High mobility transistors based on electrospray-printed small-molecule/polymer semiconducting blends

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Spray-coating techniques have recently emerged as especially effective approaches for the deposition of small semiconducting molecules toward the fabrication of organic field-effect transistors (OFETs). Despite the promising mobility values and the industrial implementation capability of such techniques, the resulted devices still face challenges in terms of morphology control and performance variation. In this work, the efficient process control of electrostatic spraying deposition (ESD) and the excellent film properties of polymer:small molecule blends were successfully combined to develop reliable and high performance transistors. Specifically, a highly efficient blended system of 2,8-difluoro-5,11-bis(triethylsilylethynyl)-anthradithiophene (diF-TES-ADT) and poly(triarylamine) (PTAA) was employed in order to realize top-gate OFETs under ambient conditions, both on rigid and on flexible substrates. The films revealed an extensive crystallization and microstructural organization implying a distinct phase separation in the electrosprayed blend. Furthermore, we investigated the effects of the processing temperature on the film-forming properties by means of film continuity and grains boundaries. Remarkably, the electrosprayed OFETs exhibited field-effect mobilities as high as 1.71 cm²/Vs, and enhanced performance consistency when compared to conventional gas-sprayed transistors. Additionally, the transistors showed excellent electrical and environmental stability, indicative of the good interface quality and the self-encapsulation capability of top-gate structure. These results highlight the great potential of electrohydrodynamic atomization techniques for implementation to large-area processing for OFETs fabrication.

I. INTRODUCTION

Organic-based transistors are the fundamental building block of all the emerging electronic technologies such as flexible active matrix displays [1] , sensors [2,3], light emitting devices [4] and RFIDs [5]. In recent years, the prospect of realizing low cost/weight, unbreakable flexible ‘plastic’ electronics paved the way for the development of solution-processed organic semiconductors towards the realization of organic FETs (OFETs). Despite their existing limitations related to their reliability and electrical stability, their potentiality for processing at low temperatures and thus at a lower cost, and their applicability with deposition techniques for high-throughput fabrication over a large area, has stimulated a huge scientific interest towards this direction [6]. Accordingly, with the investigation of new materials and processing methods as well as the optimization of the existing ones toward the improvement of the physicochemical aspects of the organic semiconductor (i.e., rheology, crystallization kinetics) we can achieve even more cost-effective routes to mass production.

High performance OFETs have been successfully realized using conventional techniques (i.e. drop-casting, spin-coating and dip coating). However, these methods face challenges regarding their implementation into existing manufacturing technologies. Consequently, well-established industrial coating methods, such as blade-metering[7,8] and spray-coating [9,10] have come to the fore for the deposition of the critical layers in organic solar cells[11], light emitting diodes[12], or even thin film transistors.[13] Among them, electrostatic spraying deposition (ESD) represents a very promising spraying approach, which is based on the electrohydrodynamic atomization of a liquid ejected through a nozzle by means of an electrical field.[14] Compared to the conventional spray deposition techniques, ESD bears the advantages of enhanced controllability and low cost processing, since no carrier gas is required for the transfer of the atomized species. The ESD method was recently used from our group, for the deposition of soluble acenes as the active layer of OFETs [15]. Particularly, an optimization on the ESD process parameters was performed, aiming to obtain well-ordered crystalline structures. Moreover, the spraying regime that was proposed, offered desirable morphological characteristics consisting of high quality crystal domains.

However, despite the improved crystalline structures obtained, the generally highly anisotropic nature of such molecular crystalline semiconductors and the incomplete coverage of the resulting films may oppose several limitations. As has been proposed in literature, a viable way to address these issues is the use of small molecules:polymer blend systems [16,17]. In such cases, the good film forming properties of the polymers can be efficiently combined with the high charge carrier mobility found in crystalline organic semiconductors and thus provide better performance consistency as well as enhanced mobilities. To our knowledge, as yet, there is only

one report on the spray deposition of small molecules:polymer blends for OFETs fabrication, although in that case a conventional air-brush system was used [18].

