ACS OMEGA

Article

Cite This: ACS Omega 2019, 4, 11657−11662

http://pubs.acs.org/journal/acsodf

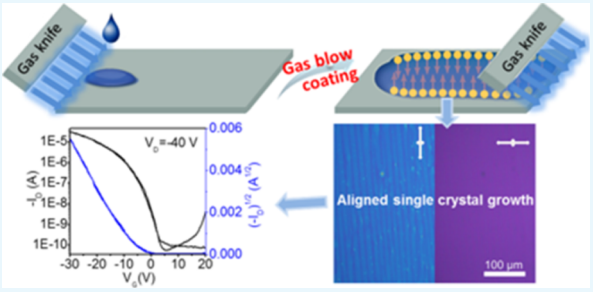
Gas Blow Coating: A Deposition Technique To Control the Crystal Morphology in Thin Films of Organic Semiconductors

Jincheng Tong,* Amadou Doumbia, Adriana Alieva, Michael L. Turner,* and Cinzia Casiraghi*

School of Chemistry, University of Manchester, Manchester M13 9PL, U.K.

Supporting Information

ABSTRACT: Rapid, large-scale, and low-cost coating methods that enable precise control of the crystal growth of organic semiconductors are essential to deliver high-performance devices that are robust and reproducible. In this work, a novel method is presented based on a gas blow coating technique, enabling the deposition of thin films of organic semiconductors, whose morphology can be optimized by adjusting the deposition parameters. We demonstrate the deposition of aligned single crystals of 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene) and 2,7-dioctyl[1]benzothieno[3,2-*b*][1]benzothiophene (C8-BTBT) by gas blow coating and their use as active layers in organic field-effect transistor (OFET) devices. The OFETs of TIPS-pentacene and C8-BTBT have charge mobilities of 0.15 and 1.4 $cm^2\ V^{-1}\ s^{-1}$, respectively, with low threshold voltages and on/off ratios exceeding 10^5. This coating method can also be extended to polymeric semiconductors: films based on poly(3-hexylthiophene) and poly[2,5-(2-octyldodecyl)-3,6-diketopyrrolopyrrole-*alt*-5,5-(2,5-di(thien-2-yl)thieno[3,2-*b*]thiophene)] are realized, establishing gas blow coating as a novel and efficient technique for the deposition of thin films of organic semiconductors.



1. INTRODUCTION

Organic electronic devices, including organic field-effect transistors (OFETs),[1,2] organic solar cells,[3] and organic light-emitting diodes,[4] have attracted tremendous attention over the last decades due to their low-cost and fabrication flexibility, ensured by the use of solution processing.[5] The performance of all of these devices is strongly dependent on the molecular arrangement within the active layer, which strongly depends on the method used to deposit the organic material on the substrate. Large variations in OFET performance have been reported by using different deposition methods and the same organic semiconductor.[6] Table S1 provides a short overview for OFETs fabricated using 6,13-bis(triisopropylsilylethynyl)-pentacene (TIPS-pentacene) and 2,7-dioctyl[1]benzothieno-[3,2-*b*][1]benzothiophene (C8-BTBT), which are highly crystalline small molecule semiconductors, by a variety of techniques. It is well known that deposition of aligned single crystals with the highest order and purity leads to devices with the highest electrical performance.[7−9] This alignment is achievable through control of the crystallization by patterning the wettability of the surface.[10,11] However, this method usually requires complex and time-consuming patterning processes, hindering practical utility. A simpler approach is based on direct control of the crystal growth using low-speed (<2 mm/s) meniscus-guided processes such as solution shearing,[8,12] dip coating,[13] and slot-die coating.[14] Alternatively, small angle drop casting[15,16] and droplet-pinned crystallization[17] have also been employed to deposit aligned single crystals by controlling the self-organization process in a specific direction with the aid of gravity or of a solid pinner. Use of antisolvents has also been used to control crystallization, using double-shot inkjet printing,[7,18] spray printing,[19] and solution-epitaxy growth.[9] Thus, there is strong interest in developing new coating methods for the deposition of films of well-aligned organic single crystals.

