

Investigation of solution-processed organic thin film transistors based on α,ω -hexyl-distyryl-bithiophene (DH-DS2T): growth and transport properties

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We have studied drops of a semiconducting oligomer as active layer in organic thin film transistor (OTFT) devices. A small molecule, α,ω -hexyl-distyryl-bithiophene (DH-DS2T), was used as a hole transporting active layer. Structure and morphology of thin films have been studied by X-ray diffraction and optical microscopy. Depending of ink's parameters (solvent, concentration), a comparative analysis of both electrical response and film crystallinity obtained under identical measurement conditions was realized.

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1. Introduction

Solution-processable electronics have attracted considerable attention and research. They combine simple additive processing with novel low-cost materials and have the potential to drastically lower the cost of integrated circuit fabrication, especially compared to conventional silicon processing. In recent years, organic materials, as small molecule and polymeric semiconductors, have been implied in low-cost solution processing techniques, as spin-coating, drop-casting, dip-coating or inkjet-printing, to form the active channel materials for organic thin-film transistors (OTFTs). Performances of OTFTs have been continually improving to the point of now being viable in integrated circuit applications [1-4], with potential use in future products such as low-cost flexible radiofrequency identification (RFID) tags [5], active matrix displays [6-8] and sensing devices [9]. More recently, soluble small-molecule systems provided the high performances of vapor deposited systems with the convenience of low-cost solution-based processing techniques. Owing to their compatibility with flexible substrates, semiconducting oligomers can be used as active materials in printed electronics. Printed flexible electronics' has the potential to be a truly disruptive technology by enabling the pervasive introduction of electronic devices in our everyday lives. From the materials standpoint, the main challenge of flexible electronics is the ability to deposit and process semiconductor layers at low temperature on large area coating and throughout satisfactory

performances. When properly designed, the oligomers dissolve in common organic solvents and can be processed from liquid solution at room temperature. A classical approach to soluble materials relies on functionalization of linearly oligomers with substituents to increase the solubility of these oligomers in common organic solvents. This leads to 'semiconducting inks' that can be deposited using low-cost technologies such as spin-coating, drop or inkjet. Spin-coating and drop-casting can offer rapid and versatile solution processed OTFTs while direct printing techniques are mentioned to be one of the key-technologies to fabricating plastic electronic devices [10].

Recently, we reported a new series of structurally simple and readily available oligothiophene derivatives end-capped with styryl units, DS_nT ($n = 2-4$), that were used as the semiconducting layer in OTFTs [11]. The devices not only showed very high field-effect mobility (up to 0.1 cm²/Vs) and on/off ratios (up to 105), but were also found to be exceptionally long-lived (more than one year of storage) and stable toward continuous operation, under atmospheric conditions. As these conjugated cores were shown to lead to long-term stability, we thus decided to synthesize and investigate di- n -hexyl-terminated analogues [12-14]. In this study, the α,ω -hexyl-distyryl-bithiophene (DH-DS2T) was used as a soluble small molecule to form the active layer (scheme 1). The substitution by alkyl chains on the α,ω -end positions of organic semiconductors has been used as a simple approach to increase their solubility and thus their processability in transistors. Using a single transistor, in a standard bottom-gate bottom-contact configuration with

source-drain electrodes as two gold plots (channel length $L = 50 \mu\text{m}$, channel width $W = 1 \text{ mm}$), the highest mobility values up to 3.5×10^{-5} and $2.5 \times 10^{-5} \text{ cm}^2/\text{V.s}$ are obtained for DH-DS2T thin films drop-casting from solutions at 0.82 mg/mL in dichloromethane and 3 mg/mL in chlorobenzene, respectively [14]. In order to investigate a simple circuit, we describe herein the transistor behavior of DH-DS2T drop-casted on interdigital structure (channel length $L = 50 \mu\text{m}$, channel width $W = 132 \text{ mm}$). Using the same solutions, a mobility up to $1.5 \times 10^{-4} \text{ cm}^2/\text{V.s}$ is obtained for DH-DS2T thin films drop-casting from the solution at 0.82 mg/mL in dichloromethane.

2. Experimental part

The synthesis of DH-DS2T has been described previously [12-13]. The chemical structure of DH-DS2T is shown on Fig. 1. The product was purified on a silica gel column eluting with a mixture dichloromethane-cyclohexane (1:4, v/v). The desired fractions were collected and evaporated to dryness to afford the *E* isomer.

