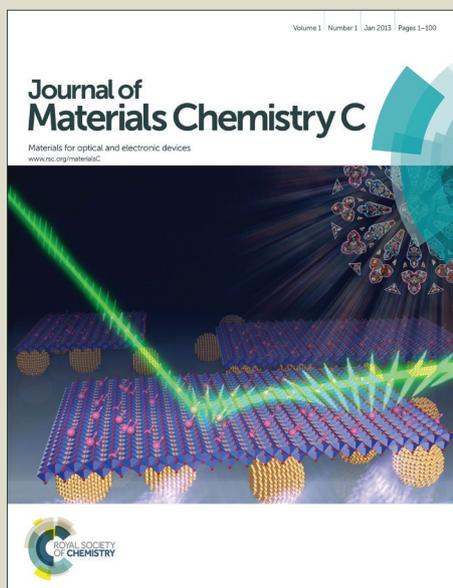


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ARTICLE TYPE

Thiophene-Tetrafluorophenyl-Thiophene- A Promising Building Block for Ambipolar Organic Field Effect Transistors

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Thiophene-tetrafluorophenyl-thiophene donor-acceptor-donor building block was used in combination with furan substituted diketopyrrolopyrrole for synthesizing polymer semiconductor PDPPF-TFPT. Due to the balance of tetrafluorophenylene/diketopyrrolopyrrole electron withdrawing and furan/thiophene electron donating moieties in the backbone, PDPPF-TFPT exhibits an ambipolar behaviour in organic thin-film transistors, with hole and electron mobilities as high as 0.40 cm²/Vs and 0.12 cm²/Vs.

Introduction

Since last decade, there are several reports on high performance polymeric semiconductors for the *p*-channel and *n*-channel organic field effect transistors (OFETs).¹⁻⁴ The highest hole and electron mobility of 13 cm²/Vs and 6 cm²/Vs has been reported for the *p*-type and *n*-type polymeric semiconducting materials.^{5,6} Meanwhile, the polymeric semiconductors for ambipolar OFETs are gaining great attention due to its capability to conduct both hole and electron charges under the positive and negative gate voltage modes.⁷⁻⁹ The ambipolar behavior in OFET devices can be achieved by three different methods such as either using a mixture of unipolar electron and hole transporting organic semiconductors,¹⁰ two stacked separate layers of electron and hole transporting semiconducting materials¹¹ or a single layer.¹² The single component polymer holds a huge potential to simplify the complexity of the organic electronic circuits such as inverter and ring oscillator based device fabrication.^{13, 14} Single component polymers are also easy to synthesize and cost effective. Multistep synthesis of discrete *p*- and *n*-channel materials will be avoided by using single component ambipolar polymer. Since the finding of single polymer based ambipolar OFETs, there are very few reports on such polymers with balanced high hole and electron mobility.^{14c} In order to achieve high ambipolar performance, the balanced yet high mobility are highly required. Both holes and electrons can be induced in the conductance channel of single layer ambipolar material by adjusting their appropriate the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The HOMO-LUMO value difference or band gap of newly synthesized polymer needs to be low in order to endorse the injection and conduction of both holes and electrons effectively.