Following this rationale, we herein propose the deposition of small molecule:semiconducting polymer blends using ESD-printing method and we combine the excellent film properties of such blends with the enhanced process control of ESD to develop reliable and high performance OFETs. Particularly, 2,8-difluoro-5,11-bis(triethylsilylethynyl) anthradithiophene (diF-TESADT) was blended with a binding semiconducting polymer poly(dimethyl-triarylamine) (PTAA), and electrosprayed onto rigid or flexible substrates in order to realize OFET devices. Under properly adjusted conditions, the ESD blends were observed to form continuous films with distinct segregated structures consisting of polymer and crystalline phases. The good crystal growth control and film uniformity resulted in improved device performance and substantially lower device-to-device variation compared to conventional sprayed OFETs based on identical blends. The remarkable electrical properties of the electrosprayed transistors are demonstrated from the improved average mobility values ($\sim 1 \text{ cm}^2/\text{Vs}$) and the performance stability under electrical stresses and long-term environmental exposure. Furthermore, OFETs fabricated on flexible substrates exhibited encouraging characteristics, which suggests ESD as a powerful technique compatible with roll-to-roll applications paving the way for large scale low-cost plastic electronics.

Experimental Details

2,8-difluoro-5,11-triethylsilylethynylanthradithiophene (diF-TESADT, **Fig.1a**) were synthesized in the Center for Applied Energy Research at the University of Kentucky, following the procedure reported elsewhere.[Ref] Poly (bis(4-phenyl)(2,4-dimethylphenyl) amine) (PTAA, $M_w = 6.3 \text{ kDa}$, **Fig.1b**) was purchased from Ossila and used without further purification. 1,2,3,4-tetra-hydronaphthalene (tetralin, anhydrous, 99%), 1,2-Dichlorobenzene (o-DCB, anhydrous, 99%) and pentafluorobenzenethiol (PFBT, $M_n = 200.13$) were purchased from Sigma Aldrich.

A top-gate, bottom-contact (**Fig.1c**) architecture was employed for the electrosprayed OFETs. Glass substrates were first ultrasonicated in detergent solution (Hellmanex TM) and sequentially rinsed with deionized water and isopropanol (IPA). Source and drain electrodes were patterned onto the glass substrates via thermal evaporation of gold (Au) (40 nm) through a shadow mask, followed by oxygen plasma for 3 min at 60 W. The contact electrodes were subsequently treated by immersing the substrates in PFBT solution (5 mmol/L in IPA, 10min) to modify the work function of the Au contacts and thus achieve better injection. The semiconducting

blend consisted of a 1:1 by weight blend of diF-TES ADT and PTAA in tetralin at a total concentration of 20 mg/ml. The solution was loaded into a 5 mL glass syringe with a 26-Gauge stainless-steel nozzle. The applied voltage power was adjusted in the range of 16–19 kV, while the flow rate ranged between 0.2 -1 $\mu\text{L}/\text{min}$. The distance between the tip of the nozzle and the collector was adjusted between 60-70 mm. For the airbrush sprayed transistors, the solution was sprayed in ambient atmosphere and temperature by hand at a distance of 30cm and Nitrogen gas pressure of 1 bar for 2 seconds. Then the film annealed at 120 °C for 2 minutes to remove the solvent. CYTOP was then spin-coated (2000 rpm for 60 sec) over the semiconductor and baked at 100 °C for 15 min in order to form the dielectric layer. Finally, aluminum gate electrodes (100 nm) were vapor-deposited through a shadow mask in an ultrahigh vacuum chamber.

The surface topography and morphology were investigated using atomic force microscopy (AFM; NTEGRA NT-MDT), polarized optical microscopy (POM; Nikon LV100) and Spectroscopic Ellipsometry (SE) measurements in the near infrared to visible and far ultraviolet (NIR–vis–fUV) spectral region. The structural properties of the crystalline films were studied using X-ray diffraction (XRD; Bruker D-5000) measurements, while the current-voltage (I-V) characteristics of the fabricated OFETs were measured using a semiconductor parameter analyzer (Keithley 4200SCS) under dark and ambient conditions at room temperature.