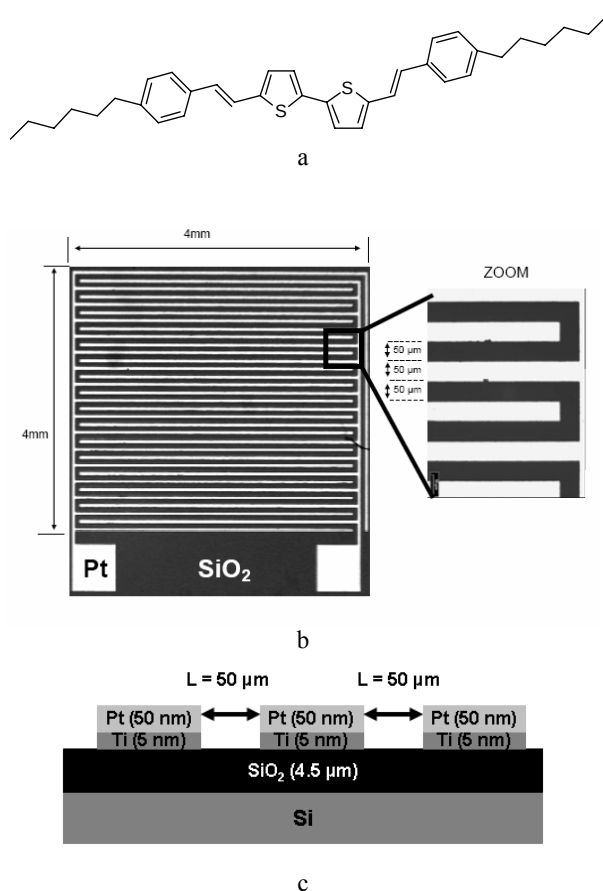


Fig. 1. (a) Molecular structure of α,ω -hexyl-distyryl-bithiophene (DH-DS2T). Top view (b) and cross section (c) of OTFT structure.

Bottom-contact (BC) configuration was used for the OTFT devices. Highly p-doped silicon wafers (gate), covered with thermally grown silicon oxide SiO_2 (4.5 μm , insulator layer), were used as bottom-gate substrates. The capacitance per unit area of silicon dioxide dielectric layers was 0.76 nF/cm^2 . The source and drain electrodes were obtained from a sputtered platinum (Pt) film, using photolithography and lift off processes. An adhesive layer of 5 nm in Titanium (Ti) is deposited prior the Pt deposition. The final interdigital structure (channel length $L = 50 \mu\text{m}$, channel width $W = 132 \text{ mm}$) is represented in Fig. 1. Current-voltage characteristics were obtained at room temperature under ambient conditions with Hewlett-Packard 4140B pico-amperemeter-DC voltage sources. The source-drain current (I_D) in the saturation regime is governed by the equation:

$$(I_D)_{\text{sat}} = (W/2L) C_i \mu (V_G - V_t)^2 \quad (1)$$

where C_i is the capacitance per unit area of the gate insulator layer, V_G is the gate voltage, V_t is the threshold voltage, and μ is the field-effect mobility. The on/off ratio values given in Table 1 were determined from the I - V transfer plots under a constant drain-source voltage $V_D = -30 \text{ V}$.

The DH-DS2T active layer was realized by vacuum evaporation and drop casting:

(i) For vapor processed OTFTs, DH-DS2T was vacuum deposited onto the substrates using a Edwards Auto 306 apparatus, at a rate of 7 nm/min under a pressure of $1.6 \times 10^{-6} \text{ mbar}$ to a nominal thickness of 80 nm as determined with a in situ quartz crystal monitor.

(ii) For drop-casting, two different solvents were used, dichloromethane (CH_2Cl_2) and chlorobenzene (CB), with boiling points (bp) of 40°C and 131°C , respectively. The solubility limit in both solvent, CH_2Cl_2 and CB, was evaluated to be 7.91 mol/L corresponding to 4.26 mg/mL [14]. DH-DS2T solutions in dichloromethane stabilized by methanol had a concentration of 0.82 and 4.26 mg/mL while in chlorobenzene a solution of 3 mg/mL was used. The DH-DS2T-solution was added dropwise at a volume of $5 \mu\text{L}$ onto the complete surface of the devices. Such volume covered entirely the channel of one OTFT. After the organic-solution deposition, different post-treatments were realized: vacuum ($1.3 \times 10^{-6} \text{ mbar}$) during 3 hours for dichloromethane-based solutions or heated to 110°C during 3 h in air for chlorobenzene-based solutions.

