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Laser Printed Organic Thin-Film Transistors

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Abstract

Solution deposition of organic opto-electronic materials enables fast roll-to-roll manufacturing of photonic and electronic devices on any type of substrate and at low cost. But controlling the film microstructure when it crystallizes from solution can be challenging. This represents a major limitation of this technology, since the microstructure, in turn, governs the charge transport properties of the material. Further, the solvents typically used are hazardous, which precludes their incorporation in large-scale manufacturing processes. Here, we report the first ever organic thin-film transistor fabricated with an electrophotographic laser printing process using a standard office laser printer. This completely solvent-free additive manufacturing method allows for simultaneous deposition, purification, and patterning of the organic semiconductor layer. Laser printed transistors using triisopropylsilylethynyl pentacene as the semiconductor layer were realized on flexible substrates and characterized, making this a successful first demonstration of the potential of laser printing of organic semiconductors.

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Organic semiconductors (OSCs) provide a platform to construct the next generation large-area, light-weight, flexible, and stretchable optoelectronic applications, including flexible displays, electronic paper, sensors, disposable and wearable electronics, renewable energy sources, medical applications, and more. The unique properties of organic materials have enabled new paradigms for 2D additive manufacturing of devices that significantly reduce the complexity of processing.^[1–8] Their fast deposition from solution using roll-to-roll fabrication may enable large-volume production at low cost per unit area, and with no restrictions on the substrate choice, expanding the use of electronics to applications currently precluded by established technologies.^[1] Solution processability indeed brings competitive advantages, but unfortunately, it also carries with it several serious complications. First, OSCs are generally only soluble in aromatic and/or halogenated solvents, which represent environmental and safety hazards, making their use in large scale manufacturing processes unattractive. Second, the crystallization of the film from solution often yields a complex microstructure, which is sensitive to drying conditions^[9–11] and a large number of polymorphs that cannot be controlled in a reliable way without very careful process engineering.^[12] It is quite common for OSCs, including some of the highest performers (2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C8-BTBT), triisopropylsilylethynyl pentacene (TIPS-Pn), or 2,8-difluoro-5,11-bis(triethylsilylethynyl)-anthradithiophene (diF-TES ADT)), to exhibit mobilities spanning several orders of magnitude, depending on the deposition method that is used, the solvent, or the

chemistry at the interfaces.^[4, 5, 13–17] Even on the same test substrate, device-to-device performance can have an unacceptably large variance, with failure rates hindering the possibility of manufacturing. It is clear that in spite of the fact that solution processing is compatible with low-cost and high-throughput manufacturing, this technique suffers from significant limitations in terms of insufficient performance, poor uniformity, and low reproducibility and, unfortunately, the uncontrollable nature of solute film formation overwhelms the fabrication benefits. Recent valiant efforts have been applied to improve film quality, including the use of higher boiling co-solvents or solvent additives, vitrifying agents, vibrating the substrate, or blending small-molecule semiconductors with insulating or semiconducting polymers.^[11, 14, 17–23] The vitrification ability of semiconductors was recently used to decouple the solution-coating step from the crystallization of the semiconductor film to pattern its microstructure and improve the device performance and reproducibility.^[24] Ultimately, these methods do not exclude the hazardous solvents, and the additional steps slow the process and/or include supplementary materials and costs, which do not always justify the improvements in performance.

Here we report on a completely solvent-free, environmentally friendly method for rapid deposition of OSC films under ambient air conditions: *laser printing*. Laser printing is a well-established, low-cost, high-throughput, and directly scalable coating and patterning technique that has not been explored for manufacturing of electronic devices. It melts a solid-state powder, known as the toner, allowing for simultaneous purification, deposition, and patterning of the semiconductor. We have formulated a toner based on the OSC TIPS-Pn and demonstrated the first