In nature, the growth of ice crystals is controlled by the air flow in the atmosphere, producing beautiful snowflakes.[20] To date only a few reports have discussed the use of a similar method, based on gas flow, for the deposition of thin films from solution.[21−24] In particular, there is no systematic study on the effect of the deposition parameters on the resulting film morphology. Herein, we report a novel deposition method based on gas blowing, using a gas knife to deposit films of organic semiconductors. Uniform films of well-aligned single crystals of small molecules can be rapidly deposited on a large scale by controlling the moving speed and gas supply pressure of the gas knife. This method gives highly aligned crystalline films of TIPS-pentacene and C8-BTBT, showing OFET charge carrier mobilities of 0.15 and 1.4 $cm^2\ V^{-1}\ s^{-1}$, respectively. In addition, thin films of poly(3-hexylthiophene) (P3HT) and poly[2,5-(2-octyldodecyl)-3,6-diketopyrrolopyrrole-*alt*-5,5-(2,5-di(thien-2-yl)thieno[3,2-*b*]thiophene)] (DPPTTT) with good uniformity have been prepared, demonstrating the utility

Received: March 26, 2019
Accepted: May 3, 2019
Published: July 5, 2019

DOI: 10.1021/acsomega.9b00835
ACS Omega 2019, 4, 11657−11662

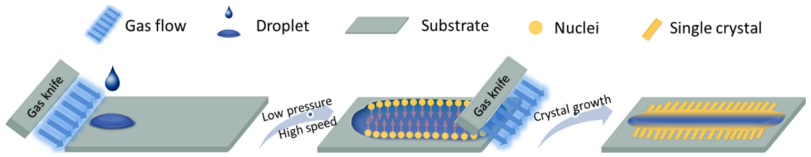


Figure 1. Schematic of the gas blow coating method for deposition of aligned crystals.

of this method for the deposition of small molecule, as well as polymeric semiconductors.

2. RESULTS AND DISCUSSION

2.1. Influence of the Gas Blow Coating Deposition Parameters on the Thin Film Morphology. The coating system is based on a modified doctor blade coater, where a gas knife (from EXAIR) supplies a uniform laminar gas-flow (Supporting Information, Figure S1). The process is conducted in ambient atmosphere (20−27 °C and 10−30% relative humidity). This deposition method is capable of preparing thin films on several substrates at the same time, thus improving the batch-to-batch reproducibility. Note that this deposition method is very different from the original doctor blade coating, as the distance from the gas knife to the substrate is more than 5 mm, in contrast to the doctor blade, where a low distance (usually below 100 μm) is usually applied to contact and guide the spreading of the solution.

There are two main deposition parameters that can strongly affect the morphology of the thin films: the speed of the knife and the gas supply pressure. The effect of these parameters was investigated by using TIPS-pentacene (8 mg/mL in *o*-xylene) as a reference material. When a relatively low gas supply pressure (0.3 bar) and a high knife speed (3.5 cm/s) are used, an elongated wet film is deposited uniformly on the substrate (Supporting Information, Figure S2). During deposition, it is observed that crystal growth starts from the two edges of the elongated wet film, and the crystals grow rapidly to the middle, in the direction perpendicular to the gas flow direction (Supporting Information, Figures S2 and S3). This fast crystal growth is favorable for the formation of aligned single crystals as the nucleation events are suppressed. Figure 1 gives a simple schematic of the growth mechanism, which seems similar to the droplet pinning method, in which a solid pinner is applied to assist the alignment of the crystals during the growth.[25] In our case, a steady contact line is formed at the edge, from which the crystals start growing. Crystals grow from the two contact lines and therefore meet together in the middle, stopping the growth process. This growth mechanism means a disruption line appears in the middle of the film (Supporting Information, Figure S4). When the gas supply pressure is increased or the knife speed is decreased, the thickness of the deposited wet layer decreases, so that the solvent evaporates faster, and thus random nucleation sites are observed, resulting in solid thin films consisting of disconnected parts with small crystals (Supporting Information, Figures S2 and S3). By further increasing the gas supply pressure and using relatively low speed, many nuclei appear on the whole film, leading to a uniform thin film of small particles (Supporting Information, Figure S5).

Note that there are also other parameters, such as the angle or the distance between the gas knife and the substrate, that could affect the crystal morphology. Our homemade setup did not allow changing of these parameters. It is expected, however, that changes in the angle or distance should have similar effects to that observed when changing the pressure, as the actual pressure guiding the droplet decreases with the increase of the distance from the exit of the air knife to the substrate.

According to these results, it is of fundamental importance to optimize the gas pressure and the knife moving speed in order to deposit a uniform wet film without any disruption. Our results also show that another important parameter that determines the size and degree of alignment of the crystals, is the nuclei density: a high nuclei density is needed to achieve uniform and aligned crystals.[25] Therefore, the effect of the solution concentration on the film morphology was investigated by depositing TIPS-pentacene with concentrations in the range of 2−8 mg/mL in *o*-xylene. When the concentration is higher than 6 mg/mL, good crystal alignment is observed (Supporting Information, Figures S6 and S7). In particular, at concentrations of 8 mg/mL, droplets were uniformly spread, resulting in stable wet films that do not recede, allowing complete crystallization. Long, well-aligned crystals over a length of 100 μm are observed (Supporting Information, Figures S4b and S7d). Contact profilometer measurements showed that the thickness of the deposited crystals increased linearly with the concentration (Supporting Information, Figure S8), as expected.

