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Toward n-channel organic thin film transistors based on a distyryl-bithiophene derivatives

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ABSTRACT

Solution and solid-state properties of two new perfluoroalkyl end-substituted analogues of distyrylbithiophene (CF₃-DS2T and diCF₃-DS2T) are presented. Vacuum deposited thin films were investigated by atomic force microscopy, X-ray diffraction, and implemented as active layers into organic thin film transistors. While physicochemical measurements in solution suggest a preferential hole injection and transport inside CF3-DS2T and diCF3-DS2T films, electrical measurements performed under high vacuum show that CF₃-DS2T behaves as n-type semiconductor while no charge transport was measured in diCF₃-DS2T. The results highlighted the importance of substituents on conjugated backbone and on the resulting fine ordering in solid state to control the charge transport.

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1. Introduction

During the last few years several studies have reported organic thin film transistors (OTFTs) based on n-channel semiconductors designed by various synthetic strategies. While initial n-type organic semiconductors suffered from two principal drawbacks, such as low carrier mobilities and poor environmental stability,1-4 new compounds as small molecules or polymers have emerged enabling airstable n-channel OTFTs.^{1,5–21} Despite lower mobilities than conventional inorganic semiconductors, the development of n-type materials is essential to enable complementary metal oxide semiconductor (CMOS) technology. Compounds with strong electron affinity are usually found to enable electron transport in the solid state. In order to predict the O₂/H₂O sensitivity of organic n-type materials, studies on arylene bisimides and other semiconductors derived an empirical method from the consideration of the

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electrochemical data obtained for a range of chemical structures.^{1,5–9} Accordingly, semiconductors with a first reduction potential $E_{\rm P1}$ ranging from -0.4 to 0.0 V versus SCE should result in OTFTs exhibiting stable electron transport in air, provided that an optimized thin film morphology is obtained. This indeed contributes to favor the generation of the anion-radical species responsible for negative charge carrier transport in the solid as electron injection into the lowest unoccupied molecular orbital (LUMO) of the semiconductor from the metal can be facilitated.²² As small molecules, oligomers of thiophene are widely known as excellent p-type semiconductors. However, by introducing appropriate electron withdrawing groups (EWGs), as fluor (-F) or perfluoroalkyl $(-CF_3)$, it is possible to switch their hole-type conductivity to the electron-type one. Chemical substitution with EWG functionalities is often considered as a versatile approach to lowering the LUMO energy level of conjugated systems. First n-type derivatives obtained in the oligothiophene family were α, ω -perfluorohexyl-quaterthiophene (DFH-4T) and α, ω -perfluorohexyl-sexithiophene (DFH-6T).^{23,24} Transistors based on vapordeposited DFH-4T and DFH-6T thin films on silicon dioxide (SiO₂), hexamethyldisilazane (HMDS), poly(styrene) (PS) and poly(vinyl alcohol)(PVA) dielectric layers showed electron mobility up to 0.06 and $0.02 \text{ cm}^2/\text{V}$ s in vacuum, respectively. Despite the presence of electron withdrawing groups and a dense crystal packing, transistors do not retain their good activity when exposed to air. An independent work has shown the air activity of n-channel DFH-4T based transistors by