The as-deposited thin films were characterized using an X-ray diffractometer (Rigaku Co., ATX-G) which was specially designed for characterization of thin films in air. The used wavelength of X-ray in the experiments was 0.1542 nm .

Table 1. Charge carrier mobility (μ), on/off ratio (I_{ON}/I_{OFF}) and threshold voltage (V_t) for OTFTs with DH-DS2T-organic active layers processed by vapor and drop-casting deposition methods on Si/SiO₂ substrates equipped by Pt interdigital source and drain electrodes.

DH-DS2T deposition method	Post-treatment of DH-DS2T film	Solvent (concentration)	μ (cm ² /Vs)	I_{ON}/I_{OFF}	V_t (V)
vapor	No	×	4.3×10^{-4}	1×10^4	21
drop-casting	vacuum ^a	CH ₂ Cl ₂ (0.82 mg/mL)	1.5×10^{-4}	4.9×10^2	48
		CH ₂ Cl ₂ (4.26 mg/mL)	8.7×10^{-5}	6.5×10^2	68
	Heating ^b	CB (3 mg/mL)	2.1×10^{-5}	1.2×10^0	117

No = no post treatment

^avacuum at 1.3×10^{-6} mbar during 3 hours

^bheating at 110°C during 3 hours

3. Results and discussion

Structure of the DH-DS2T based drops, deposited on interdigital structures, was investigated by optical microscopy. A direct influence of solvent is observed. The microstructure of OTFT processed by drop-casting from dichloromethane-based solutions present a pronounced “coffee-staining effect” with the formation of multiple rings (Fig. 2a), while OTFT processed from chlorobenzene-based solution present a uniform surface as evidenced by the slight change in shading (figure 2b). Such formation of successive rings is due to a concomitant effect of (i) an evaporation rate enhanced near the drop’s edge compared to that at the center and (ii) geometrical constraints of the drying drop to the edge due to existing solids [15]. This phenomenon produces ring like stains and occurs for a wide range of surfaces, solvents, and solutes. However, using a solvent with a high boiling point, as chlorobenzene (bp = 131°C), this phenomenon disappears as the evaporation rate strongly decreases.

The ability to deposit and tailor reliable semiconducting films is indispensable for contemporary solid-state electronics where vacuum-evaporated organic thin films are commonly show as reference in term of charge transport properties. This study is correlated with the fabrication and the characterization of OTFTs based on vacuum-evaporated DH-DS2T thin films as active layer on interdigital substrates. Fig. 3a shows the optical microscopy image of a thin film deposited by vacuum evaporation. Both electrodes and channel are covered by a uniform organic thin film while a large number of crystals are formed in thin films deposited by drop-casting from both solutions (Fig. 3b and c). A random orientation of crystals on the surface is observed for both DH-DS2T based drops with bigger crystals for processed by drop-casting from the chlorobenzene-based solution.

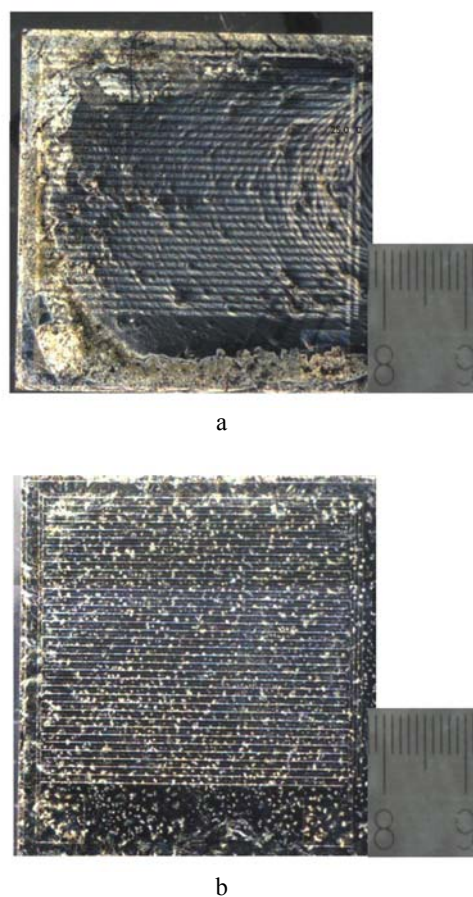
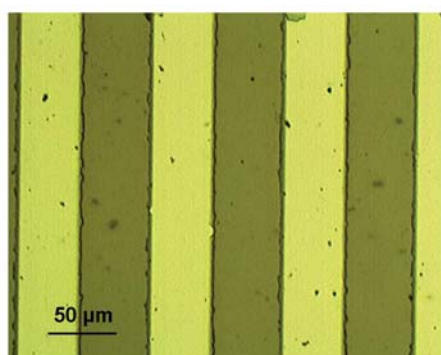
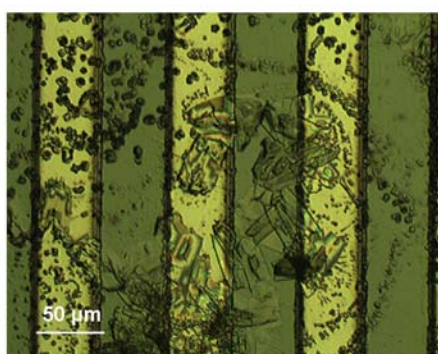