The results indicate that in the case of TIPS-pentacene in *o*-xylene, the best crystal morphology is obtained by using a concentration of 8 mg/mL, a moving speed of 3.5 cm/s, and a gas pressure of 0.3 bar. Figure 2a,b shows polarized optical microscopy (POM) images of the crystals. This figure shows that the contrast of individual crystals changes from light to dark as the polarizer was rotated from 0° to 90°, suggesting that the single crystal domains are highly oriented over several millimeters in length. Figure 2c shows the atomic force microscopy (AFM) image of a crystal with well-defined crystal boundaries are visible. The roughness (R_a) of the surface of the crystal is ∼0.18 nm and the thickness is 130 nm. The highly crystalline nature of the thin film was further confirmed by thin film X-ray diffraction measurements (Figure 2d). Intense diffraction peaks corresponding to the (00*l*) planes of crystalline TIPS-pentacene are observed.[26] The strong diffraction peak at 5.4° is assigned to the identical *d*-spacing of 16.8 Å of TIPS-pentacene.[14,19] The formation of these aligned single crystals by fast crystal growth revealed that the gas blow coating technique is capable of processing molecular semiconductor thin films with high crystallinity.

To evaluate the charge transport properties of the above aligned single crystals, OFET devices with a bottom-gate top-contact configuration were fabricated on a doped silicon substrate, with a 290 nm thermally grown oxide layer as dielectric. Gold electrodes were deposited perpendicular to the aligned crystals (inset Figure 2e). Typical transfer and output characteristics of the devices are shown in Figure 2e,f, respectively: the devices show p-type field effect behavior with a small hysteresis. Over 20 devices were fabricated by deposition of TIPS-pentacene onto six substrates with different

DOI: 10.1021/acsomega.9b00835
ACS Omega 2019, 4, 11657−11662

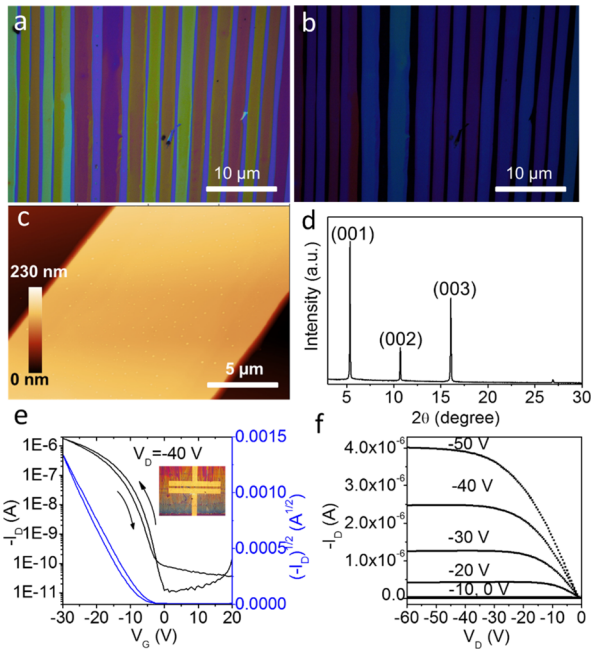


Figure 2. (a) Bright field microscope image; (b) cross-polarized microscope image; (c) AFM image of a single crystal; (d) X-ray diffraction pattern of films of TIPS-pentacene deposited by gas blow coating, using 8 mg/mL in *o*-xylene, a moving knife speed of 3.5 cm/s and gas pressure of 0.3 bar. (e) Typical transfer (V_D = −40 V) and (f) output characteristics of an OFET device made with the film of TIPS-pentacene (inset panel (e): optical micrograph of the device).

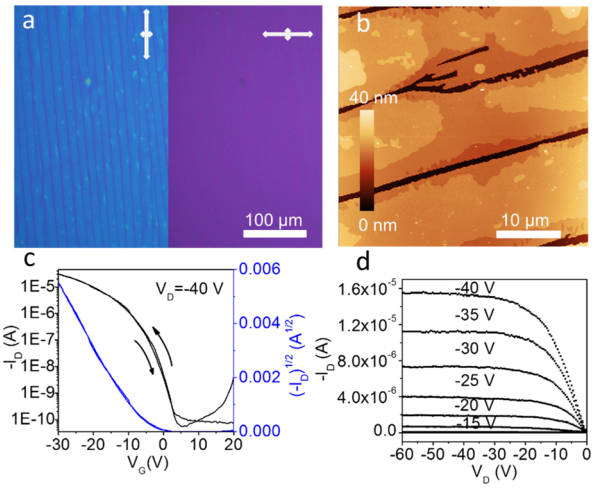


Figure 3. (a) Bright and cross-polarized microscope images and (b) corresponding AFM images of the C8-BTBT films deposited from 4 mg/mL solution of *o*-xylene on silicon wafer by gas blow coating with knife speed of 3.75 cm/s and gas pressure of 0.18 bar. Typical (c) transfer (V_D = −40 V) and (d) output characteristics of the OFET device.