II. RESULTS AND DISCUSSION

Figure 1(d) shows a schematic illustration of the ESD technique and an image (inset) of the nozzle during the spraying process. In principle, ESD is a well-known method used for the electrostatic atomization of liquids. Particularly, the established electrical field between the conductive nozzle and a grounded collector causes the elongation of the droplet hanging out of the nozzle capillary and its subsequent break up into fine droplets due to the shear stress on the liquid surface. By tailoring the electrospraying parameters, such as the applied voltage between the nozzle and the collector (at a constant liquid flow rate), various electrospraying modes (i.e., micro-dripping, jet-spraying) and spraying profiles occur as the disintegration effect on the pendant droplet changes [19].

Among the several ESD modes, jet and multi-jet spraying have been applied for applications where high throughput and uniform film deposition over a large area is required, due to the efficient atomization and the good size dispersity of the emitted droplets. However, as we described elsewhere,[15] the extensive atomization in jet-spraying mode induces small-sized droplets which tend to evaporate relatively fast, leading to the formation of smaller and disrupted domains, when crystalline semiconductors such as diF-TES-ADT are deposited. Interestingly, the introduction of a polymer such as PTAA in the solution, was found to encounter this drawback,

since the diffusion of semiconductor in the polymeric matrix inhibits the rapid anisotropic crystallization, rendering jet-spraying mode a viable deposition condition for semiconducting blends.

The selection of the appropriate solvent is a crucial step in ESD, since it influences not only the critical voltage at which the transition between different spraying schemes occurs, but also the radius of the spraying cloud, as well as the stability of the produced jet. According to Rayleigh limit equation [$q_R = 8\pi(\epsilon_o\sigma d^3)^{0.5}$, where ϵ_o permittivity, σ surface tension of the liquid and d the droplet diameter], the maximum surface charge a droplet could carry is highly depended on the physical properties of the solution. The abovementioned aspect becomes more complicated in the case of crystalline semiconductors, due to solvent compatibility and/or other processing issues (i.e., solubility, film drying) that should be also taken into account. More specifically, functionalized acenes are generally well soluble in non-polar solvents (low dielectric constant), which means that higher electrical field is required for the charging/discharging of the droplets while simultaneously the transfer efficiency is rather low. The spraying characteristics can be significantly improved when common polar solvents, such as acetone or IPA, are used. In that case, the solubility is poor and the drying rate is exceptionally high due to the droplets miniaturization and the relatively low boiling point of such solvents. To cope with this issue, a mixture of non-polar (tetralin, $T_e = 207\text{ }^\circ\text{C}$, $\epsilon_r = 2.4$) and polar (o-DCB, $T_e = 180\text{ }^\circ\text{C}$, $\epsilon_r = 9.8$) solvent (95:5) was used, to provide sufficient control over the drying process and enhanced spraying stability. In order to further improve the coverage over the substrates and simultaneously limit the sequential merge of the drops in the same area, the collector was set to follow a programmable motion while the capillary tube was kept fixed. The optimized speed of the collector was around 10 mm/sec, while the relatively large movement range of the stage in the x-y plane (0.1 -200 mm) allowed us to prepare multiple samples at once.

Fig. 1. (a) Schematic diagram of the electrospayed transistor structure with a top-gate/bottom-contact geometry and the chemical structures of the used materials. (b) Illustration of the electro spray printing method. The inset image shows a magnified view of the nozzle during spraying.

A critical aspect that determines the crystal growth and the topographical properties of solution-processed films is the solvent evaporation rate, the effects of which have been thoroughly studied in similar, spin-coated, blend systems [20]. Indeed, in ESD method it is feasible to tune the crystalline morphology, in terms of grain size and boundaries density, by adjusting the induced temperature during the spraying process. In order to investigate that, two different conditions were studied: (a) fast drying (sprayed and annealed at 80 °C) and slow drying (sprayed at 40 °C) films. **Figure 2** shows the POM images of the electrospayed diF-TES-ADT:PTAA blends. Both images exhibit strong optical birefringence, clearly indicating the crystalline nature of the deposited films. The visible color and brightness deviation inside the grains are attributed to the anisotropic crystal orientation and/or thickness fluctuations at the grain edges or near the nucleation points. The absence of the spherulitic growth typically observed in the spin-coated blends is likely related to the substantially lower drying rate and the domination of small molecule crystallization. By comparing the two morphologies, it can be seen that higher processing temperature (**Fig.2a**, fast drying) induces smaller crystalline domains, which are mainly defined by the size of the individual droplets or by their overlap, indicating that the landed drops cannot maintain the liquid state