transistor fabricated by laser printing, achieving a field-effect mobility of $1.7 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The processing steps did not exceed 180°C , allowing us to package our devices on a flexible substrate using a simple office laser printer. Grazing incidence wide angle x-ray scattering (GIWAXS) analysis reveals partial lamellar texturing of the TIPS-Pn films which is crucial for effective in-plane transport and successful organic thin-film transistor (OTFT) device operation. The implementation of laser printing technology therefore promises to be a viable option for organic electronics and can be achievable with minimal investment, as laser printing technologies are mature, very low cost, operate in ambient air, and use an operating temperature range (140°C to 210°C) compatible with the melting point (T_m) of many existing OSCs. Further developments in the laser printing of OSC films are expected to improve film structure and morphology and achieve performance on par with champion solution-printed films. Moreover, control over the process temperature in laser printing could help achieve superior control over the crystallization and microstructure of OSCs as compared with the drying of volatile inks in conventional solution processes.

We fabricated bottom-contact, bottom-gate laser printed OTFT devices on flexible substrates consisting of polyethylene terephthalate (PET) sheets pre-coated with indium tin oxide (ITO), which was used as the gate electrode. Cytop was spin-coated to form the gate dielectric layer and gold source and drain electrodes were thermally evaporated through a shadow mask. The substrates were taped to a piece of multipurpose 75 g m^{-2} (common 20 lb bond) paper and inserted into the printer paper tray for OSC deposition. The OSC layer was printed at the surface of the pre-fabricated device substrates from a toner consisting of a solid-state mixture of several components,

as described below, and formulated to facilitate good transfer, continuity and uniformity of the film onto these substrates. The OSC incorporated in the toner was TIPS-Pn, a widely-used material in solution-deposited OTFTs.^[5, 25–28] Since this compound melts at a higher temperature ($T_m = 261\text{ °C}$)^[29] than most printer fuser rollers apply, we added another component to the toner that melts at a lower temperature to ensure proper transfer to the substrate (details on the printing process are provided below). We chose carnauba wax as the low-melt material based on several favorable properties: it has a low melting point $\sim 85\text{ °C}$,^[30] it is inert, it is brittle, therefore allowing for better grinding instead of caking, it has low adhesion, which prevents bonding of the toner to the rollers, and it is a low-cost material.

Laser printers work on the principle of electrostatic cling of toner particles on a rotating cylindrical drum typically coated with an organic photoconductor (OPC). The printer's OPC drum is charged (Figure 1a) and the areas in which the toner will be applied are selectively discharged with the use of the laser (Figure 1b). The toner electrostatically adheres to those areas which the laser has discharged on the OPC (Figure 1c). As the OPC continues to rotate, this toner is transferred to the substrate which has been taped to the printing paper (Figure 1d) and then melted to it during the final step with a hot fusing roller to ensure that the toner fuses to the substrate (Figure 1e). While in this work we have not modified the design of the office printer, the temperature of the fusing roller can be tuned by altering the temperature setpoint of the heating element through either firmware editing or adjusting the reading used in the controller's feedback loop, thus allowing the use of the printer for a broad range of materials.

Fabrication of a semiconductor layer requires the toner powder to have very fine particle size. This ensures the highest print resolution and maximizes the surface area for charges and additives to accumulate. It also results in a large charge to mass ratio, q/m , which increases the yield of the mass transfer steps and achieves high quality printing.^[31] To obtain a fine toner powder, we explored two methods that are popular in the laser printing industry, namely the mechanical grinding and the chemical processing in environmentally benign solvents such as isopropyl alcohol (IPA). The choice of the toner fabrication method depends on the properties of the starting materials that will be part of the final composition. The toner ingredients, when combined and processed, must have the proper triboelectric charging characteristics, powder flowability (i.e. it must not clump or “cake” together into agglomerates), and adequate rheology (the toner should melt or undergo a glass transition within the temperature window of the fuser roller). The mechanical grinding is typically accomplished in the dry state of the material using mortar and pestle, ball-milling, or air jet-milling.^[32] The toner materials are mixed in a melt phase, cooled, and broken down in the grinding device. This setup is advantageous for the simplicity and often lower cost, but produces irregularly shaped particles with a wide size distribution. TIPS-Pn by itself does not grind easily into a fine powder. We therefore mixed it with carnauba wax and fumed silica charge control agent (CCA), which prevents the particles from sticking together, and improve the flowability of the powder. The mixture was chemically treated with hexamethyldisilazane (HMDS) to aid in charge control and increase its hydrophobicity. While we were able to print TIPS-Pn films from this toner, unfortunately we did not obtain any working devices using this technique, most likely due to the particle size of the powder being too large.