channel lengths (20−100 μm). The devices with a channel length of 60 μm show an average saturation mobility of 0.07 ± 0.04 $cm^2 V^{-1} s^{-1}$, threshold voltage (V_{th}) of 5 ± 3 V, and on/off ratios >10^5 (V_D = −20 V). The highest mobility calculated is 0.15 $cm^2 V^{-1} s^{-1}$ (Supporting Information, Table S2). It should be noted that as most of the papers in Table S1 use the width of the electrodes to estimate the carrier mobilities for a better comparison, we also use the width of the electrode as channel width. In this way, the carrier mobility obtained is slightly underestimated as the crystals do not fully cover the channels.[12] It is noticed that the mobility value achieved here is lower than that reported by solution shearing method, in which a higher carrier mobility is obtained by increasing the electron orbital overlap between the molecules through the application of strain.[27] Our process is very different because the aligned crystals are formed by the self-organization of TIPS-pentacene molecules, and no lattice strain is applied.[8,25] Indeed, the values of mobility reported here are comparable to those reported for self-organized crystals[13,15,28] or single crystals of TIPS-pentacene deposited by double-shot inkjet printing[18] or spray-printing[19] (Supporting Information, Table S1).

The utility of the gas blowing coating technique was then tested for deposition of C8-BTBT, which is a p-type semiconductor showing excellent performance in OFET devices.[9,29,30] In this case, *o*-xylene was used as the solvent. The ideal deposition parameters found for this material are: knife speed of 3.75 cm/s, gas pressure of 0.18 bar, and concentration of 4 mg/mL (Supporting Information, Figure S9). We note that these values are rather close to those used for the deposition of TIPS-pentacene, probably because these are both molecular semiconductors deposited from the same solvent.

POM images (Figure 3a) show that the absorption intensity of the film becomes totally dark after the polarizer changes from 0° (left) to 90° (right), demonstrating essentially mm-size single crystals. AFM measurements show that the C8-BTBT film has a thickness of ∼18 nm and is characterized by terraced structures with a 2.6−2.8 nm molecular step (Supporting Information, Figure S9d,e) and faceted edges (Figure 3b), in agreement with previous results.[7,9] Additionally, some defects are observed on the individual layers, which mainly derive from the fast growth of the crystals (Figure S9d).

OFETs fabricated from these crystalline films show ideal transfer characteristics with very little hysteresis (<0.1 V) and a subthreshold slope of 1.7 V/decade (Figure 3c). The output characteristics (Figure 3d) show excellent linear source/drain current−voltage dependence at low voltages, in contrast to previous reports,[7] showing that there is almost no injection barrier at the contacts.[29,31] More than 25 devices with different channel lengths were fabricated. An average mobility of 0.7 ± 0.31 $cm^2 V^{-1} s^{-1}$ was extracted, with a threshold voltage of −4.6 ± 0.9 V for a channel length of 100 μm. The on/off ratio is in the range of 10^6−10^7. The highest mobility extracted is 1.4 $cm^2 V^{-1} s^{-1}$ (Supporting Information, Table S3), which is higher than that obtained with standard deposition methods, such as spin coating or vacuum deposition. Higher mobilities have been reported, but these have been obtained with either more complex or expensive deposition methods or by using blends (Supporting Information, Table S1).

2.2. Deposition of P3HT and DPPTTT Films. To further demonstrate the utility of this novel coating technique, we also performed the deposition of conjugated polymeric semiconductors, such as P3HT[32,33] and DPPTTT.[34,35]

P3HT thin films, with around 250 mm width and several centimeters length, were deposited on glass or hexamethyldisilazane (HMDS)-treated silicon wafers from *o*-xylene, with a knife speed of 0.6 cm/s and a gas supply pressure of 1.8 bar (Supporting Information, Figures S10−S12). DPPTTT thin films with a similar area were deposited from chlorobenzene on octadecyltrichlorosilane (OTS)-treated silicon wafers by gas blow coating with a knife speed of 0.6 cm/s and gas pressure of

DOI: 10.1021/acsomega.9b00835
ACS Omega 2019, 4, 11657−11662

1.6 bar (Supporting Information, Figures S13−S14). It can be noted that the same solvent (*o*-xylene) has been used for deposition of TIPS-pentacene, C8-BTBT, and P3HT, however, a higher pressure and lower speed is required for P3HT in order to achieve a uniform thin film. In the case of P3HT, the thin films are directly obtained when the gas knife drags the droplet forward, that is the solvent evaporates almost instantaneously, rather than leaving a uniform wet film for aligned crystal to grow, as observed for TIPS-pentacene and C8-BTBT. In the case of DPPTTT, chlorobenzene is used as solvent, but the deposition parameters are close to those used for P3HT, possibly due to the similar solution behavior of the polymers and the use of a hydrophobic treated substrate.

