

# Towards solution-processed ambipolar organic thin film transistors based on $\alpha,\omega$ -hexyl-distyryl-bithiophene (DH-DS2T) and a fluorocarbon-substituted dicyanoperylene (PDIF-CN<sub>2</sub>)

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Drop casting of solutions based on oligomers as active layers in organic thin film transistors (OTFTs) was studied towards the realization of solution-processed ambipolar devices. As p- and n-type semiconductors,  $\alpha,\omega$ -hexyl-distyryl-bithiophene (DH-DS2T) and *N,N'*-1H,1H-perfluorobutyl dicyanoperylene diimide (PDIF-CN<sub>2</sub>) were used, respectively. Solutions were prepared by mixing different ratios of PDIF-CN<sub>2</sub> versus DH-DS2T. Structure and morphology of thin films were studied by X-ray diffraction (XRD) and atomic force microscopy (AFM). With the fine tuning of PDIF-CN<sub>2</sub> amount, both p- and n- charge carrier transport could be measured in OTFT devices based on blend DH-DS2T:PDIF-CN<sub>2</sub> as active layer to form so-called ambipolar OTFTs.

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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 molecules and polymeric semiconductors, have been implied in low-cost solution processing techniques, as spin-coating, drop-casting, dip-coating or inkjet-printing, to form active materials in organic thin-film transistors (OTFTs). Performances of OTFTs have been continually improving up to the point of now being viable in integrated circuit applications, with potential use in future products such as low-cost flexible radiofrequency identification (RFID) tags, display drivers, smart cards and sensing devices [1-6]. Additionally, the joint use of p-channel transistors combined with n-channel transistors, opens new perspectives in the field of organic electronics, in particular through the realization of organic complementary logic. Compared to circuits using only one type of transistors, complementary circuits can be more easily designed and secondly it expected to improve

performances in terms of speed and consumption devices. From the point of view of organic materials, some soluble small-molecule systems provided similar or even highest performances than 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. 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 oligomer solubility.

A new series of structurally simple and readily available oligothiophene derivatives end-capped with styryl units, DS<sub>n</sub>Ts (n = 2-4), were used as p-type semiconducting layers in OTFTs [7]. The devices not only showed high field-effect mobility (up to 0.1 cm<sup>2</sup>/V.s) and on/off ratios (up to 10<sup>5</sup>), but were also found to be exceptionally long-lived (more than one year of storage) and stable toward continuous operation, under atmospheric

conditions. The substitution by alkyl chains on  $\alpha,\omega$ -end positions of the bithiophene derivative to obtain the  $\alpha,\omega$ -hexyl-distyryl-bithiophene (DH-DS2T) has been used as a simple approach to increase its solubility and thus its processability in transistors [8-11]. A hole mobility up to  $1.5 \times 10^{-4} \text{ cm}^2/\text{V.s}$  was obtained for DH-DS2T thin films drop-casting, from a solution at 0.82 mg/mL in dichloromethane, on source and drain interdigital structure (channel length  $L = 50 \text{ }\mu\text{m}$ , channel width  $W = 132 \text{ mm}$ ) [11]. Concerning n-type semiconductors, there have been so far few reports on high performing n-type OTFTs [12-14], notable among them, the perylene alkyldiimide (PDIR) family holds the distinction of having one of the highest n-type mobilities known, 0.2-0.6  $\text{cm}^2/\text{V.s}$ , uncorrected for contact resistance and 1.7  $\text{cm}^2/\text{V.s}$  when corrected [15-17]. In addition to these outstanding electrical properties reported for vapor deposited films, PDIR-based materials, particularly those core-functionalized with cyano groups (PDIR-CN<sub>2</sub>), have demonstrated great promise due to their ability to yield high performing semiconductor films from solution, but also due to their air-stable device operation [18-20]. Usually fluorocarbon- versus hydrocarbon-functionalization of the aromatic cores leads to far less processable materials in conventional organic solvents. However in the fluorocarbon-substituted dicyanoperylene series, the compound *N,N'*-1*H*,1*H*-perfluorobutyl dicyanoperylene diimide (PDIF-CN<sub>2</sub>, Polyera ActivInk™ N1100) is unique since it combines solution processability characteristics and excellent semiconductor properties with electron mobilities up to 0.15  $\text{cm}^2/\text{V.s}$  when deposited by spin-coating [21,22].