The second approach for toner formulation was based on a chemical method that makes use of an emulsion and results in spherical particles of a narrow size distribution.^[30] This method is more elaborate than the mechanical one, but it grants increased control of the particle size, since the growth can be stopped once the precipitate has reached the target size, a process which is manipulated by reaction duration time, temperature, and/or mixing shear. Each part of the dispersed liquid component in the emulsion attempts to minimize its area to balance the cohesive forces, resulting in spherical shapes. After the dispersed phase solidifies, the suspensions are dried to remove any solvents using a freeze- or spray-drying procedure. The toner formulation was developed by empirically testing several ratios for the three toner components (TIPS-Pn, carnauba wax and fumed silica), and varying the temperature and processing time. We achieved the most favorable toner powder by first preparing an emulsion of the carnauba wax in hot IPA (**Figure 2a**), followed by mixing in the TIPS-Pn (Figure 2b), then fumed silica in a 5:10:4 mass ratio (Figure 2c). The particles in suspension were dried using a spray-dryer apparatus that was designed and fabricated in our lab (Figure 2d), as detailed in experimental methodology.

To print the OSC layer we first filled a toner cartridge of an unmodified office laser printer with one of our OSC toner formulations. In order to confine the print to a desired region, we designated a target section of the paper by first printing a square border with regular printer toner using a digital design of the print patterns. This square served as the reference for our PET/ITO/Cytop transistor substrate with gold source/drain electrodes. The substrate was taped to the printing paper with Kapton tape. An image of a laser printed layer obtained after one print run is

included in Figure S1, Supporting Information; it can be observed that the film is not continuous.

While it appears that the film adheres well to the highly hydrophobic Cytop surface, since the first generation OSC toner developed herein is not sufficiently optimized, we were unable to print a continuous layer. Therefore, multiple prints were required to create a continuous film. We printed solid squares designed to cover the transistor substrate in order to ensure overlap of each of the repeated prints (typically 10-15 passes). The unmodified office printer is not designed for multiple passes and therefore lacks precise alignment for the paper feed. This resulted in registration errors when multiple prints on the same substrate were attempted. Thus, the ability to print precise OSC patterns requires further optimization of the printing process in a single-pass or the use of a printer capable of precise alignment of repeated prints. An example of a laser printed TIPS-Pn layer can be seen in Figure 1f in which the OSC toner was printed in the form of text on standard paper.

The printed samples were removed from the printer and transferred to a semiconductor probe station for electrical characterization without any further modification. The structure of the OTFT used in this study is shown in **Figure 3a**, and a digital photograph of an array of devices is shown in Figure 3b. The current-voltage characteristics of a device are shown in Figs. 3c and 3d. It can be observed that the current between the source and drain electrodes (I_D) is modulated with the applied source-gate voltage (V_{GS}) and p-type behavior is recorded, which is typical for this material. This device exhibited a mobility of $\mu = 1.5 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, current on/off ratio of 4×10^3 , sub-threshold swing of 2 V dec^{-1} , and threshold voltage of 6 V .