AFM measurements (Figure 4a) show that the P3HT film has uniform morphology with a thickness of 12 ± 1 nm and an

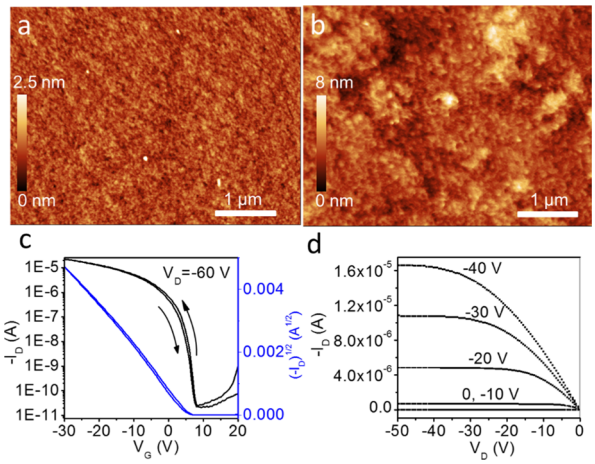


Figure 4. AFM images of (a) P3HT thin film deposited from 10 mg/mL solution of *o*-xylene on HMDS-treated silicon wafer and (b) DPPTTT thin films deposited from 7 mg/mL solution of chlorobenzene on OTS-treated silicon wafer by gas blow coating. Typical (c) transfer (V_D = −60 V) and (d) output characteristics of the FET device for DPPTTT thin films.

average surface roughness of 0.2 nm. OFET devices fabricated using such P3HT films show mobility in the range 0.0007−0.02 $cm^2\ V^{-1}\ s^{-1}$ (Supporting Information, Table S4), which is comparable to that reported for devices prepared using spin- or drop-coating processes.[32,33]

The DPPTTT thin film has a thickness of 26 ± 3 nm and an average surface roughness of 0.7 nm (Figure 4b). Figure 4c,d shows representative transfer and output characteristics of OFETs fabricated using these films—minimal hysteresis is observed and the subthreshold slope is steep (0.7 V/decade). Over 60 devices with different channel lengths were fabricated and in all cases the mobility exceeded 0.3 $cm^2\ V^{-1}\ S^{-1}$ (average mobility is 0.4 ± 0.26 $cm^2\ V^{-1}\ s^{-1}$ for channel length of 60 μm). The highest mobility calculated is 1.5 $cm^2\ V^{-1}\ S^{-1}$ (Supporting Information, Table S5), which agrees with the reported values (by the supplier) for DPPTTT.[36]

3. CONCLUSIONS

In summary, this work presents a new method, based on a gas blow-assisted technique, for the deposition of small molecule and polymeric organic semiconductors on a wide range of substrates. Well-aligned single crystals of molecular semiconductors and uniform continuous films of polymeric semiconductors can be deposited by optimizing the deposition parameters. OFETs based on TIPS-pentacene, C8-BTBT, P3HT, and DPPTTT have been demonstrated, showing comparable performances to those fabricated by traditional deposition techniques.

Gas blow coating is a unique, noncontact coating method, suitable for the deposition of thin films with different morphologies, showing tremendous potential for the fabrication of thin films from organic molecules in solution. As organic crystals are used in several fields (pharmaceuticals, food industry, and so forth), this technique may be useful to produce controlled films or crystals on a substrate without using expensive equipment.

4. EXPERIMENTAL SECTION

4.1. Materials. All materials and solvents were bought from Sigma-Aldrich and used as received if not otherwise specified. TIPS-pentacene and C8-BTBT have been selected to investigate deposition of small molecule thin films, and P3HT and DPPTTT with molecular weight around 30 kDa (purchased from Ossila) have been selected to investigate deposition of high-performance small conjugated polymers. Aceton and isopropanol (IPA) were used to wash the substrates. Microscope glass slides were purchased from Fisherbrand, and oxidized Si wafers are bought from IDB Technologies Ltd.

4.2. Characterization of the Gas Blow-Coated Thin Films. A Nikon Eclipse LV100 microscope equipped with a polarizer was used to take optical images. A Bruker Dektak XT stylus profilometer was used to measure the film thickness. A Bruker MultiMode 8 AFM in tapping mode was used to analyze the morphology of the films. X-ray diffraction measurements were carried out with a PANalytical X'PERT MRD system.