sufficiently long in order to coalesce and form a complete layer. This fact has detrimental effects in the quality of the sprayed films, since empty domains (gaps) as well as coalesced crystalline stains may dominate the semiconducting layer, resulting in an extensive number of structural defects and voids. On the contrary, reducing the processing temperature (**Fig.2b**, slow drying) gives rise to the merge of the individual neighboring droplets prior drying, thus enhancing the formation of a complete wet layer over the substrate. In that case, the electrosprayed films exhibit a more extensive crystallization with significantly larger grains size ($> 250\ \mu\text{m}$) and elongated crystals. A similar morphology was also observed when the same blends were deposited using conventional airbrush spraying method. POM images of various airsprayed samples are provided in the Supplementary **Fig. S1**. Thus, we conclude that slow dried films demonstrate better film uniformity while retaining optimal morphological characteristics across crystalline grains.

Fig. 2. POM images of the electrosprayed blends developed using (a) fast and (b) slow drying conditions. Schematic cartoons showing the various morphological features observed in each case based on visual inspection of the films.

To gain better insight into the morphological characteristics of the electrosprayed films we also performed SEM and AFM measurements. Specifically, the SEM imaging in **Fig.3a** shows the presence of well-defined facets on the top surface of the films which correspond to crystalline structures, demonstrating the evidence of vertical segregation between the two components and the domination of diF-TES-ADT phase on the upper interface. By using AFM measurements (**Fig. 3b**) in several different film areas, we calculated the root-mean-square (RMS) roughness, which was found to range from 7.2 to 25.1 nm. Such high values are expected, since ESD processing

provides more time for drying and consequently the crystallites arising upon phase separation are significantly larger. Another factor that may contribute to the increased roughness of the films is the crystals overlapping caused by the superpositioning of the adjacent sprayed droplets. In the corresponding phase imaging of **Fig. 3c** a strong contrast between two different origins is depicted, confirming the effects of phase segregation. Overall, the presence of well-formatted grains and interconnected crystals on the top surface can be interpreted as better charge percolation pathways, implying a high conductivity film profile.

Figure 3d shows the out-of-plane XRD spectra of the electrosprayed blends obtained in $\theta/2\theta$ mode. A series of well-resolved ($00l$) peaks was observed, confirming the highly crystalline nature of the deposited films. The primary diffraction peak at $2\theta = 5.32$ corresponds to an interplanar distance of $16.6 \text{ \AA}$ and is attributed to the (001) reflection of the diF-TES-ADT. This value is consistent with the c -axis length of the single crystal unit cell (triclinic structure, $a = 7.1153 \text{ \AA}$, $b = 7.2342 \text{ \AA}$, $c = 16.626 \text{ \AA}$, $\alpha = 97.522^\circ$, $\beta = 91.361^\circ$, and $\gamma = 107.491^\circ$) [21]. Also, by comparing this XRD pattern with that from a blade-coated diF-TES-ADT textured films (dotted line in the same figure) a good matching between the diffraction peaks is revealed, confirming that the electrosprayed blends maintain the polycrystalline acene phase. The absence of metastable phases and/or significant peaks shift, implies the good microstructural formation of the molecules, derived by the efficient phase separation phenomena between polymer and semiconductor. It should be noted that the apparent difference in peaks intensity is likely related to the film thickness and the smaller crystalline grains appeared in the blended films.