The modest performance recorded in these devices is attributed to the coarseness of the toner. We therefore modified the spray-drying process by altering key parts of our apparatus to improve the heat flow into the drying chamber, increase the overall pressure gradient with a larger air blower (roughly 3 times the power), and enhance particle separation by decreasing the upper and lower radii of the cyclone separator from 15 cm to 7 cm and 7.5 cm to 2 cm, respectively. These modifications further refined the toner fabrication procedure, leading to decreased particle size and distribution spread. As a result, OTFTs were realized with two orders of magnitude improvement in mobility, with a value of $1.7 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ (Figure S2, Supporting Information). This value aligns with that achieved in the solid-state processing of Baklar *et al.*,^[33] who created a TIPS-Pn film at temperatures as low as 100 °C by applying high pressure (10 kN cm^{-2}).^[34] TIPS-Pn can exhibit mobility values ranging from 10^{-4} to $1.8 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ in OTFTs, depending on the deposition method, surface treatments, substrate temperature, or solvent used^[25, 26, 34, 35] and between 10^{-6} to $0.01 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ in various blends with insulating polymers.^[27] Further, under different solution-shearing or blade coating conditions the TIPS-Pn film can achieve enhanced microstructure and assume one of three polymorphs, with subsequent mobilities between 10^{-2} to $11 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.^[5, 23, 28] While the mobility we achieved in our laser printed TIPS-Pn OTFT is modest in comparison to values that were reported in this material from other methods, this result is important since it represents the **first** OTFT made by laser printing the semiconductor layer and was obtained with no extensive optimization. As such, it is on par with early generation vacuum-deposited small-molecule and solution deposited polymeric OTFT devices dating back to the late 1980s.^[2, 36] Unfortunately, the yield of our first generation laser printed OTFTs was low, which precluded us from performing a rigorous statistical analysis. Below,

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we will discuss a few key factors that affect the device yield and the value of the measured charge carrier mobility and which can be improved through additional optimization.

In Figure 4a we plot the dependence of mobility on the longitudinal electric field F , i.e. between the source and drain contacts. Such dependence, following the relation $\mu(F) = \mu_0 \exp(\gamma \sqrt{F})$, where μ_0 is the zero-field mobility and γ is a pre-factor, is referred to as the Poole-Frenkel (PF)-like effect, and results from intrinsic disorder within the OSC film.^[37, 38] The value of γ that we obtained ($\gamma = 10^{-4} \text{ m}^{1/2} \text{ V}^{-1/2}$) is on par with those reported on similar small molecule organic semiconductors.^[39, 40] In light of this result, we performed density of states (DOS) analysis to better understand the landscape of the electronic traps present in our film. We used Grünewald's method and the results are shown in Figure 4b in which the DOS is plotted as a function of the energy above the valence band ($E_v - E_f$).^[41] Measurement of the DOS is a sensitive tool to probe defects and impurities in OSCs, as we have shown elsewhere.^[42, 43] The obtained spectra suggest that the trap densities at the laser printed OSC/Cytop interface is about one order of magnitude greater than that obtained in spin-coated devices with the same dielectric.^[42]

Microstructure, texture and morphology play a crucial role in charge transport of organic semiconductors. As charge transport in OSCs tends to be highly anisotropic and transport in OTFTs occurs at the OSC-dielectric interface, any changes in the crystal packing structure and texture near this interface will have significant implications on the device performance. We investigated the structure and texture of the laser printed OSC using grazing incidence wide angle X-ray scattering (GIWAXS) to explain the low-end carrier mobility achieved in the first generation laser printed

devices demonstrated in this study. GIWAXS measurements reveal lamellar order in these films, as it can be seen by (00 l) scattering rings ($l = 1, 2, 3, 4$) with interplanar spacing of $d = 16 \text{ \AA}$ nm for (001) Bragg Sheet ($q_z = 0.38 \text{ \AA}^{-1}$) shown in **Figure 5a**. The presence of (00 l) powder rings however highlights the fact that many of the TIPS-Pn crystallites are randomly oriented, lacking the pure lamellar texture commonly found in solution printed films of the same OSC prepared by drop-casting, spin coating or blade coating.^[10, 12, 23, 44] In particular, the GIWAXS image reveals the presence of <111> textured crystallites along with <001> crystallites. <111> oriented crystallites represent the face-on π -stacking texture, which exhibits poor in-plane transport.^[45] Nevertheless, the polycrystalline film appears to exhibit a preferential lamellar crystallite orientation, especially as so far as (00 l) peaks are concerned, as seen in Figure 5d. While many crystals are randomly oriented, a substantial fraction are clearly textured with the lamellar plane parallel to the semiconductor-dielectric interface. These are likely to be the crystals in direct contact with the substrate and are thus responsible for achieving good in-plane transport in the channel.