4.3. Device Fabrication and Measurement. Bottom-gate, top-contact OFET configuration was used for device fabrication. Heavily doped n-type silicon substrate served as bottom gate, and ∼290 nm oxide with the capacitance (C) of 10 nF/cm^2 was used as the dielectric layer. The silicon substrates used for gas blow coating of TIPS-pentacene and C8-BTBT solution were washed and sonicated using acetone and IPA and further cleaned by argon plasma treatment. The silicon substrates used for P3HT and DPPTTT were treated using HMDS and OTS, respectively. After deposition, the samples were annealed to eliminate the residual solvents under different conditions: TIPS-pentacene and C8-BTBT films are put in vacuum at 50 °C overnight, whereas P3HT films were annealed in vacuum at 70 °C overnight; finally, DPPTTT films are annealed at 140 °C under N_2 for 40 min. Then, 70 nm thickness of Au was thermally deposited through a shadow mask with the channel length (L) of 20, 40, 60, 80, 100 μm and channel width (W) of 1000 μm for TIPS-pentacene. In the case of C8-BTBT, P3HT, and DPPTTT, 50 nm of Au was used. Electrical measurements were obtained by using an Agilent B1500A semiconductor parameter analyzer in conjunction with a probe station. All measurements were carried out in the ambient environment at room temperature. A straight line fit of $(I_D)^{1/2}$ versus $(V_G - V_{th})$ was used to extract the field-effect mobility (μ) at the saturation regime. The threshold voltage (V_{th}) was extracted from the intercept at zero current.

DOI: 10.1021/acsomega.9b00835
ACS Omega 2019, 4, 11657−11662

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00835.

Details of the setup of gas blow coating system, digital images, optical images, and AFM images of the thin films of small molecular and polymeric OSCs obtained in different conditions, and OFET device performance of TIPS-pentacene, C8-BTBT, P3HT, and DPPTTT (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: Jincheng.tong@manchester.ac.uk (J.T.).
*E-mail: Michael.Turner@manchester.ac.uk (M.L.T.).
*E-mail: cinzia.casiraghi@manchester.ac.uk (C.C.).

ORCID

Jincheng Tong: 0000-0001-7762-1460
Michael L. Turner: 0000-0003-2853-5632
Cinzia Casiraghi: 0000-0001-7185-0377

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

J.T. gratefully acknowledges the University of Manchester for the President Scholarship Award (PDSA). J.T. also thanks Dr. Chaochao-Dun for useful discussions. This work is partially supported by the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme under grants agreement nos. 648417 and 770047.

■ REFERENCES

(1) Sirringhaus, H. 25th Anniversary Article: Organic Field-Effect Transistors: The Path Beyond Amorphous Silicon. *Adv. Mater.* **2014**, *26*, 1319−1335.

(2) Doumbia, A.; Webb, M.; Turner, M.; Behrendt, J.; Wilson, R. *A Printed Electronic Platform for the Specific Detection of Biomolecules, Organic Sensors and Bioelectronics X*; International Society for Optics and Photonics, 2017; p 103640N.

(3) Benduhn, J.; Tvingstedt, K.; Piersimoni, F.; Ullbrich, S.; Fan, Y. L.; Tropiano, M.; McGarry, K. A.; Zeika, O.; Riede, M. K.; Douglas, C. J.; Barlow, S.; Marder, S. R.; Neher, D.; Spoltore, D.; Vandewal, K. Intrinsic non-radiative voltage losses in fullerene-based organic solar cells. *Nat. Energy* **2017**, *2*, 17053.

(4) Tao, Y.; Yang, C.; Qin, J. Organic host materials for phosphorescent organic light-emitting diodes. *Chem. Soc. Rev.* **2011**, *40*, 2943−2970.

(5) Günes, S.; Neugebauer, H.; Sariciftci, N. S. Conjugated polymer-based organic solar cells. *Chem. Rev.* **2007**, *107*, 1324−1338.

(6) Diao, Y.; Shaw, L.; Bao, Z.; Mannsfeld, S. C. B. Morphology control strategies for solution-processed organic semiconductor thin films. *Energy Environ. Sci.* **2014**, *7*, 2145−2159.

(7) Minemawari, H.; Yamada, T.; Matsui, H.; Tsutsumi, J. y.; Haas, S.; Chiba, R.; Kumai, R.; Hasegawa, T. Inkjet printing of single-crystal films. *Nature* **2011**, *475*, 364−367.

(8) Giri, G.; Verploegen, E.; Mannsfeld, S. C. B.; Atahan-Evrenk, S.; Kim, D. H.; Lee, S. Y.; Becerril, H. A.; Aspuru-Guzik, A.; Toney, M. F.; Bao, Z. Tuning charge transport in solution-sheared organic semiconductors using lattice strain. *Nature* **2011**, *480*, 504−508.

(9) Xu, C.; He, P.; Liu, J.; Cui, A.; Dong, H.; Zhen, Y.; Chen, W.; Hu, W. A General Method for Growing Two-Dimensional Crystals of Organic Semiconductors by Solution Epitaxy. *Angew. Chem., Int. Ed.* **2016**, *55*, 9519−9523.