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using polymethylmethacrylate (PMMA) as organic insulating layer.²⁵ On the base of the guaterthiophene conjugated core, a complete work investigated how the placement of the perfluoroarene unit in the conjugated skeleton could trigger the sign of the majority charge carrier. With the perfluoroarene units located at both termini of the quaterthiophene oligomer, the diperfluorophenyl-quaterthiophene DF-4T was found to be n-type under argon or under vacuum (moderate vacuum ~20 mTorr or high vacuum ~ 10^{-5} Torr).^{26,27} Gold source and drain electrodes-containing transistors exhibited excellent parameters for DF-4T with an electron mobility up to 0.43 cm^2 V s and on/off ratio of 10,⁸ while the two others with fluoroarene units incorporating in the oligothiophene chain are p-type with no ambipolar property. A theoretical study on such diperfluorophenyl substituted quaterthiophenes has stressed not only the major role of the intermolecular contributions (transfer integrals, reorganization energies, dependencies on intermolecular separation and arrangement) to control the charge transport properties of materials, but they have also emphasized the critical role played by several macroscopic properties within the device architecture, which could overwhelm the electronic effect of the perfluoroarene unit depending on its location in the conjugated structure.²⁸ Following the same synthetic approach perfluoroarene-containing analogues of distyryloligothiophenes (DFSnT, n=2, 4) were studied.^{29,30} The incorporation of perfluoroarene rings in DSnTs series (n=2, 3, 4), where an exceptional stability of p-channel OTFTs has been shown,³¹ was found to lower the LUMO energies, consistently with the electron withdrawing influence of the fluorine atoms. Nevertheless. **DFS2T** and **DFS4T** thin films exhibit a p-type semiconducting behavior as active laver implemented in OTFT devices under identical conditions as DF-4T for accurate comparison.³⁰ Such p-type transport was observed not only in air,²⁹ but also under high vacuum.³⁰ In contrast to DF-4T, the incorporation of double bonds between perfluoroarene units and oligothiophene cores fails to produce the similar trend in vacuum. In such perfluoroarene-terminated oligothiophene derivatives, an efficient electron density confinement at the molecular scale is advanced to affect the final transport properties.³⁰ As efficient EWGs, -CF₃ substitutions on aryl naphthalenetetracarboxylic diimide (NTCDI) enable to lower LUMO level and help to improve electron charge injection. Resulting mobilities and air stability on nchannel OTFTs have been considerably increased.³² In order to expand the series of fluorinated distyryl-bithiophenes, two new perfluoroalkyl end-substituted analogues of distyryl-bithiophene (CF3-DS2T and diCF₃-DS2T) were synthesized by introducing -CF₃ groups on arene end-units with various numbers and position. Scheme 1 gives the chemical structure of DS2T, DFS2T, CF3-DS2T and diCF3-DS2T.

A comparative study in solution and in solid state based on DFS2T, CF3-DS2T and diCF3-DS2T reveals the great influence of perfluorination by alkyl chains on the arene moieties of distyrylbithiophene skeleton on electronic structure, physical properties, and device efficiencies. As expected, the incorporation of perfluoroalkyl chains was found to lower the LUMO energies but not dramatically to predict a preferential electron injection from gold metal electrodes to the LUMO level. While any obvious electron density confinement occurred in both CF3-DS2T and diCF3-DS2T, nchannel OTFTs can be observed only for CF₃-DS2T in high vacuum. In the series of fluorinated oligomers, a particular attention was taken to realize and measure the OTFT devices in the same conditions for a more accurate discussion. Classical dielectrics, bare and HMDS-treated Si/SiO₂ substrates instead of PS, PVA or BCB, were chosen as n-channel OTFTs were observed with DF-4T under vacuum.^{26,27} The main result coming out of this comparative study is the influence of the high electronic effect of -CF₃ groups together with a fine molecular arrangement in CF3-DS2T-based thin films to control the charge carrier type, i.e., electrons, transported in organic active layers.



Scheme 1. Chemical structure of DS2T, DFS2T, CF3-DS2T and diCF3-DS2T.

diCF₃-DS2T

2. Results and discussion

To understand and quantify the effects of the perfluoroalkyl substitutions on the aromatic backbone of distyryl-bithiophene derivatives, absorption spectroscopy and cyclic voltammetry measurements in solution were carried out. All data were compared to those obtained for previous reported distyryl-bithiophenes (**DS2T** and **DFS2T**).^{29–31} Optical and electrochemical data of **DS2T**, **DFS2T**, **CF3-DS2T** and **diCF3-DS2T** based solutions are reported in Table 1 and the energy diagram of LUMO and HOMO (highest orbital molecular orbital) levels for the four oligomers is shown in Fig. 1.

In a simple Schottky-type injection barrier model, as presented on Fig. 1, the relative carrier injection barriers should be described as the difference between the molecular HOMO energy and the metal electrode work function, here gold with $E_{\rm f} \sim 4.9$ eV, for the hole injection ($\Delta E_{\rm h}$), and the difference between the molecular LUMO energy and the metal work function for the electron injection ($\Delta E_{\rm e}$). Compounds designated to give rise to air-stable nchannel OTFTs may possess a LUMO level lying near the metal work function to facilitate the electron injection into the semiconductor from the metal.²² The overall picture resulting from the physicochemical measurements in solution of **CF₃-DS2T** and **diCF₃-DS2T** compared to **DFS2T** is the similar influence of perfluorination by