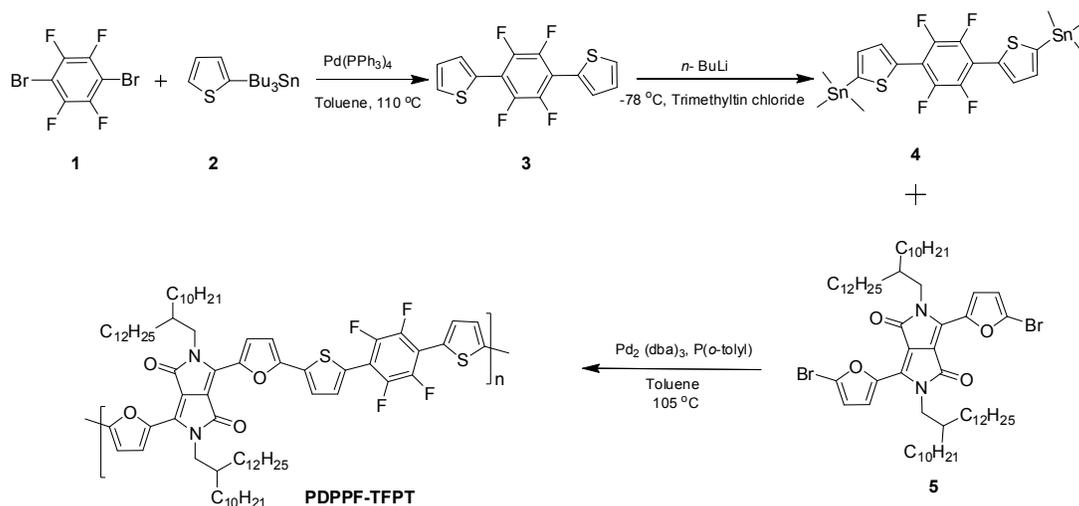
The electron donating (donor) and electron accepting (acceptor) conjugated building blocks can be attached in an alternate fashion *via* organometallic coupling and this has been demonstrated to be one of the most successful strategies for designing a lower band gap single component ambipolar material. Among reported ambipolar polymers, most of the polymers are based on “diketopyrrolopyrrole (DPP)” based donor-acceptor functional low band gap materials.^{15, 16} For DPP based materials, so far thiophene moiety used as a flanking group widely than any other heterocyclic group. Our group is designing and synthesizing novel furan flanked DPP based copolymers as semiconducting material for organic electronic devices.^{17, 18} Furan is analogous functional group as like thiophene with comparable aromaticity but very little work has been done so far on this moiety for preparing organic semiconductors.^{19,20} By combining furan with DPP it is easily possible to make stable derivatives which are highly promising fused building block for making high performance organic semiconductors. In addition to that, furan moiety is more appropriate for ambipolar charge transport.^{7a,21} In earlier reports, 3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DBF) core has been successfully used by us and other groups for unipolar *p*-channel and ambipolar OFETs. DBF based copolymer has exhibited highest hole mobility of 4 cm²/Vs in *p*-channel OFETs^{18a} whereas highest hole and electron mobility of 0.61 and 0.67 cm²/Vs was reported for ambipolar OFETs.^{7a} Fluorinated building blocks are promising strong electron withdrawing group and has been previously used by various groups for synthesizing *n*-type polymers for OFET devices.²² Fluorine atom demonstrates exceptional properties such as the small atom size and highest electron negativity. Due to small atom size, the fluorine substitution doesn't hamper the molecular packing due to minimal steric hindrance. In addition to that, fluorine atom can enhance the intermolecular interaction between C-F and H-C, which is helpful for better molecular organization and charge transport.²³ Due to fluorine, the HOMO can be lowered which is useful for inducing oxidative stability whereas LUMO would be lowered for easy electron injection.²⁴

Tetrafluorophenyl is also one of the attractive groups for designing new polymeric structure. Recently, alternating copolymers composed of thiophene flanked DPP and a tetrafluorophenyl unit was reported and this polymer exhibits a high *n*-type charge-transport property with an electron mobility of 2.36 cm² V⁻¹ s⁻¹.²⁵ In this communication, we used furan

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Scheme 1 Synthesis of thiophene-tetrafluorophenyl-thiophene with furan flanked diketopyrrolopyrrole (**PDPFF-TFPT**) alternating copolymer.

flanked DPP (DBF) and thiophene-tetrafluorophenyl-thiophene building blocks for making novel solution processable copolymer **PDPFF-TFPT** and its use in OFETs. Upon using this newly synthesized polymer **PDPFF-TFPT** in OFET devices, it exhibits ambipolar behaviour with balanced high mobilities of hole and electron mobilities as high as 0.40 cm²/Vs and 0.12 cm²/Vs, respectively.