Herein we report the realization of bottom-gate bottom-contact ambipolar OTFTs based on drop-casted films from either single DH-DS2T and PDIF-CN<sub>2</sub> solutions or mixed ones. Different mixed solutions based on both DH-DS2T and PDIF-CN<sub>2</sub> compounds were performed according to a defined ratio (% of PDIF-CN<sub>2</sub> versus DH-DS2T) and deposited by drop casting on substrates equipped by interdigital source and drain electrodes. The fine tuning of amounts of both oligomers contained in the mixed solution led us to the realization in air of solution-processed ambipolar OTFTs.

## 2. Experimental part

The DH-DS2T synthesis has been described previously [8,9]. 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. PDIF-CN<sub>2</sub> was synthesized at Polyera Corporation and it is commercially available under the trade name of ActivInk™ N1100 [23]. The chemical structures of DH-DS2T and PDIF-CN<sub>2</sub> are shown on Figure 1a.

Bottom-gate bottom-contact (BG-BC) configuration was used for the OTFT devices. Highly p-doped silicon wafers (gate), covered with thermally grown silicon dioxide SiO<sub>2</sub> (4.5  $\mu\text{m}$ , insulator layer), were used as

bottom-gate substrates. The capacitance per unit area of SiO<sub>2</sub> dielectric layers was 0.76 nF/cm<sup>2</sup>. 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 to the Pt deposition. The final interdigital structure (channel length  $L = 50 \text{ }\mu\text{m}$ , channel width  $W = 132 \text{ mm}$ ) is represented in Fig. 1b and 1c. Current-voltage characteristics were obtained at room temperature under ambient conditions with Hewlett-Packard 4140B pico-ampere-meter-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  $\mu$  is the field-effect mobility.

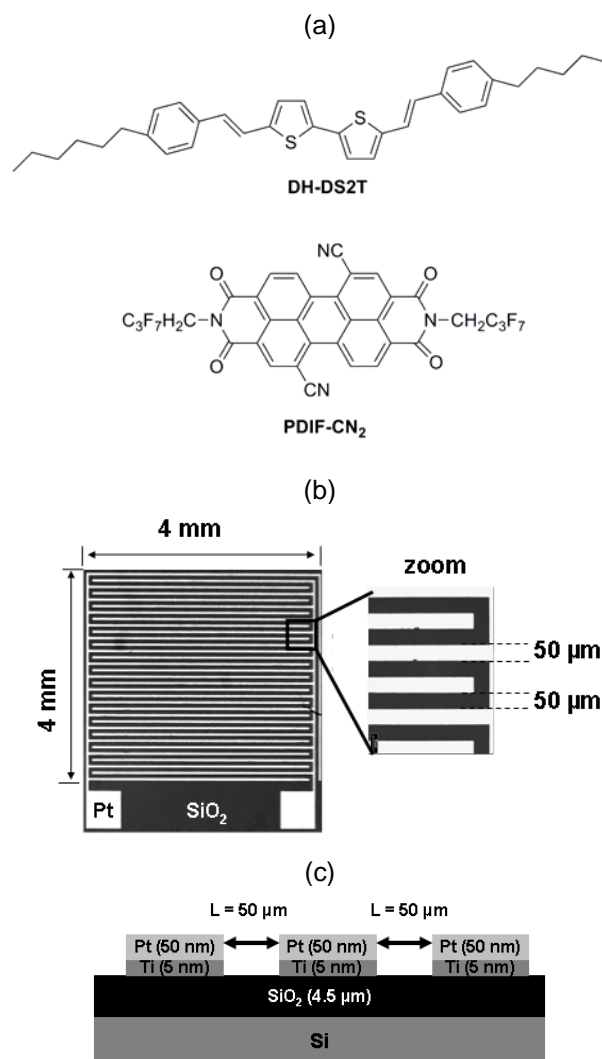


Fig. 1. (a) Molecular structure of  $\alpha,\omega$ -hexyl-distyryl-bithiophene (DH-DS2T) and *N,N'*-1*H*,1*H*-perfluorobutyl dicyanoperylene diimide (PDIF-CN<sub>2</sub>). Top view (b) and cross section (c) of OTFT structures.