Table 1 Optical and electrochemical data of distyryl-bithiophene (DS2T) and its derivatives (DFS2T, CF3-DS2T and diCF3-DS2T)					
	$\lambda_{\max} \left(nm ight)^{a}$	$E_{g_{opt}}$ (eV)	$E_{1/2}(\mathrm{ox1})(\mathrm{V})$	<i>E</i> _{1/2} (red1) (V)	HOMO (eV) ^b

R R' R DS2T н н н 425 2 60 0 48 -2.26 430 2.55 0.59 DFS2T F F F -2.10CF₃-DS2T CF₃ н н 429 2 5 5 0.63 -2.10 diCF₃-DS2T 2 5 2 Н 430 0.62 -2.02Н CF₂

^a In CH₂Cl₂.

^b Estimated from experimental data with LUMO (eV)=-4.84 eV-E_{1/2} (red1) and HOMO (eV)=LUMO-E_g.



Fig. 1. Energy diagram of LUMO and HOMO levels for distyryl-bithiophene (**DS2T**) and its derivatives (**DFS2T**, **CF**₃-**DS2T** and **diCF**₃-**DS2T**). The horizontal thick line corresponds to Fermi level of gold electrode (~4.9 eV). LUMO and HOMO energies are estimated from experimental data with LUMO (eV)= $-(4.84 \text{ eV}+E_{1/2} \text{ (red)})$ and HOMO (eV)=LUMO- E_g where E_g optical band gap.

alkyl groups (–CF₃) than by fluorine atoms (–F) on arene end-units of DS2T π -core. It is worth noting that the LUMO and HOMO energies are identical for **DFS2T** and **CF₃-DS2T**, while those of **diCF₃-DS2T** are even ~0.05–0.08 eV lower. The molecular orbital plots of **CF₃-DS2T** and **diCF₃-DS2T** obtained by DFT reveal highly delocalized HOMOs and LUMOs having aromatic and quinoidal configurations, respectively (Fig. 2).

Lowest HOMO and LUMO energies for **diCF₃-DS2T** than for **CF₃-DS2T** underline the results obtained by experimental data. Based on the strictly schematic representation of orbital energies, **CF₃-DS2T** involved as active layer in OTFT devices with Au-based electrodes should operate identically as **DFS2T** i.e., both hole injection and



-5.18

-5.29

-5.29

-5.34

LUMO (eV)^b

-2 58

-2.74

-2.74

-2.82

Ref

33 34

29,30

This ref.

This ref.

Fig. 2. DFT-optimized geometries, frontier orbitals, and orbital energies (eV vs vacuum) of CF₃-DS2T and diCF₃-DS2T.

transport to confer a p-channel activity in air and in vacuum. With a lower LUMO level, **diCF₃-DS2T** should be more appropriated for an electron injection from gold electrodes although a high ΔE_e value of 2.08 and 2.2 eV, obtained by, respectively, the experimental data and DFT computations, is predicted as a limiting factor. In order to classify a compound as n-type organic semiconductor, transport properties in solid state have to be investigated to identify the majority charge carriers (holes or electrons) involved.

The Bottom-Gate Top-Contact (BGTC) configuration was used for the OTFT devices based on CF3-DS2T and diCF3-DS2T. Au-based source and drain electrodes were deposited on top of the semiconducting layer after the latter was evaporated onto bare or HMDS-treated Si/SiO₂ substrates at different substrate temperatures (T_{sub} =30 and 80 °C). While no transistor activity was observed in air or in moderate vacuum (270-300 mTorr) for both CF3-DS2T and **diCF₃-DS2T**, the only one operating channel is observed in high vacuum (below 6×10^{-6} Torr) with **CF₃-DS2T** as active layer in OTFTs based on SiO₂ insulator layer coated with HDMS for either T_{sub} =30 or 80 °C. In comparison with bare Si/SiO2 substrates, HMDS-treated ones posses less electron trapping sites at the semiconductor/insulator interface to be filled before the carriers become mobile.³⁵ Unexpectedly, by application of positive drain and gate voltages OTFTs operate in the accumulation mode demonstrating that CF₃-DS2T behaves as n-type semiconductor in high vacuum. Any ambipolar property was observed in either air or vacuum. For an identical BGTC configuration, DFS2T behaved as a p-type semiconductor directly in air on bare SiO₂ dielectric.³⁰ Typical output characteristics of OTFT devices fabricated with **CF₃-DS2T** at *T*_{sub}=30 and 80 °C on HMDS-treated Si/SiO₂ substrates are shown in Fig. 3a and b, respectively.