10 Results and Discussion

The synthesis of polymer **PDPFF-TFPT** is depicted in Scheme 1. First, 2,2'-(perfluoro-1,4-phenylene)dithiophene (**3**) was synthesized in a good yield by reacting 1,4-dibromo-2,3,5,6-tetrafluorobenzene (**1**) and tributyl(thiophen-2-yl)stannane (**2**) via Stille coupling. Compound **3** was converted to the bistannyl derivative (5,5'-(perfluoro-1,4-phenylene)bis(thiophene-5,2-diyl))bis(trimethylstannane)(**4**) using *n*-butyllithium (*n*-BuLi) and trimethyl tin chloride in anhydrous THF at -78 °C. Compound 3,6-bis(5-bromofuran-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)-dione (**5**) was synthesized according to previously reported procedure.^{17a} Stille coupling polymerization of compounds **4** and **6** resulted in polymer poly{3,6-difuran-2-yl-2,5-di(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,4-dione-alt-2,2'-(perfluoro-1,4-phenylene)dithiophene} (**PDPFF-TFPT**) in 77% yield. In order to remove the catalytic impurities and oligomer fractions, the **PDPFF-TFPT** was purified by sequential Soxhlet extraction using various polar (methanol and acetone) and non-polar (hexane) solvents. Finally, the pure polymer fraction was obtained from the bulk polymer sample by dissolving it in chloroform. The chloroform fraction was removed under rotavap and precipitated in methanol. The molecular weight of the purified polymer was determined by high temperature gel permeation chromatography (GPC). The recorded number

average (M_n) and weight average molecular weight (M_w) are 12083 and 20689 g/mol, respectively, at a column temperature of 160 °C using trichlorobenzene as eluent.

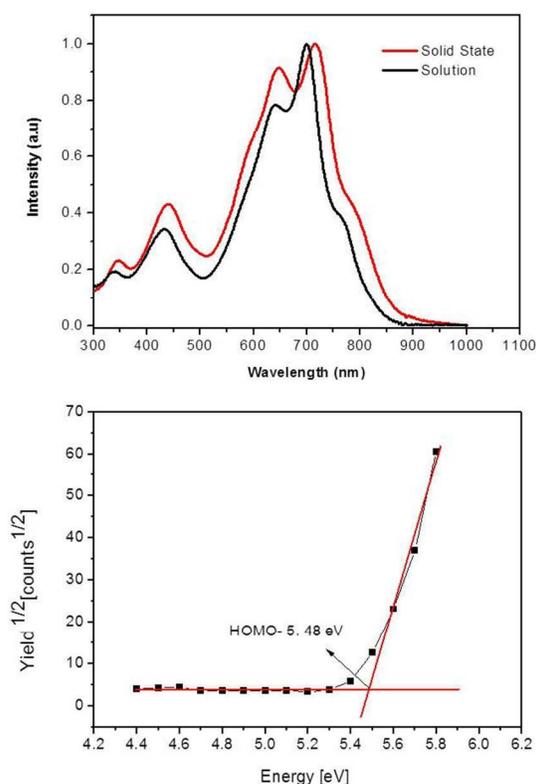


Fig.1 (a) UV-vis absorption spectra of **PDPFF-TFPT** in chloroform solution and in thin film. (b) Photoelectrospectroscopy in air (PESA) analysis of **PDPFF-TFPT** spin coated thin films on glass.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques were used for studying the thermal properties of **PDPPF-TFPT** polymer. The 5% weight loss of **PDPPF-TFPT** was measured at 410 °C under nitrogen indicating the high thermal stability of polymer. Such a higher thermal stability is attributed with the tetrafluoro robust conjugated building block incorporated in the backbone. During both (first and second) heating and cooling cycles, the two exothermic (at 283 °C and 292 °C) and endothermic peaks (at 230 °C and 254 °C) observed which suggests that **PDPPF-TFPT** polymer might be crystalline by nature.