The optical properties of the diF-TES-ADT:PTAA blends were investigated by NIR-Vis-fUV SE method in the spectral region (0.7–6.5 eV) with steps of 20 meV at an angle of incidence of 70° . The measurement principle of SE relies on the measurement of the polarization changes in a light beam of a known polarization state, caused by its reflection or transmission from a material structure. This polarization change is represented as an amplitude ratio Ψ and a phase difference Δ and is the measurement commonly written as $\rho = \tan\Psi e^{i\Delta}$, where Ψ and Δ are the ellipsometric angles. The final optical properties are represented by the complex pseudo-dielectric function $\langle\tilde{\epsilon}(\omega)\rangle = \langle\epsilon_1(\omega)\rangle + i\langle\epsilon_2(\omega)\rangle$, where ω is the photon energy. **Figure 3e** shows the measured pseudo-dielectric function $\langle\tilde{\epsilon}(\omega)\rangle$ of the diF-TESADT:PTAA blend deposited by the ESD technique onto a glass substrate. As it can be seen, the measured $\langle\tilde{\epsilon}(\omega)\rangle$ is dominated by optical absorptions that are attributed to the different electronic transitions of the diF-TES-ADT and PTAA components of the blend. The strong absorption located at 307 nm is attributed to the $B_1 \rightarrow A_1$ electronic transition that is polarized along the long axis of the conjugated core, whereas the broad absorption at the range 350–400 nm is attributed to the PTAA. In addition, the lower absorption at 550 nm is attributed to the $A_1 \rightarrow A_1$ electronic transition polarized along the short axis of the conjugated core

[22]. The spectra consistency with previous reported values of diF-TES-ADT and PTAA highlights the potentiality of this process to develop high quality semiconducting films.

Fig. 3 (a) SEM, (b) AFM topography and the corresponding (c) phase image of the electrospayed diF-TES-ADT:PTAA films. (d) Out-of-plane XRD spectra and (e) the pseudodielectric function $\langle \epsilon(\omega) \rangle$ of the blended films measured by SE.

Transistors in top-gate/bottom-contact configuration based on diF-TES-ADT:PTAA blends were realized onto glass or PEN substrates via ESD. **Figure 4a** shows the transfer curves of the best performing device ($L = 50 \mu\text{m}$, $W = 1000 \mu\text{m}$) in the linear ($V_{DS} = -5 \text{ V}$) and saturation regimes ($V_{DS} = -50 \text{ V}$), measured under ambient and dark conditions. The field-effect mobility values were calculated in the saturation regime from the following equation:

$$\mu = \frac{2L}{WC_i} \left(\frac{\partial \sqrt{I_{DS}}}{\partial V_{GS}} \right)^2 \quad (1)$$

where W ($1000 \mu\text{m}$) is the width of the channel, L ($30\text{--}80 \mu\text{m}$) the length of the channel, C_i is the total measured capacitance per unit area ($\sim 2.2 \text{ nF/cm}^2$), V_{GS} is the applied gate voltage and I_{DS} is the drain current. From the shape of the output curves, it is evident that the transistors exhibit unipolar p-type FET behavior with distinct linear and saturation regimes. Hardly any current hysteresis in the transistor characteristics is observed, which is likely attributed to the low density of energetically shallow charge carrier traps at the interface between semiconducting layer and the CYTOP. The best performing electrospayed transistor yielded a saturation field-effect mobility of $1.71 \text{ cm}^2/\text{Vs}$, while the calculated mean mobility value from 16 different OFETs was $1.01 \pm 0.22 \text{ cm}^2/\text{Vs}$.

Additionally, a turn-on voltage of around 2-4 V, threshold voltage of -7.2 V and on/off current ratio of 7.9×10^3 , were obtained from this specific device.