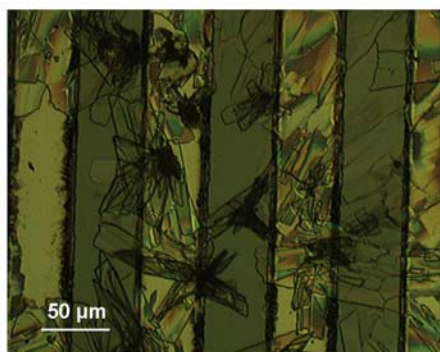
Fig. 2. Optical microscopy images of thin films deposited by drop-casting on OTFT structure. For (a): from a solution in dichloromethane at 0.82 mg/mL and vacuum during 3 hours as post-treatment. For (b): from a solution in chlorobenzene at 3 mg/mL and heating to 110°C during 3 hours as post-treatment.



a



b



c

Fig. 3. Optical microscopy images of thin films deposited by vacuum evaporation (a) and drop-casting (b and c) on Si/SiO₂ substrates. For (b): from a solution in dichloromethane at 0.82 mg/mL and vacuum during 3 hours as post-treatment. For (c): from a solution in chlorobenzene at 3 mg/mL and heating to 110°C during 3 hours as post-treatment.

The structure of DH-DS2T films grown on Si/SiO₂ substrates by vacuum evaporation and drop-casting were studied by XRD. As already reported for solid state thin films based on DH-DSnT ($n = 2$ and 4), patterns present the occurrence of (00l) progressions which means that the *ab*-planes of the grains are mainly oriented parallel to the

substrate surface [12-14]. Figure 4 compares the out-of-plane patterns obtained for vapor-deposited and drop-casted films. X-ray diffraction patterns of DH-DS2T drop-casted thin films are characterized by sharp and strong reflections as observed for vacuum-deposited films. Additionally to an identical crystal structure, the occurrence of progressions up to (0013) is indicative of long-range ordering in vacuum deposited and drop-casted thin films. Thin films consist of highly oriented polycrystals having an interplanar *d*-spacing of 3.45 nm. A molecular length of $\sim 3.4 - 3.5$ nm indicates that DH-DS2T adopts mainly an upright orientation on the substrate as schematically represented in Fig. 5.

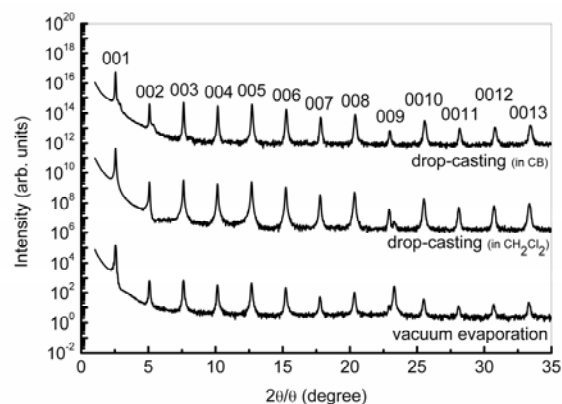


Fig. 4. Out-of-plane X-ray diffraction patterns of DH-DS2T-based films deposited onto Si/SiO₂ substrates by vacuum evaporation and drop-casting.