In Figure 5b we plot the intensity vs q and summarize the peaks in **Table 1** along with peak positions for Form-1 of TIPS-Pn polymorphs.^[28] The diffraction peak positions of laser printed films are the same as found for the Form-1 TIPS-Pn polymorph.^[28] In top-contact bottom-gate (SiO_2 as a dielectric) devices prepared by blade coating this polymorph typically realizes mobility in the range of $1\text{-}3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ when its texture is highly lamellar and exhibits well-aligned crystallites parallel to channels.^[28] However, the existence of many crystallites exhibiting powder texture and the coexistence of different crystal orientations, especially <111> textured crystals, points to significant

grain boundary misorientation in the plane of transport. The origin of the powder texture likely comes from the fact that solidification of the melted TIPS-Pn does not occur entirely on the surface of the substrate, likely because the recrystallization on the substrate occurs very quickly. These results show that further optimization of the toner and printing processes can help achieve more textured and ideal microstructures through melt recrystallization which approach those of the higher performing solution-printed OSCs.

The DOS measurements performed on laser printed OSCs (Figure 4b) reveal that these films exhibit an order of magnitude greater trap density than spin-cast films at the interface with the same dielectric.^[42] This might suggest the different components of the toner do not segregate vertically very well, and the channel contains residual toner components in addition to TIPS-Pn. Note, however, that the solution-deposited OSC films/Cytop dielectric interface could only be obtained in a top-gate geometry since the low surface energy of the Cytop layer induced serious dewetting unless a chemical treatment was performed.^[46] On the contrary, laser printed allowed us to coat the OSC layer on the hydrophobic dielectric with no prior surface treatment being necessary. Another likely explanation for the higher density of trap states is the more powder-like microstructure adopted by the TIPS-Pn film as opposed to the purely lamellar texture typically achieved through solution-processing methods. These observations are encouraging as they point to ways in which higher performance laser printed devices can be obtained in the future with better control of the toner, the film quality, and of the processes taking place at the semiconductor-dielectric interface.

Print coverage remains one of the primary challenges due to the fact that the OSC toner powder being too coarse, even in the best case presented in this study, coupled with limited alignment capabilities. This is partially the cause of the increased film roughness, and the significant variations in the quality of the film processed identically, as it can be observed from the atomic force microscopy (AFM) measurements included in Figure S3, Supporting Information. The non-uniformity of the particle sizes causes a spread in the q/m per particle since a greater volume implies a lower surface area in proportion. Static charges collect on the outer surfaces of each particle, so when the particles are too large, there is not a sufficient amount of charge to compensate for the additional mass. Under these conditions, the powder is not efficiently transferred by the Coulombic forces applied by the charged rollers. Further, if the cross-section is too large, the particles are removed by the doctor blade used to meter the thickness of accumulated powder on the transfer roller. This has a tendency to clog up that sector of the roller and results in streaks in the print. To address this challenge, future studies will focus on the use of flash precipitation to achieve smaller particle size.^[47]

Another opportunity for device improvement will be provided through transition to other materials. TIPS-Pn is unstable in a liquid state at high temperatures, and while we do not find signatures of decomposition in our films, they may still be present in small quantities and negatively affect charge carrier transport.^[48] Polymer semiconductors are particularly attractive in this respect since standard toner is already composed of 85-95% of a polymer resin, so the technology should be

transferable to a large number of polymer semiconductors given that they have a suitable

rheology.^[49]