The performance of the ESD OFETs was further assessed by comparing the extracted electrical parameters with those of airbrushed transistors (of the same device structure). As can be observed in the I-V data of **Fig. S2**, a similar electrical behavior with well defined linear and saturation regimes, negligible hysteresis was obtained. Furthermore, the airbrushed transistors exhibited a maximum saturation mobility of $1.60 \text{ cm}^2/\text{Vs}$ and a mean value of approximately $0.94 \text{ cm}^2/\text{Vs}$. The statistics data based on the characterization of 16 transistors from each spraying method is shown in **Fig. 4c**. Despite the insignificant variation in the average and the maximum saturation mobility between the two spraying approaches, the evident difference in the standard deviation values cannot be excluded, since it is directly related to the performance consistency of the fabricated transistors. By calculating the ratio of standard deviation to measured average mobility (μ_{std}/μ_{avg}) we found a decrease by a factor of about 1.4 (0.38 versus 0.27) in the ESD transistors, implying a significantly lower variation compared to airbrush transistors. Following this trend, the threshold voltage data of ESD transistors displayed much narrower distribution as well as a lower average value. In contrast, the on/off current ratio of ESD devices appeared to be around one order of magnitude lower than airbrush transistors, even though the values exhibited low variation. Nevertheless, such on/off values are similar to those of spin-coated transistors using the same blend system. The electrical parameters of the electrospray printed OFETs are summarized in **Table 1**. Top-gate OFETs based on TIPS-PEN:PTAA using similar process conditions and solution properties, were also realized by the ESD technique. **Fig. S3** depicts the POM image in the channel area of the transistor while **Fig. S4** shows the electrical characteristics of those devices. The maximum saturation mobility was significantly lower compared to diF-TES-ADT:PTAA blends with a value of $0.55 \text{ cm}^2/\text{Vs}$. This is most likely related to the different crystallization scheme of TIPS-PEN and the worse charge injection properties, due to the absent of fluorine interactions[23].

Fig. 4 (a) Transfer (I_{DS} - V_{GS}) and (b) output (I_{DS} - V_{DS}) characteristic curves of electrospray printed diF-TES-ADT:PTAA OFETs, with top-gate, bottom-contact architecture. (c) Comparative histogram plots with statistical data of the mobility (μ), threshold voltage (V_T) and I_{on}/I_{off} , of the ESD and the air-brush sprayed OFETs.

The ESD based diF-TES-ADT:PTAA transistors were subjected to continuous bias stress for 18000 sec (3h) under high gate voltage conditions ($V_{GS} = -50$ V). Typical instability characteristics with a time-dependent current decay and a gradual shifting toward negative values were observed in the evolution of the transfer curves in **Fig.5a**. One possible explanation is the presence of deep traps at the semiconductor-dielectric interface and/or at the grain boundaries of semiconductor that can disturb the free charge carriers and immobilize them in the channel. Nevertheless, no significant degradation in the saturation mobility was observed after almost 1h of bias stress, while after 18000 sec an acceptable decrease of about 12.5 % were measured. Additionally, only marginal changes were found in the on/off ratio and the hysteresis of the transistors in the forward and backward sweep.

Figure 5b shows the dependence of the threshold voltage shift (ΔV_T) on the stress time, as extracted from the $\sqrt{I_{DS}}$ vs. V_{GS} plots (inset graph). Specifically, the ESD based OFETs yielded a ΔV_T of -9.6 V after 18000 sec, with a tendency to saturate, as the trapping rate reduced due to the gradual occupation of the vacant states. In order to quantify the threshold voltage instability, we fitted the data using the stretched exponential equation (2)[24],

$$\Delta V_T(t) = \Delta V_o \left\{ 1 - \exp \left[-\left(\frac{t}{\tau} \right)^\beta \right] \right\} \quad (2)$$

where $\Delta V_o = V_{GS} - V_{T0}$, where V_{GS} is the applied gate and V_{T0} the initial threshold voltage, τ is the relaxation time and β ($0 < \beta < 1$) is the stretching parameter. **Fig. 5c** shows the relative threshold voltage ($\Delta V_T/\Delta V_o$) versus time and the corresponding fit (dashed line). The τ and β parameters were found to be approximately 7×10^5 and 0.36, respectively. The relaxation time is higher or of the same order to that of previously reported pentacene [25], TIPS-Pentacene [7] or PTAA [26] OFETs, even though the bias-stress conditions in the present study were more severe and the measurements took place in ambient environment.

