2, Supporting Information). Noticeably, the HTM doped with **f-SWCNT** allows the achievement of performances very close to the spiro-MeOTAD standard doping with LiTFSI (9.6% *vs* 10.9%), also in terms of statistical distribution (1.0 *vs* 1.1). Besides the comparable efficiency, the most relevant advantage conferred by the SWCNTs doping is the improved chemical stability of the perovskite material, with respect to the one underneath the Li-doped spiro-MeOTAD. We compare the effect of the two different dopings (NTs *vs* LiTFSI) on the stability of perovskite ﬁlms by exposing them continuously for 45 days to the environment (ambient air ≈ 70% relative humidity, room temperature = 25±1 °C).68,69 We monitored perovskite degradation by recording XRD spectra of the complete devices doped with NTs and with the standard Li salt (Figures 4b-c) and found that the perovskite active layer is severely damaged by moisture and by the possible migration of Li+ from the HTM (Figure 4b). The final products of the degradation process contain large amounts of PbI2, as evidenced by the appearance of its characteristic (001) peak at 12.65° and the yellowish device color (inset Figure 4b). The intensity of MAPbI3 main reﬂection at 14.1° is massively reduced after 45 days exposure. It can also be noticed the appearance of a broad background in the 2Ө window between 20 and 30°, ascribable to the evolution of the crystalline perovskite phase into an amorphous form. For the aged devices doped with **f-SWCNTs**, instead, the PbI2 peak is significantly smaller and the perovskite XRD peaks maintain the same shape and intensity, indicating a negligible degree of decomposition. The improved moisture resistance combined to the comparable efficiency with the standard doping demonstrates the suitability of this material as a valid doping agent for spiro-MeOTAD, representing a viable alternative to the conventional Li-salt.

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**Figure 4**. (a) Characteristic curves of the best performing devices; XRD patterns of (b) HTM STD and (c) HTM + **f-SWCNT** device from 0 to 45 days exposition at ambient conditions (rt, RH% = 70%). The combination of the (002)/(110) planes is found at ∼14.1° and that of the (004)/(220) planes at ∼28.4°. The other low-intense diffraction peaks at ∼ 23.5°, 31.9°, 40.5° and 43.20° are assigned to the (211), (312), (224) and (006)/(330) planes.14 Peaks at 26.5°, 33.8° and 37.9° are assigned to FTO.

The morphology of the hole transporting layers used for the solar cell fabrication was studied by means of Atomic Force Microscopy (AFM, Figure 5), which reasonably explains the performance of the cells. The pristine spiro-MeOTAD shows a very smooth and homogeneous morphology (Rq = 1.1 nm), whereas the LiTFSI doping induces the formation of big aggregates and pinholes in the film, due to the poor solubility of the Li-salt. Overall, the SWCNT doping increases the spiro-MeOTAD roughness, while keeping a homogeneous film morphology if compared to that of LiTFSI. The Ox-SWCNT and f-SWCNT doped samples show a roughness Rq of 2.6 and 2.2 nm respectively. Such a slight difference could be due to a more homogeneous dispersion of f-SWCNT in the spiro-MeOTAD matrix conferred by the organic chromophore. The photophysical characterization of the modified SWCNTs demonstrates that the derivatization strongly affects the excited state properties of the molecules. In fact, an efficient quenching of the SWCNT luminescence is recorded when OPVs terminals are introduced. On the other hand, the OPV insertion is necessary to enhance the solubility of the nanocarbon material and favor the interactions with the hosting hole transporting matrix. Notably, the perturbation of the SWCNT excited states does not affect the charge transport capability of the HTMs. In fact, unmodified SWCNT exhibit poorer performances when included in PV devices due to worst dispersion in spiro-MeOTAD. This result can be relevant for researchers working on the synthesis of new doping materials for HTMs, as it shows that the excited state behavior of such materials has little or no impact on the final HTM carrier mobility.

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**Figure 5**. AFM characterization of the spiro-MeOTAD films.

**CONCLUSIONS**

Here we report on a new covalently functionalized SWCNT as dopant for spiro-MeOTAD to i) reduce the chemical instability of perovskite material embedded in the common perovskite solar cell configuration, bearing LiTFSI doped HTM; ii) enhance the affinity of CNTs with Spiro-MeOTAD. The selected material, (7,6)-enriched SWCNTs functionalized with oligophenylenevinylenes bearing alkoxy groups in the central ring and amine residues at the extremities, allows the fabrication of well performing and reproducible perovskite-based solar cells, with respect to the pristine SWCNT, the latter undergoing a large scattering of the PCE values. Noticeably, our results demonstrate a maximum PCE value of 9.6%, which is in line with the Li-doped spiro-MeOTAD system but significantly improved in terms of chemical stability of perovskite layer.

ASSOCIATED CONTENT

Supporting Information

Technical and experimental details along with all the synthetic procedures. Device fabrication and characterization and morphological and structural analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

T.M. performed all the synthesis and prepared all the materials for the different studies. E.P. performed all the photophysical studies in solution. The fabrication and characterization of the flat perovskite solar cell based on f-SWCNTs-doped spiro-MeOTAD and the XRD characterization has been performed by V.T., A.R. A.L and S.C. S.C., N.A. and D.B. programmed, designed and coordinated all the scientific activities and wrote the paper through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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