The active layers were realized by drop casting of solutions prepared in chloroform ( $\text{CHCl}_3$ ). DH-DS2T based solution in  $\text{CHCl}_3$  had a concentration of 0.82 mg/mL, while PDIF-CN<sub>2</sub> based solutions in  $\text{CHCl}_3$  had a concentration of 3-5 mg/mL. Different mixed DH-DS2T and PDIF-CN<sub>2</sub> containing solutions in  $\text{CHCl}_3$  (called mixed DH-DS2T:PDIF-CN<sub>2</sub> solutions) were preparing by varying the molar fraction of PDIF-CN<sub>2</sub> versus DH-DS2T. The as-prepared solutions contained 0, 37, 55, 70 and 100% of PDIF-CN<sub>2</sub>. The solution was added dropwise at a volume of 30  $\mu\text{L}$  onto the complete surface of the devices. After the organic-solution deposition, a heating to 110°C during 30 min under argon of devices was realized.

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. Atomic force microscopy (AFM) measurements were done on thin films in air with a SII NanoTechnology inc., S-image operating in tapping mode.

### 3. Results and discussion

Thin film morphology was investigated by AFM for DH-DS2T, PDIF-CN<sub>2</sub> and DH-DS2T:PDIF-CN<sub>2</sub> thin films grown on Si/SiO<sub>2</sub> substrates by drop-casting (Figure 2). For drop-casted DH-DS2T thin films (Fig. 2a), AFM pictures show a polycrystalline morphology where monolayer terraces are clearly observed with an average value of 3.2 nm as determined for the steps height and corresponding to the molecular length ( $\sim 3.4$ -3.5 nm) [10]. On the contrary, PDIF-CN<sub>2</sub> film exhibit small rounded protrusions even after thermal annealing without evidence of microstructural organization (Fig. 2b). Fig. 2c shows the AFM picture of a thin film deposited on bare Si/SiO<sub>2</sub> from a DH-DS2T:PDIF-CN<sub>2</sub> mixed solution in  $\text{CHCl}_3$  containing 50% of PDIF-CN<sub>2</sub>. The film presents the coexistence of small rounded protrusions and larger domains without reaching a polycrystalline morphology.

In order to get details in microstructure-function relationships between ordering in organic thin films and charge transport properties, X-ray diffraction experiments are crucial. The structure of DH-DS2T, PDIF-CN<sub>2</sub> and DH-DS2T:PDIF-CN<sub>2</sub> films grown on Si/SiO<sub>2</sub> substrates by drop-casting were studied by XRD (Figure 3). As already reported for solid state thin films based on DH-DS2T, patterns present the occurrence of (001) progressions which means that the *ab*-planes of the grains are mainly oriented parallel to the substrate surface [10,11]. 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 (0010) is indicative of long-range ordering in drop-casted thin films. Thin films consist of highly oriented poly-crystals 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 [11]. On the contrary for PDIF-CN<sub>2</sub>, any

significant peak reflections are recorded confirming the AFM observations.