In summary, we successfully realized the first OTFT in which the organic semiconductor layer was laser printed using a commercially available office laser printer that was not modified in any way. The process outlined in this study is fundamentally different than other processing techniques requiring the use of a laser, such as laser-induced forward transfer (LIFT) and laser ablation, in which a laser is used to energetically heat, evaporate, and/or ablate a layer of interest.^[50–53] In our work, the laser in the office laser printer never interacts directly with the toner; it is used as a light source to discharge the OPC drum prior to transferring the toner. We obtained a mobility of $1.7 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ with no prior material purification or post-processing steps, such as vapor or thermal annealing, or any modification of the office laser printer. This method has the advantage of being low-cost, environmentally friendly, and compatible with roll-to-roll manufacturing. While our results consist a proof of concept for the integration of laser printed technologies with organic electronic devices, the performance and yield are limited and further optimisation of the toner formulation and insrtument design are necessary in order for this method to be technologically relevant. In addition, this technology can be expanded for depositing all layers of the device, which would allow the realization of an “all printed” device.

Experimental Section

OTFT Fabrication and Characterization

The laser printed OTFT devices were fabricated on ITO coated PET substrates with a surface resistivity of $60 \Omega \text{ sq}^{-1}$ and a thickness of $127 \mu\text{m}$ (Sigma Aldrich). Because PET films shrink when exposed to elevated temperatures, we heated these substrates to 200°C for 5 minutes prior to printing, to make them dimensionally stable for the temperatures reached in the laser printer ($\sim 180^\circ\text{C}$).^[54, 55] The fluoro-polymer Cytop was spin-coated over this substrate at 2,000 rpm for 60 sec in a nitrogen glovebox to act as the gate dielectric. The Cytop covered substrate was heated at 50°C for 30 min in nitrogen and then transferred to a vacuum oven and heated to 110°C for 2 hours under vacuum. The PET/ITO/Cytop sheets were cut into $2 \times 2 \text{ cm}$ squares followed by thermally evaporating Au source and drain electrodes through a shadow mask to complete the bottom-gate, bottom-contact test structure as seen in Figs 3a and 3b (Note: in some tests, a 5 nm Ti layer was deposited by electron-beam evaporation and used as an adhesion layer for Au, but was not necessary, as we later found that Au adheres well on Cytop). The OSC layer was laser printed in the last step of the device fabrication, as we will describe later.

The I-V characteristics of the printed OTFT devices were measured in ambient air using a probestation connected to an Agilent 4155C Semiconductor Parameter Analyzer. The field-effect

mobility was extracted from the resulting I_D vs V_{GS} in the saturation regime with $V_{DS} = -60$ V using the equation:

$$I_D = \frac{W}{L} \frac{C_i}{2} \mu (V_{GS} - V_T)^2$$

where W and L are the channel width and length, respectively, C_i is the areal dielectric capacitance of 1.30 nF cm^{-2} , and V_T is the threshold voltage.

Toner formulation and preparation

To obtain the toner, first, 2 g of carnauba wax flakes (Alfa Aesar) were added to 200 mL IPA in an open beaker on a magnetic stirrer hotplate set to 125°C and stirred at 350 rpm. A clear emulsion formed typically within 30 minutes. The beaker was then transferred to a water-bath sonicator warmed to 60°C and the emulsion was sonicated for 20 minutes, which resulted in the transformation from a clear liquid into a cloudy suspension as the wax cooled into fine particles. Next, 4 g of TIPS-Pn were added with continued sonication for 20 minutes. Then, 1.6 g of fumed SiO_2 (Thomas Scientific) that has been vapor treated with HMDS was added, followed by another 20 minutes of sonication. The silica was treated by filling a 100 mL amber jar with the fumed silica along with 200 μL of HMDS which was capped, placed on a hotplate set to 130°C , and set to stir at 350 rpm for 30 min. The silica is added in the last step to attach to the outer surfaces of the particulates.

The IPA/OSC toner suspension was dried in a spray-drying apparatus. This instrument consists of a venturi-fed paint sprayer that sprays the warm liquid into a stainless-steel drying chamber. The chamber was heated with hot air from a heat-gun, which rapidly evaporates the IPA from the spray. A pressure gradient created by a high-speed centrifugal air blower carried the solvent vapor and dried particulate through a cyclone separator. The separator generated a vortex (Figure 2d) in which the heavier particles were centrifugally pushed to the wall of an inverted cone while the lighter gas and vapor were expelled through the exhaust in the top-center. A collection jar was connected to the bottom of the cone for the powder to spiral into.