It is nevertheless essential to mention that high drain-source (V_d) and gate (V_g) voltages up to 200 V have to be applied in order to observe a drain current (I_d) as high as 0.3 μ A on heated substrates. At this stage of the study, it remains consistent to suggest that a contact resistance should have an effect on the measured data as high voltages were applied to observe an accumulation mode for a high drain-source voltage (V_d >25 V). Nevertheless, such contact resistance should not have a direct influence on the active



Fig. 3. Output characteristics of **CF₃-DS2T** based-OTFTs on HMDS-treated Si/SiO₂ substrate at T_{sub} =30 °C (a) and 80 °C (b) measured in vacuum (below 6×10⁻⁶ Torr).

layer behavior i.e., p- or n-type. An electron mobility up to 8.1×10^{-4} cm²/V s together with an I_{on}/I_{off} ratio of ~10⁷ were measured for CF3-DS2T films deposited at 80 °C as against 5.2×10^{-4} cm²/V s and 10^{6} for **CF₃-DS2T** films deposited at 30 °C. The average mobilities and standard deviations are 5.6×10^{-4} (cm²/ V s) $\pm 2.5 \times 10^{-4}$ and 4.1×10^{-4} (cm²/V s) $\pm 1.1 \times 10^{-4}$ for OTFTs with CF3-DS2T deposited on HMDS-treated Si/SiO2 substrates at 80 and 30 °C, respectively. A good reproducibility of measured data was obtained as five individual OTFTs were tested for each substrate temperature. Despite modest mobility values, the most significant result is the observation for the first time of n-channel OTFTs in the distyryl-oligothiophene series where any obvious electron density confinement occurs compared to DSF-2T.²⁹ By changing the substituents by -CF₃ on arene end-units, the electron density is delocalized on the overall molecular backbone without any hindering due to the presence of double bonds. The electronic effect of such -CF3 groups has been demonstrated in arene-end substituted NTCDI compounds where the electron mobility increased with the number of -CF₃. However, such results were associated with unique morphological features, including plate-like and rod-like morphologies.32

AFM pictures of 50 nm thick-vapor-deposited CF_3 -DS2T and diCF_3-DS2T films grown on either HMDS-treated or bare Si/SiO₂ substrates at 30 and 80 °C are presented on Figs. 4 and 5, respectively. CF₃-DS2T exhibits plate-like small grains with some high out-of-plane grains at 30 °C regardless of the Si/SiO₂ substrate nature, bare or treated-HMDS. By increasing the substrate temperature during the organic vacuum deposition up to 80 °C, the same trends are observed but with an increased grain size together



Fig. 4. AFM pictures and corresponding AFM profiles of **CF₃-DS2T** and **diCF₃-DS2T** thin films deposited at T_{sub} =30 °C (a, b) and 80 °C (c, d) on HMDS-treated Si/SiO₂ substrates with a nominal thickness of 50 nm.

with better defined grain edges. On the contrary, increasing substrate temperature leads to an opposite effect for **diCF₃-DS2T** films as the high number of small needles like grains observed at 30 °C give way to 5 μ m-long grains unconnected to each other and randomly dispersed on the surface. Based on AFM images observed at 30 °C for both oligomers, **CF₃-DS2T** and **diCF₃-DS2T**, the macroscopic morphology is not sufficient to explain the lack of charge transport in **diCF₃-DS2T**-based thin films as continuous films were observed.