(10) Janneck, R.; Vercesi, F.; Heremans, P.; Genoe, J.; Rolin, C. Predictive Model for the Meniscus-Guided Coating of High-Quality Organic Single-Crystalline Thin Films. *Adv. Mater.* **2016**, *28*, 8007−8013.

(11) Park, S.; Giri, G.; Shaw, L.; Pitner, G.; Ha, J.; Koo, J. H.; Gu, X.; Park, J.; Lee, T. H.; Nam, J. H.; Hong, Y.; Bao, Z. Large-area formation of self-aligned crystalline domains of organic semiconductors on transistor channels using CONNECT. *Proc. Natl. Acad. Sci. U.S.A.* **2015**, *112*, 5561−5566.

(12) Diao, Y.; Tee, B. C.-K.; Giri, G.; Xu, J.; Kim, D. H.; Becerril, H. A.; Stoltenberg, R. M.; Lee, T. H.; Xue, G.; Mannsfeld, S. C. B.; Bao, Z. Solution coating of large-area organic semiconductor thin films with aligned single-crystalline domains. *Nat. Mater.* **2013**, *12*, 665−671.

(13) Sele, C. W.; Kjellander, B. K. C.; Niesen, B.; Thornton, M. J.; van der Putten, J. B. P. H.; Myny, K.; Wondergem, H. J.; Moser, A.; Resel, R.; van Breemen, A. J. J. M.; van Aerle, P.; Anthony, J. E.; Gelinck, G. H. Controlled deposition of highly ordered soluble acene thin films: effect of morphology and crystal orientation on transistor performance. *Adv. Mater.* **2009**, *21*, 4926−4931.

(14) Chang, J.; Chi, C.; Zhang, J.; Wu, J. Controlled Growth of Large-Area High-Performance Small-Molecule Organic Single-Crystalline Transistors by Slot-Die Coating Using A Mixed Solvent System. *Adv. Mater.* **2013**, *25*, 6442−6447.

(15) Lee, W. H.; Kim, D. H.; Jang, Y.; Cho, J. H.; Hwang, M.; Park, Y. D.; Kim, Y. H.; Han, J. I.; Cho, K. Solution-processable pentacene microcrystal arrays for high performance organic field-effect transistors. *Appl. Phys. Lett.* **2007**, *90*, 132106.

(16) Uemura, T.; Hirose, Y.; Uno, M.; Takimiya, K.; Takeya, J. Very high mobility in solution-processed organic thin-film transistors of highly ordered [1] benzothieno [3, 2-b] benzothiophene derivatives. *Appl. Phys. Express* **2009**, *2*, 111501.

(17) Li, H.; Tee, B. C.-K.; Giri, G.; Chung, J. W.; Lee, S. Y.; Bao, Z. High-Performance Transistors and Complementary Inverters Based on Solution-Grown Aligned Organic Single-Crystals. *Adv. Mater.* **2012**, *24*, 2588−2591.

(18) Minemawari, H.; Yamada, T.; Hasegawa, T. Crystalline film growth of TIPS-pentacene by double-shot inkjet printing technique. *Jpn. J. Appl. Phys.* **2014**, *53*, 05HC10.

(19) Rigas, G.-P.; Payne, M. M.; Anthony, J. E.; Horton, P. N.; Castro, F. A.; Shkunov, M. Spray printing of organic semiconducting single crystals. *Nat. Commun.* **2016**, *7*, 13531.

(20) Albert, M. R.; Mcgilvary, W. R. Thermal Effects Due to Air-Flow and Vapor Transport in Dry Snow. *J. Glaciol.* **1992**, *38*, 273−281.

(21) Huang, F.; Dkhissi, Y.; Huang, W.; Xiao, M.; Benesperi, I.; Rubanov, S.; Zhu, Y.; Lin, X.; Jiang, L.; Zhou, Y.; Gray-Weale, A.; Etheridge, J.; McNeill, C. R.; Caruso, R. A.; Bach, U.; Spiccia, L.; Cheng, Y.-B. Gas-assisted preparation of lead iodide perovskite films consisting of a monolayer of single crystalline grains for high efficiency planar solar cells. *Nano Energy* **2014**, *10*, 10−18.

(22) Ding, J.; Han, Q.; Ge, Q.-Q.; Xue, D.-J.; Ma, J.-Y.; Zhao, B.-Y.; Chen, Y.-X.; Liu, J.; Mitzi, D. B.; Hu, J.-S. Fully Air-Bladed High-Efficiency Perovskite Photovoltaics. *Joule* **2018**, *3*, 402.

(23) Seok, J. Y.; Yang, M. A Novel Blade-Jet Coating Method for Achieving Ultrathin, Uniform Film toward All-Solution-Processed Large-Area Organic Light-Emitting Diodes. *Adv. Mater. Technol.* **2016**, *1*, 1600029.