In order to evaluate the environmental stability characteristics, the devices were exposed to ambient conditions ($T=22^\circ\text{C}$ & high relative humidity R_H of around 55 %) for 60 days. As can be seen by the transfer curves of **Figure 5d**, a slight shift toward positive values is accompanied by a transition in their slope and an increase in the off-current level of the transistors. These results led to a variation of just 1.8 V in the threshold voltage values, as well as to a decrease in the mobility of approximately 10% (from 1.37 to 1.23 cm^2/Vs). We assume that a multitude of factors related to the device structure and the nature of the materials contribute to the good operational and environmental stability of those devices. Specifically, the top-gate configuration along with the inherent properties of the CYTOP (hydrophobicity, chemical stability, smooth surface) provide an excellent self-encapsulation layer for the transistors by limiting the diffusion of oxygen and water molecules in the critical interfaces of the device. Additionally, since the presence of structural defects and voids may strongly define the stability of the transistors, our findings indirectly imply that the electrosprayed blends maintain optimum morphological characteristics, providing a good interface with the dielectric layer.

Fig. 5 Environmental and operational stability measurements. (a) Evolution of the transfer curves (at fixed $V_{DS} = -50$ V) under negative gate bias-stress of $V_{GS} = -50$ V. (b) Threshold voltage shift (ΔV_T) as a function of bias stress time (0-18000 sec). The inset shows the $\sqrt{I_{DS}}$ vs. V_{GS} plot used for the extraction of threshold voltage shift. (c) Relative threshold voltage shift ratio ($\Delta V_T/\Delta V_o$) as a function of stress time. The solid curve is the fit of the stretched-exponential time dependence. All the stress measurements took place in dark and ambient conditions.

(d) Comparative transfer characteristics of ESD blended OFETs right after fabrication and after 60 days of storage in air ($T=22\text{ }^{\circ}\text{C}$ & high relative humidity R_H of around 55 %).

ESD technique was also used for the fabrication of OFETs on flexible PEN substrates. The flexible transistors exhibited similar electrical behavior with a maximum saturation mobility of $0.45\text{ cm}^2/\text{Vs}$, an average value of $0.31\text{ cm}^2/\text{Vs}$, near zero threshold voltage and on/off current ratio between 10^2 and 10^3 , as shown in the transfer characteristics of **Fig.6a**. The output curves of **Fig. 6b** show a clear pinch-off and good saturation characteristics, while the apparent linear behavior at low V_{DS} values implies a minimum Schottky barrier and consequently good carrier injection properties. We should note that the functional flexible transistor yield exceeded 75%, with the rest of the devices showing either abnormal electrical behavior or being nonfunctional due to excessive leakage currents or topographical defects.

Fig. 6 (a) Transfer and (b) output electrical characteristics of diF-TES-ADT:PTAA OFETs fabricated via ESD printing on flexible PEN substrates, depicted in the inset image.

Table 1. Summary of the electrical parameters obtained from the electrospray printed OFETs

Substrate	Method	$\mu_{\max}$ (cm^2/Vs)	μ_{avg} (cm^2/Vs)	V_T (V)	Ion/Ioff (Log_{10})
Glass	Electrospraying	1.71	1.01 ± 0.27	-7.9 ± 2.8	3.28 ± 0.27
	Air-brush spraying	1.60	0.94 ± 0.38	-17.9 ± 9.3	4.97 ± 0.25
PEN	Electrospraying	0.45	0.31 ± 0.09	0.7 ± 2.7	2.61 ± 0.28

III. CONCLUSIONS

In summary, we herein propose the realization of high performance and reproducible OFETs via ESD printing of diF-TES-ADT:PTAA blend. The resulting films exhibited excellent film-forming properties, resulting in continuous and well-ordered crystalline structures. The fabricated OFETs yielded remarkably lower device-to-device variations compared to conventional air-brush sprayed OFETs, indicative of the enhanced control over morphology evolution during our process. A maximum saturation mobility of $1.71 \text{ cm}^2/\text{Vs}$ and a mean mobility value of about $1.01 \text{ cm}^2/\text{Vs}$ were achieved. This performance is comparable to equivalent spin-cast devices while it is among the highest values obtained by spraying technique, reported to date. Further, investigations on the electrical and environmental stability of the electrospray printed OFETs have shown minimal performance degradation, given the fact that the entire processing and measurements (apart from electrodes deposition) were carried out in ambient air. Overall, this work underlines the great versatility of acene:polymer systems and their compatibility with ESD, toward mass-manufacture of low-cost printed electronics.

ACKNOWLEDGEMENTS

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