In order to understand how the solid-state ordering in the semiconductor affects thin film microstructure and charge transport properties, X-ray diffraction experiments were carried out. X-ray diffraction (XRD) was performed on **CF₃-DS2T** and **diCF₃-DS2T** thin films as 50 nm thick vacuum deposited layers at 30 and 80 °C on bare and HMDS-treated Si/SiO₂ substrates (Fig. 6). The XRD scans show that thin films present different textures depending on



Fig. 5. AFM pictures and corresponding AFM profiles of **CF₃-DS2T** and **diCF₃-DS2T** thin films deposited at $T_{sub}=30$ °C (a, b) and 80 °C (c, d) on bare Si/SiO₂ substrates with a nominal thickness of 50 nm.

the position of perfluoroalkyl groups and the nature of the dielectric surface. No significant peak reflections are recorded for diCF₃-DS2T at either T_{sub}=30 or 80 °C on both bare and HMDStreated Si/SiO₂ substrates. The lack of n-channel behavior of diCF₃-DS2T may be due to unfavorable molecular packing in thin solid film, which generates in particular a less-effective $\pi - \pi$ stacking as already observed for a NTCDI with fluorinated phenylethyl groups.³⁶ On the contrary, textured patterns are observed with CF3-DS2T but only for films deposited on HMDS-treated Si/ SiO₂ at either T_{sub} =30 or 80 °C agreeing with an effective charge transport activity observed for a dielectric surface containing less electron trapping sites as HMDS-treated Si/SiO₂. Despite comparable XRD patterns,²⁹ DFS2T and CF₃-DS2T give rise to drastic different electrical responses. While **DFS2T** behaved as a p-type semiconductor in air and under vacuum,^{29,30} **CF₃-DS2T** presents an electron transport activity but exclusively under high vacuum. Additionally to the measurement conditions (air or vacuum), the



Fig. 6. $\theta/2\theta$ mode of X-ray diffraction patterns of **CF₃-DS2T** and **diCF₃-DS2T** based thin films deposited at $T_{sub}=30$ °C (a) and 80 °C (b) on bare and HMDS-treated Si/SiO₂ substrates with a nominal thickness of 50 nm.

nature of the dielectric seems to be a relevant parameter as pchannel DFS2T-based OTFTs operated on bare or HMDS-treated Si/ SiO₂ substrates and PMMA,²⁹ a charge transport activity in CF₃-DS2T-based thin films is observed only on HMDS-treated Si/SiO₂ substrates. Another main difference between CF3-DS2T and DFS2T is the observation of a second polymorphism on Fig. 6 as determined by the dominate diffraction peak (001) and its shoulder (001') corresponding to a principal *d*-spacing of 2.25 nm together with an additional d'-spacing of 2.03 nm, respectively. Some specific intermolecular interactions in CF₃-DS2T-based thin films give rise to a fine ordering in the solid state where the occurrence of (001) progressions means that the *ab*-planes of the grains are oriented parallel to the substrate surface with a small tilted angle for the second polymorphism. Such ordering is favorable to a $\pi - \pi$ stacking in solid film for an efficient electron transport in OTFT devices.

Recent work reported in the literature the great effect of the halogenated moieties on the packing of molecules with S–F interactions involved in the solid state assembly of organic semiconducting materials.^{37,38} Based on structural parameters in thin film phase obtained for the three fluorinated compounds **DFS2T**, **CF₃-DS2T** and **diCF₃-DS2T**, the major difference is the great impact of the fine crystalline environment, which is achieved in the solid state. While substitutions with –CF₃ lowered LUMO level in both **CF₃-DS2T** and **diCF₃-DS2T** compounds, the lack of n-channel behavior of **diCF₃-DS2T** thin films even in vacuum is due to the less-effective π – π stacking. Contrary to **DFS2T**, any efficient electron

density confinement at the molecular scale occurred confirming the high electronic effect of such $-CF_3$ groups on conjugated backbone. From specific intermolecular interactions resulting in high ordering in **CF₃-DS2T**-based thin films emerge n-channel OTFTs on HMDS-treated Si/SiO₂ substrates. **CF₃-DS2T** is the first electron transporting derivative observed in the distyryloligothiophene series. Indeed, more extensive studies demonstrated that different chemical substitutions on the distyryloligothiophene core with EWGs as fluoro-atoms (-F),^{29,30} cyano groups $(-CN)^{39}$ or carbonyl groups $(-C=O)^{40}$ failed to produce ntype organic semiconductors. Therefore, this approach aiming at switching the sign of the majority carriers in oligothiophenes using EWGs cannot be considered as general and the particular structure of the conjugated backbone as well as the resulting solid state microstructure has to be taken in account.