(24) He, Z.; Chen, J.; Sun, Z.; Szulczewski, G.; Li, D. Air-flow navigated crystal growth for TIPS pentacene-based organic thin-film transistors. *Org. Electron.* **2012**, *13*, 1819−1826.

(25) Li, H.; Tee, B. C.-K.; Cha, J. J.; Cui, Y.; Chung, J. W.; Lee, S. Y.; Bao, Z. High-mobility field-effect transistors from large-area solution-grown aligned C60 single crystals. *J. Am. Chem. Soc.* **2012**, *134*, 2760−2765.

(26) Xiao, C.; Kan, X.; Liu, C.; Jiang, W.; Zhao, G.; Zhao, Q.; Zhang, L.; Hu, W.; Wang, Z.; Jiang, L. Controlled formation of large-area single-crystalline TIPS-pentacene arrays through superhydro-

DOI: 10.1021/acsomega.9b00835
ACS Omega 2019, 4, 11657−11662

phobic micropillar flow-coating. *J. Mater. Chem. C* **2017**, *5*, 2702−2707.
(27) Giri, G.; Li, R.; Smilgies, D.-M.; Li, E. Q.; Diao, Y.; Lenn, K. M.; Chiu, M.; Lin, D. W.; Allen, R.; Reinspach, J. One-dimensional self-confinement promotes polymorph selection in large-area organic semiconductor thin films. *Nat. Commun.* **2014**, *5*, 3573.
(28) Lim, J. A.; Lee, W. H.; Lee, H. S.; Lee, J. H.; Park, Y. D.; Cho, K. Self-organization of ink-jet-printed triisopropylsilylethynyl pentacene via evaporation-induced flows in a drying droplet. *Adv. Funct. Mater.* **2008**, *18*, 229−234.
(29) Haase, K.; Teixeira da Rocha, C.; Hauenstein, C.; Zheng, Y.; Hambsch, M.; Mannsfeld, S. C. B. High-Mobility, Solution-Processed Organic Field-Effect Transistors from C8-BTBT: Polystyrene Blends. *Adv. Electron. Mater.* **2018**, *4*, 1800076.
(30) Wang, Q.; Qian, J.; Li, Y.; Zhang, Y.; He, D.; Jiang, S.; Wang, Y.; Wang, X.; Pan, L.; Wang, J.; Wang, Z.; Nan, H.; Ni, Z.; Zheng, Y.; Shi, Y. 2D Single-Crystalline Molecular Semiconductors with Precise Layer Definition Achieved by Floating-Coffee-Ring-Driven Assembly. *Adv. Funct. Mater.* **2016**, *26*, 3191−3198.
(31) Liu, C.; Minari, T.; Lu, X.; Kumatani, A.; Takimiya, K.; Tsukagoshi, K. Solution-processable organic single crystals with bandlike transport in field-effect transistors. *Adv. Mater.* **2011**, *23*, 523−526.
(32) Wang, G.; Swensen, J.; Moses, D.; Heeger, A. J. Increased mobility from regioregular poly (3-hexylthiophene) field-effect transistors. *J. Appl. Phys.* **2003**, *93*, 6137−6141.
(33) Yang, H.; Shin, T. J.; Yang, L.; Cho, K.; Ryu, C. Y.; Bao, Z. Effect of Mesoscale Crystalline Structure on the Field-Effect Mobility of Regioregular Poly(3-hexyl thiophene) in Thin-Film Transistors. *Adv. Funct. Mater.* **2005**, *15*, 671−676.
(34) Chen, Z.; Lee, M. J.; Shahid Ashraf, R.; Gu, Y.; Albert-Seifried, S.; Meedom Nielsen, M.; Schroeder, B.; Anthopoulos, T. D.; Heeney, M.; McCulloch, I. High-Performance Ambipolar Diketopyrrolopyrrole-Thieno[3,2-b]thiophene Copolymer Field-Effect Transistors with Balanced Hole and Electron Mobilities. *Adv. Mater.* **2012**, *24*, 647−652.
(35) Sirringhaus, D.; Nikolka, M.; Sadhanala, A.; Lemaur, V.; Zelazny, M.; Kepa, M.; Hurhangee, M.; Kronemeijer, A. J.; Pecunia, V.; Nasrallah, I.; Broch, K.; McCulloch, I.; Emin, D.; Olivier, Y.; Cornil, J.; Beljonne, D.; Sirringhaus, H. Approaching disorder-free transport in high-mobility conjugated polymers. *Nature* **2014**, *515*, 384.
(36) https://www.ossila.com/products/dpp-dtt-polymer.

DOI: 10.1021/acsomega.9b00835
ACS Omega 2019, 4, 11657−11662