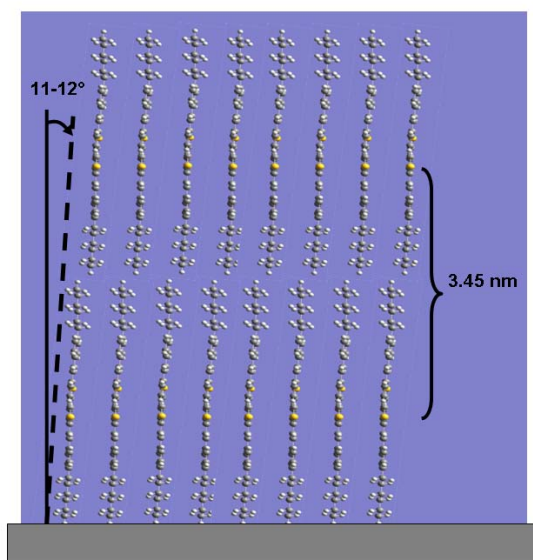


Fig. 5. Schematic organization of DH-DS2T in thin films processed by vacuum evaporation and drop-casting (from solution in dichloromethane and in chlorobenzene).

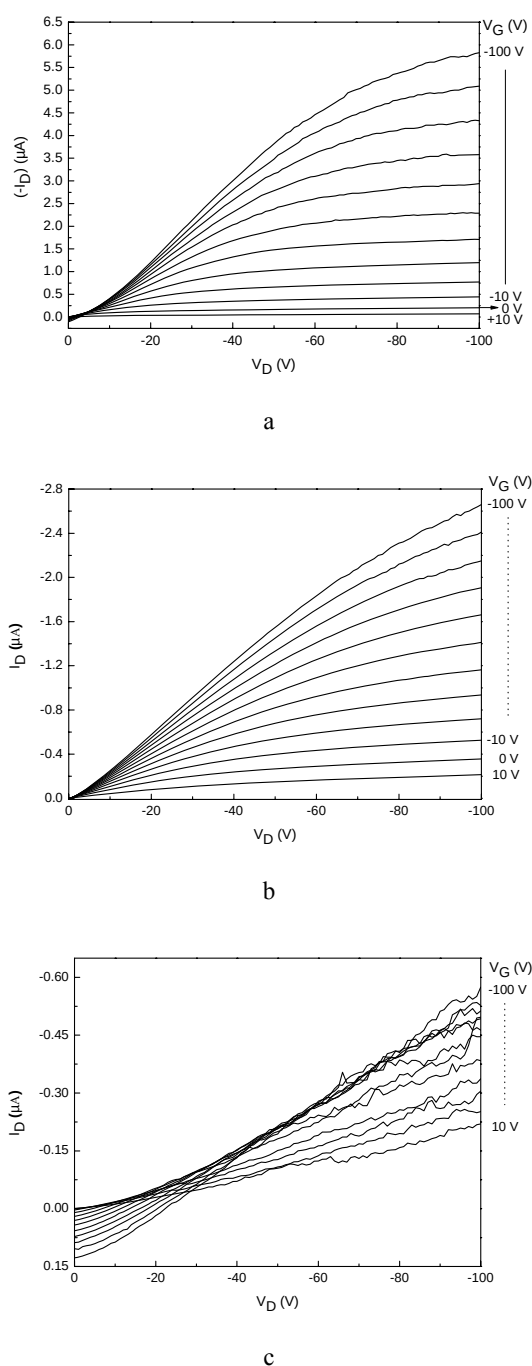


Fig. 6. Output characteristic of OTFTs with DH-DS2T as active layer processed by vacuum evaporation (a) and drop-casting (b and c) on OTFT structure. For (b): from a solution in dichloromethane at 0.82 mg/mL and vacuum during 3 hours as post-treatment. For (c): from a solution in chlorobenzene at 3 mg/mL and heating to 110°C during 3 hours as post-treatment.

Current-voltage characteristics were performed in air at room temperature on OTFTs as active layer processed by vacuum evaporation and drop-casting (Fig. 6). Table 1

collects the electrical data in terms of mobility (μ), threshold voltage (V_t) and current on/off ratio (I_{ON}/I_{OFF}) obtained with equation (1). Transistor responses were obtained only for negative bias, which is indicative that DH-DS2T is a p-type semiconductor. As a reference, devices based on vacuum-evaporated organic thin films work in the accumulation mode with the presence of a well-defined linear regime at $V_D < V_G$ followed by a saturation regime at $V_D > V_G$. Hole mobilities as high as $4.3 \times 10^{-4} \text{ cm}^2/\text{V.s}$ with a positive threshold voltage (V_t) of 21 V and a high on/off ratio (up to 10^4) are achieved. A comparative mobility is obtained for an OTFT with DH-DS2T as active layer processed by drop-casting from a solution in dichloromethane at 0.82 mg/mL. By increasing the concentration to the solubility limit (4.26 mg/mL) lower performances are obtained. While chlorobenzene is often used in inkjet printing processes, the current-voltage characteristic loses its feature and the transport properties decreased by one order for μ and even four orders for I_{ON}/I_{OFF} . The dichloromethane remains the solvent the more appropriate for OTFTs processed by drop-casting form a small soluble organic semiconductor as DH-DS2T.