3. Conclusion

In conclusion, two novel distyryl-bithiophenes with perfluoroalkyl groups (-CF₃) were synthesized: E,E-5,5'-(bis((4trifluoromethyl)phenyl)-ethenyl)-2,2'-bithiophene (CF3-DS2T) and *E,E*-5,5'-bis(2-(3,5-di-(trifluoromethyl)phenyl)-ethenyl)-2,2'-bithiophene (diCF₃-DS2T). A comparative study with the perfluoroarenecontaining distyryl-bithiophenes analogue (DFS2T) underlines the influence of perfluorination by either alkyl groups $(-CF_3)$ or by fluorine atoms (-F) on arene end-units of DS2T π -conjugated core. While **DFS2T** implemented as active laver into OTFTs behaves as a ptype organic semiconductor. **CF₃-DS2T** leads to n-channel OTFTs. With a fine microstructure observed by AFM and XRD of CF₃-DS2Tbased thin films deposited on HMDS-treated Si/SiO2 substrates heated to 80 °C, electron injection can occur from gold electrodes to LUMO level generating an electron transport. A mobility up to 9.8×10^{-4} cm²/V s together with an I_{on}/I_{off} ratio of ~ 10⁷ were measured under high vacuum. The absence of a fine solid-state ordering in diCF₃-DS2T thin films at either 30 or 80 °C revealed by XRD leads to a total absence of charge transport in such films. Analyses of these materials reveal a direct relationship between molecular structure, solid state microstructure and electrical properties. The results of this study indicate that the molecular geometry and intermolecular interactions in the crystalline state govern the electrical properties of OTFTs by directly influencing key factors as interface states and morphology of organic thin films.

4. Experimental section

4.1. Synthesis

Perfluoroalkyl-distyryl-bithiophene derivatives were prepared by Wittig–Horner olefinations between adequate phosphonate and 2,2'-bithienyl-2',5'-dicarboxaldehyde (Scheme 2).

Methylenechloride, methanol, tetrahydrofurane (THF), chloroform, were purchased from CarloErba. Tetrabutylamonium hexafluorophosphate (TBHP) was purchased from Fluka. Silica gel (240–400 mesh) was obtained from Merck. Trimethylphosphite, butyllithium in hexane, *p*-trifluoromethylbenzylbromide and 3,5-di(trifluoromethyl)benzylbromide were purchased from Sigma–Aldrich. 2,2'-bithienyl-5,5'-dicarboxaldehyde were prepared as described in the literature.⁴¹ Melting points are uncorrected and were obtained from an Electrothermal 9100 apparatus. ¹H NMR and ¹³C NMR spectra were recorded on Bruker AC 250 at, respectively, 250 MHz and 62.5 MHz. UV spectra were obtained on Varian Cary 50.

4.1.1. Dimethyl p-trifluoromethylbenzylphosphonate **1a**. The suitable benzylbromide (3.00 g, 12.55 mmol) was mixed with trimethylphosphite (10.76 mL, 62.75 mmol) and refluxed at 112 $^{\circ}$ C for



Scheme 2. Synthetic scheme for the perfluoroalkyl-DS2T oligomers (CF_3-DS2T and $diCF_3$ -DS2T).

6 h. The mixture was then distilled under reduced pressure to eliminate the excess of phosphite and the oily residue purified by column chromatography using chloroform/methanol (1/1) as the eluent. ¹H NMR (250 MHz, CDCl₃) δ : 3.10 (d, 2H, *J*=21.75 Hz, CH₂-P), 3.63 (s, 3H, OCH₃), 3.64 (s, 3H, OCH₃), 7.34 (d, 2H, *J*=8.25 Hz, H_{benz}), 7.48 (d, 2H, *J*=8.25 Hz, H_{benz}). ¹³C NMR (67.5 MHz, CDCl₃) δ : 31.50 (CH₂), 33.70 (CH₂), 52.77 (CH₃), 52.88 (CH₃), 122.00 (CF₃), 125.45 (C_{benz}), 129.92 (C_{benz}), 130.03 (C_{benz}), 137.70 (C_{benz}). MS (FAB+) *m/z*: calcd 268, found 269.