Printing

After the toner was processed, it was poured into an empty toner cartridge. Our test printer was a four-color (cmk) Magicolor 2490MF made by Konica Minolta. Each of the four cartridges reside in a quadrant of a carousel that revolves according to which pigment is required for the printing process.

Printers have a series of rollers in order to feed substrates through the mechanisms, often in serpentine routes. Because of that, substrates must be flexible, such as the PET which we have chosen as the supporting layer. Several device structures were attempted and the most favorable results were obtained when using a layer of the transparent conductor indium tin oxide (ITO, 130 nm) on top of the PET (5 mil) for the purpose of the gate electrode (Sigma-Aldrich, $60 \Omega \text{ sq}^{-1}$). These

structures were taped with ¼" Kapton tape to a standard piece of 8.5" x 11" office printer paper in a specific location to register with the desired print region on the sheet.

We filled the cyan toner cartridge with our OSC toner, so computer software was used to print a square of pure cyan to cover the region between contacts. Complete coverage could not be established with one pass and would require between 5-10 passes to achieve film continuity.

Atomic Force Microscopy

The surface topography of laser printed thin films was evaluated using the Veeco dimension Icon atomic force microscope operating in tapping mode at KAUST solar center. Image planarization and statistical analyses were performed using Gwyddion V2.44.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. Laser printing process. a) Electrically charging OPC drum. b) Laser selectively discharges image areas. c) Toner electrostatically transferred and adhered to OPC drum. (d) Toner pattern transferred to substrate. e) Toner thermally fused to substrate. f) TIPS-Pn based toner printed on standard paper.

Figure 2. Organic semiconductor toner fabrication. a) Carnauba wax flakes added to hot IPA and stirred to create a wax emulsion. b, c) Addition of TIPS-Pn and HMDS-treated fumed silica, respectively, to the wax suspension in 60 °C IPA and sonicated. d) Suspension sprayed as a mist into spray drying chamber and powder recovered in cyclone separator collection jar.

Figure 3. Laser-printed device geometry and electrical measurements. a) Transistor geometry of laser-printed device. b) Photograph of laser-printed transistor array. c) Transfer electrical measurement taken in the saturation regime, at a constant source-drain voltage $V_{DS} = -60 V$. d) Transport electrical measurements.

Figure 4. Poole-Frenkel and DOS plots. a) Mobility extracted from the saturation regime as a function of applied electric field. b) Density of trap states within the bandgap of laser-printed device.

Figure 5. Grazing Incidence Wide Angle X-Ray Scattering. a) Grazing incidence wide angle X-Ray scattering (GIWAXS) map of laser printed TIPS-Pn film. b) Intensity (log) vs q plot extracted from (a). c) GIWAXS map showing the azimuthal integration. d) Extracted plot from (c).

Table 1. Peak positions of laser printed and solution printed TIPS-Pn film (Ref.21). The peak positions are determined from q ($\text{\AA}^{-1}$) vs Intensity plots.

	(001) [$\text{\AA}^{-1}$]	(002) [$\text{\AA}^{-1}$]	(010) [$\text{\AA}^{-1}$]	(101) [$\text{\AA}^{-1}$]	(011) [$\text{\AA}^{-1}$]
This work	0.38	0.76	0.84	0.9	1.0
Ref. 21	0.38	0.76	0.83	0.91	0.98-1.0

Organic thin-film transistors are fabricated by laser printing and characterized. This solvent-free additive manufacturing method allows for simultaneous deposition, purification, and patterning of the organic semiconductor layer in field-effect transistors realized on flexible substrates, making this a successful first demonstration of the use of laser printing for organic device processing.

Keywords

organic thin-film transistors, printed electronics, organic semiconductors, charge carrier mobility

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Laser Printed Organic Thin-Film Transistors

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