4. Conclusion

We have investigated p-channel OTFTs in an interdigital structure based on α,ω -hexyl-distyryl-bithiophene (DH-DS2T) fabricated using drop-casting as deposition method. The presence of the terminal alkyl chains allows the introduction of properties such as solubility in organic solvents. DH-DS2T dissolves in common organic solvents and can be processed from liquid solution at room temperature in OTFTs. A low and a relatively high boiling point solvent, dichloromethane and chlorobenzene, were chosen, respectively. The electrical performances (μ , V_t and I_{ON}/I_{OFF}) and thin films morphology of OTFTs realized by drop casting were studied. Different parameters linked directly to the process (solvent, concentration,...) are identified as key factors controlling film quality/crystallinity and device performances.

References

- [1] H. Sirringhaus, N. Tessler, R.H. Friend, *Sciences* **280**, 1741 (1998).
- [2] H. Sirringhaus, N. Tessler, R.H. Friend, *Synth. Met.* **102**, 857 (1999).
- [3] C. D. Sheraw, L. Zhou, J. R. Huang, D.J. Gundlach, T. N. Jackson, M. G. Kane, I. G. Hill, M. S. Hammond, J. Campi, B.K. Greening, J. Francel, J. West, *Appl. Phys. Lett.* **80**, 1088 (2002).
- [4] W. Fix, A. Ullmann, J. Ficker, W. Clemens, *Appl. Phys. Lett.* **81**, 1735 (2002).
- [5] E. Cantatore, T.C.T. Geuns, G.H. Gelinck, E. van Veenendaal, A.F.A. Gruijthuijsen, L. Schrijnemakers, S. Drews, D.M. De Leeuw, *IEEE J. Solid-State Circ.* **42**, 84 (2007).

- [6] G. H. Gelinck, H. Edzer A. Huitema, E. van Veenendaal, E. Cantatore, L. Schrijnemakers, J. B. P. H. van der Putten, T. C. T. Geuns, M. Beenhakkers, J. B. Giesbers, B.-H. Huisman, E. J. Meijer, E. M. Benito, F. J. Touwslager, A. W. Marsman, B. J. E. van Rens, D.M. de Leeuw, *Nature Mater.* **3**, 106 (2004).
- [7] P. van Lieshout, E. van Veenendaal, L. Schrijnemakers, G. Gelinck, F. Touwslager, E. Huitema, *Solid-State Circuits Conference, Digest of Technical Papers ISSCC*, **1**, 578 (2005).
- [8] L. Zhou, A. Wanga, S.-C. Wu, J. Sun, S. Park, T. N. Jackson, *Appl. Phys. Lett.* **88**, 083502 (2006).
- [9] B. Crone, A. Dodabalapur, A. Gelperin, L. Torsi, H. E. Katz, A. J. Lovinger, Z. Bao, *Appl. Phys. Lett.* **78**, 2229 (2001).
- [10] Y. Wu, Y. Li, B.S. Ong, *J. Am. Chem. Soc.* **129**, 1862 (2007).
- [11] C. Videlot-Ackermann, J. Ackermann, H. Brisset, K. Kawamura, N. Yoshimoto, P. Raynal, A. El Kassmi, F. Fages, *J. Am. Chem. Soc.* **127**, 16346 (2005).
- [12] C. Videlot-Ackermann, H. Brisset, J. Ackermann, J. Zhang, P. Raynal, F. Fages, G.H. Mehl, T. Tnaniawa, N. Yoshimoto, *Org. Elect.* **9**, 591 (2008).
- [13] Y. Didane, C. Videlot-Ackermann, H. Brisset, J. Ackermann, P. Raynal, F. Fages, G. H. Mehl, *Mol. Cryst. Liq. Cryst.* **507**, 178 (2009).
- [14] Y. Didane, C. Martini, M. Barret, S. Sanaur, P. Collot, J. Ackermann, F. Fages, A. Suzuki, N. Yoshimoto, H. Brisset, C. Videlot-Ackermann. Submitted.
- [15] R. D. Deegan, O. Bakajin, T. F. Dupont, G. Hber, S. R. Nagel, T.A. Witten. *Nature*, **389**, 827 (1997).

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