4.1.2. Dimethyl 3,5-di(trifluoromethyl)benzylphosphonate **1b**. The suitable benzylbromide (1.00 g, 3.26 mmol) was mixed with trimethylphosphite (2.79 mL, 16.28 mmol) and refluxed at 112 °C for 6 h. The mixture was then distilled under reduced pressure to eliminate the excess of phosphite and the oily residue purified by column chromatography using chloroform and methanol (1/1) as the eluent. ¹H NMR (250 MHz, CDCl₃) δ : 3.10 (d, 2H, *J*=22.50 Hz, CH₂-P), 3.65 (s, 3H, OCH₃), 3.68 (s, 3H, OCH₃), 7.70 (s, 3H, H_{benz}). ¹³C NMR (67.5 MHz, CDCl₃) δ : 31.30 (CH₂), 33.51 (CH₂), 52.83 (CH₃), 52.94 (CH₃), 120.88 (CF₃), 125.20 (C_{benz}), 129.84 (C_{benz}), 131.5 (C_{benz}), 134.5 (C_{benz}). MS (FAB+) *m/z*: calcd 336, found 337.

4.1.3. Typical procedure Wittig–Horner. Into a flask of 100 mL, 0.9 mmol of 2,2'-bithienyl-5,5'-dicarboxaldehyde and 2.07 mmol of phosphonate were dissolve in 60 mL of anhydrous tetrahydrofurane under argon. At 0 °C 4.14 mmol of *t*-BuOK are added. After 10 h of agitation at room temperature the solvent was evaporated in vacuo. The crude product was dissolved in methylene chloride and water was added. The mixture is extracted with methylene chloride. The combined organic phases were washed with water, dried (MgSO₄), and evaporated in vacuo. The product was purified on a silica gel column. The desired fractions were pooled and concentrated to afford *E* isomers.

4.1.4. *E*,*E*-5,5'-(*Bis*((4-trifluoromethyl)phenyl)-ethenyl)-2,2'-bithiophene (**CF₃-DS2T**). Yield: 55%. Mp 224–226 °C; ¹H NMR (250 MHz, CDCl₃) δ : 6.83 (d, 2H, *J*=16.25 Hz, H_{eth}), 6.97 (d, 2H, *J*=3.75 Hz, H_{thio}), 7.05 (d, 2H, *J*=3.75 Hz, H_{thio}), 7.21 (d, 2H, *J*=16.50 Hz, H_{eth}), 7.49 (d, 4H, *J*=8.75 Hz, H_{benz}), 7.54 (d, 4H, *J*=9.00 Hz, H_{benz}). HMRS: calcd 506.0598, found 506.0609. Elemental Anal. calcd for C₂₆H₁₆F₆S₂: C, 61.65; H, 3.18; S, 12.66. Found: C, 61.60; H, 2.98; S, 12.94.

4.1.5. *E,E*-5,5'-*Bis*(2-(3,5-di-(trifluoromethyl)phenyl)-ethenyl)-2,2'bithiophene (**diCF₃-DS2T**). Yield: 21%. Mp 222–224 °C; ¹H NMR (250 MHz, CDCl₃) δ : 6.85 (d, 2H, *J*=16.25 Hz, H_{eth}), 6.97 (d, 2H, *J*=3.75 Hz, H_{thio}), 7.05 (d, 2H, *J*=3.75 Hz, H_{thio}), 7.21 (d, 2H, *J*=16.50 Hz, H_{eth}), 7.65 (s, 2H, H_{benz}), 7.80 (s, 4H, H_{benz}). ¹HMRS: calcd 642.0345, found 642.0367. Elemental Anal. calcd for $C_{28}H_{14}F_{12}S_2$: C, 52.34; H, 2.20; S, 9.98, F, 35.48. Found: C, 52.79; H, 2.00; S, 10.07.

4.1.6. Physicochemical measurements in solution. UV-visible absorption spectra were obtained on a Varian Carv 1E spectrophotometer. The electronic absorption maximum (λ_{max}) and the optical band gap (E_g) are directly extracted from absorption spectra of CF₃-DS2T and diCF₃-DS2T based solution. Cyclic voltammetry (CV) data were acquired using a BAS 100 Potentiostat (Bioanalytical Systems) and a PC computer containing BAS100W software (v2.3). A threeelectrode system based on a platinum (Pt) working electrode (diameter 1.6 mm), a Pt counter electrode and an Ag/AgCl (with 3 M NaCl filling solution) reference electrode was used. Tetrabutylammonium hexafluorophosphate (TBHP) (Fluka) was used as received and served as supporting electrolyte (0.1 M). All experiments were carried out in anhydrous 1,2-dichlorobenzene (electronic grade purity) at 20 °C. Ferrocene was used as internal standard. Electrochemical reduction/oxidation potential versus Fc/Fc⁺ $(E_{1/2}(\text{red1}) \text{ and } E_{1/2}(\text{ox1}))$ values are determined from the cyclic voltammogram at a concentration of 1×10^{-3} M with a scan rate of 50 mV s^{-1} .