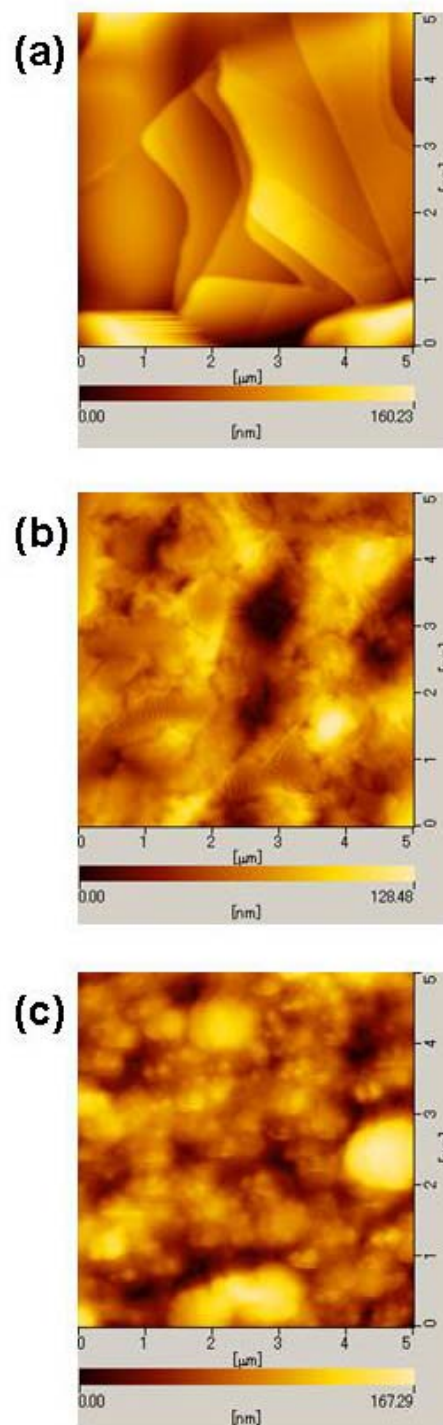


Fig. 2. AFM pictures of thin films deposited on bare Si/SiO<sub>2</sub> from (a) DH-DS2T based solution in  $\text{CHCl}_3$  at 0.82 mg/mL, (b) PDIF-CN<sub>2</sub> based solution in  $\text{CHCl}_3$  at 5 mg/mL and (c) DH-DS2T:PDIF-CN<sub>2</sub> mixed solution in  $\text{CHCl}_3$  containing 50% of PDIF-CN<sub>2</sub>.

For the DH-DS2T:PDIF-CN<sub>2</sub> blend film realized from a mixed solution containing 50% of PDIF-CN<sub>2</sub>, the single

(001) peak observation of DH-DS2T underlines the fact that films are not highly textured. Nevertheless, the emergence of a new peak corresponding to an interplanar  $d$ -spacing of 2.66 nm highlights a microstructural reorganization between DH-DS2T and PDIF-CN<sub>2</sub> in blend thin films taking roots in interactions or relaxations between DH-DS2T and PDIF-CN<sub>2</sub> molecules. As an additional observation, it is worse to specify that such new peak is only observed for thin films based on DH-DS2T:PDIF-CN<sub>2</sub> mixed solution in CHCl<sub>3</sub> containing 50-55% of PDIF-CN<sub>2</sub>. Figure 4 shows the optical microscopy image of a thin film deposited on bare Si/SiO<sub>2</sub> from a DH-DS2T:PDIF-CN<sub>2</sub> mixed solution in CHCl<sub>3</sub> containing 55% of PDIF-CN<sub>2</sub>. Both electrodes and channel are covered by a smooth and uniform organic thin film which can provide the charge injection and transport.

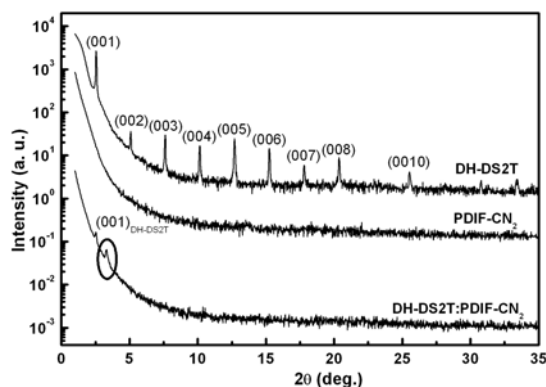


Fig. 3.  $\theta/2\theta$  mode of X-ray diffraction patterns of thin films deposited on bare Si/SiO<sub>2</sub> by drop casting from (a) DH-DS2T based solution in CHCl<sub>3</sub> at 0.82 mg/mL, (b) PDIF-CN<sub>2</sub> based solution in CHCl<sub>3</sub> at 5 mg/mL and (c) DH-DS2T:PDIF-CN<sub>2</sub> mixed solution in CHCl<sub>3</sub> containing 50% of PDIF-CN<sub>2</sub>.

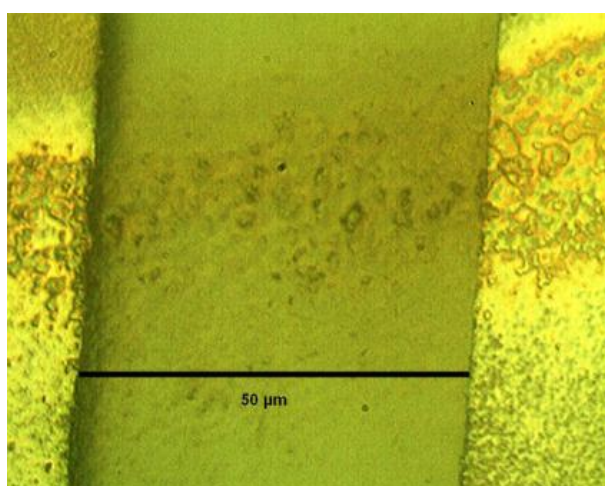


Fig. 4. Optical microscopy images of a DH-DS2T:PDIF-CN<sub>2</sub> blend thin film deposited on bare Si/SiO<sub>2</sub> by drop casting from a DH-DS2T:PDIF-CN<sub>2</sub> mixed solution in CHCl<sub>3</sub> containing 55% of PDIF-CN<sub>2</sub>. The 50  $\mu\text{m}$  scale bar shows the channel length between source and drain electrodes.