4.1.7. OTFTs fabrication. The Bottom-Gate Top-Contact (BGTC) configuration was used for the OTFT devices based on CF3-DS2T and **diCF₃-DS2T** derivatives. Highly n-doped silicon wafers (gate), covered with thermally grown silicon oxide SiO₂ (3000 Å, insulating layer), were purchased from Vegatec (France) or WRS materials (USA) and used as device substrates. Trimethylsilation of the Si/SiO₂ surface was carried out by either exposing the silicon wafers to hexamethyldisilazane (HMDS) vapor at room temperature in a closed air-free container under nitrogen for greater than one week or by immersing the Si/SiO₂ in a pure solution HMDS at room temperature overnight. The capacitance per unit area of either bare or HMDS deposition silicon dioxide dielectric layers was $1.0-1.3 \times 10^{-8}$ F/cm². The semiconductor layer was vacuum deposited onto the insulating layers to a nominal thickness of 50 nm as determined with an in situ quartz crystal monitor. Substrate temperature (T_{sub}) during deposition was controlled by heating the block on which the substrates are mounted. The deposition control occurred in a three steps' process: (i) during the evaporator reached the right pressure, the substrates were covered by a shuttle to prevent deposition in the first stages of evaporation, (ii) once the evaporation rate was constant at about 0.1–0.2 A/s, and (ii) the shuttle was opened and the deposition on the substrates started. The first two steps are to prevent the deposition of a high amount of impurities in the deposited layers. The Au source and drain electrodes were evaporated on top of the organic thin film through a shadow mask with specific channel length and channel width W.

For OTFT, current-voltage characteristics were obtained with either a Hewlett–Packard 4140B pico-amperemeter-DC voltage source at room temperature in air and/or under moderate vacuum (270–300 mTorr); or under high vacuum (below 6×10^{-6} Torr) in a customized probe-station using a Keithley 6340 subfemtoamp Remote SourceMeter and a Keithley 2400 SourceMeter. Different channel lengths and channel widths varying from 50 to 100 μ m and 1–5 mm, respectively, were deposited using shadow masks. The gold evaporation rate was kept lower that 0.05 Å/s for the first 10 nm and below 0.30 Å/s for the rest of the film. This method gives well-defined channel lengths and channel widths, that are checked by microscopy.

The source-drain current (I_D) in the saturation regime is governed by the following equation:

$$(I_D)_{sat} = (W/2L)C_i \mu (V_G - V_t)^2$$
(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. All the data were obtained by randomly measuring five individual OTFTs for each substrate temperature.

4.1.8. Film characterizations. Atomic force microscopy (AFM) measurements were done on thin films in air with a Nanoscope III Multimode (Instrument, Inc.), operating in the tapping mode. Furthermore, thin films were analyzed by X-ray film diffractometry (XRD) where thin films of **CF₃-DS2T** and **diCF₃-DS2T** were fabricated by vacuum deposition in a pressure of 5×10^{-5} Pa using K-cell type crucible. Si wafer (covered by SiO₂ layer 300 nm thick) was used as substrates, which were kept at room temperature ($T_{sub}=RT$) or heated to 80 °C ($T_{sub}=80$ °C). The deposition rate and final film thickness were 1.2 nm/min and 50 nm, respectively. The asdeposited thin films were characterized using X-ray diffraction in air using an X-ray diffractometer (Regaku Co., ATX-G), which was specially designed for characterization of thin films. The used wavelength of X-ray in the experiments was 0.1542 nm.

4.1.9. Computational Methodology. DFT calculations were carried out using the Gaussian 03 program.⁴² Becke's three-parameter exchange functional combined with the LYP correlation functional (B3LYP) was employed.⁴³ We also made use of the standard 6–31G^{**} basis set.⁴⁴

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