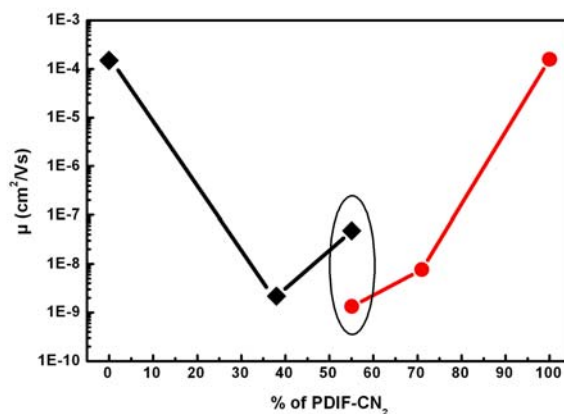


Fig. 5. Plots of hole ( $\blacklozenge$ ) and electron ( $\bullet$ ) mobility ( $\mu$ ) vs. % of PDIF-CN<sub>2</sub> containing in solutions deposited by drop casting on bare Si/SiO<sub>2</sub>.

Current-voltage characteristics were performed in air at room temperature. Fig. 5 collects the electrical data in terms of hole and electron mobilities ( $\mu$ ) vs. % of PDIF-CN<sub>2</sub> containing in mixed solutions deposited by drop casting on bare Si/SiO<sub>2</sub>. Purely p-channel OTFTs were realized from a DH-DS2T based solution in CHCl<sub>3</sub> at 0.82 mg/mL with hole mobility up to  $1.5 \times 10^{-4}$  cm<sup>2</sup>/V.s. A comparative mobility is obtained for OTFTs with DH-DS2T as active layer processed by drop-casting from a solution in dichloromethane at 0.82 mg/mL [11]. By adding 37% of PDIF-CN<sub>2</sub> in the solution, transistor responses were obtained only for negative bias indicating that the blend active layer gives rise to only a p-type charge carrier transport with a decreased hole mobility up to  $2.16 \times 10^{-9}$  cm<sup>2</sup>/V.s. Despite low hole and electron mobilities, an ambipolar transport is measured when the mixed solution is formed by  $\sim 50\%$  of each oligomer. A hole mobility up to  $4.82 \times 10^{-8}$  cm<sup>2</sup>/V.s together with an electron mobility of  $1.33 \times 10^{-9}$  cm<sup>2</sup>/V.s were measured for a DH-DS2T:PDIF-CN<sub>2</sub> blend active layer deposited on bare Si/SiO<sub>2</sub> by drop casting from a mixed solution in CHCl<sub>3</sub> containing 55% of PDIF-CN<sub>2</sub>. By increasing the amount of PDIF-CN<sub>2</sub> to 71%, transistor responses were obtained only for positive bias indicating that the blend active layer has switched in an unipolar n-type charge carrier transport with an electron mobility of  $7.66 \times 10^{-9}$  cm<sup>2</sup>/V.s against a value of  $1.57 \times 10^{-4}$  cm<sup>2</sup>/V.s for purely n-channel OTFTs based on PDIF-CN<sub>2</sub>. Despite low mobilities, solution-processed ambipolar OTFTs based on DH-DS2T:PDIF-CN<sub>2</sub> blend active layer were realized by drop casting of a properly solution where an intimate mixture between DH-DS2T and PDIF-CN<sub>2</sub> is ensured.

#### 4. Conclusion

We have investigated OTFTs in an interdigital source and drain structure based on  $\alpha,\omega$ -hexyl-distyryl-bithiophene (DH-DS2T) and  $N,N'$ -1H,1H-perfluorobutyl dicyanoperylenediimide (PDIF-CN<sub>2</sub>) by using drop-

casting as liquid deposition method. The presence of the terminal alkyl chains allows the introduction of properties to oligomers such as solubility in organic solvents. Both organic compounds, DH-DS2T and PDIF-CN<sub>2</sub>, dissolve in common organic solvents and can be processed from liquid solution at room temperature in OTFTs. The fine tuning of molecular fraction of both oligomers contained in mixed solutions led us to the realization in air of solution-processed ambipolar OTFTs. Future studies will focus on increasing charge transport properties by using dielectric surface treatments and/or others dielectrics in order to reduce both hole and electron interfacial trapping states at the semiconductor/dielectric interface.

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