The optical properties of **PDPPF-TFPT** were studied by solution and thin film UV-Vis-NIR absorption spectroscopy. In chloroform solution, **PDPPF-TFPT** exhibits maximum absorption peak (λ_{max}) at 700 nm, while its thin film showed λ_{max} at 716 nm (Fig. 1a). The red shift of 16 nm in the film compared to solution also indicates the some degree of solid state ordering. The optical band gap was calculated from the thin film absorption cut-off (~900 nm) and was found to be 1.37 eV. The HOMO energy level for **PDPPF-TFPT** was determined by photoelectron spectroscopy in air (PESA) using thin film spin coated from chloroform solution on glass. The obtained HOMO value is to be 5.48 eV (Fig. 1b). The LUMO energy value was calculated from the difference between the HOMO and optical band gap. The LUMO value was obtained as 4.11 eV and as per HOMO-LUMO values concern, **PDPPF-TFPT** can be either ambipolar or *n*-type organic semiconductor. The reasonably low-lying LUMO energy level is due to the incorporation of tetrafluorophenyl strong electron accepting conjugated block.

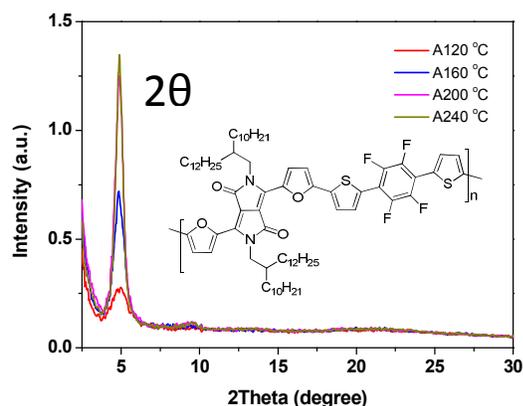


Fig. 2 XRD data obtained from spin-coated **PDPPF-TFPT** thin films (~35 nm) on OTS modified SiO₂/Si substrates annealed at different temperatures.

The solid state ordering of **PDPPF-TFPT** was studied by conventional X-ray diffraction (XRD) measurements. The XRD study was conducted at 120, 160, 200 and 240 °C preannealed thin film of **PDPPF-TFPT** on octadecyltrichlorosilane (OTS) treated Si/SiO₂ substrate as shown in Fig. 2. Weak diffractions was observed for the as spun polymer thin film indicating disordered structure. When the **PDPPF-TFPT** films were subjected to thermal annealing, the primary diffraction peak became stronger and enhances crystallinity. The thin film annealed at 240 °C showed a strong primary diffraction peak at $2\theta = 4.90^\circ$, which is assigned for the interlayer *d*-spacing of 18.02 Å. We didn't observe any secondary diffraction peak for π - π stacking in conventional XRD diffractogram. In order to confirm π - π stacking peak and its distance, two-dimensional X-ray diffractometry (2D XRD) measurements were conducted. The 2D

XRD images and 2D-XRD diffraction pattern of **PDPPF-TFPT** is shown in Fig. 3, where the incident X-ray was parallel to the polymer flakes. The 2D XRD image clearly exhibits a sharp pattern for interlayer and π - π stacking spacing. The primary diffraction peak (100) was observed at $2\theta = 4.94^\circ$ which is consistent with spin coated polymer thin film XRD data. Additionally, secondary diffraction peak (010) was observed at $2\theta = 23.92^\circ$ which can be associated to the π - π stacking distance ($d \sim 3.71$ Å). XRD results clearly signify the signature of highly ordered layer-by-layer lamellar formation with an edge-on orientation.

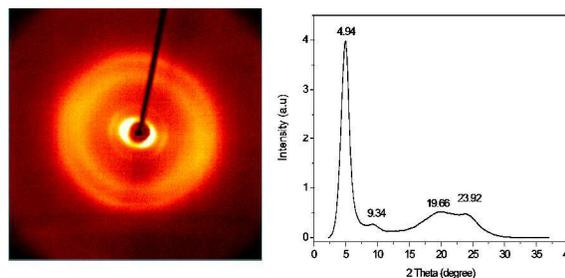


Fig. 3 2-D XRD image (left) and 2-D XRD pattern intensity graphs (right) obtained with the incident X-ray parallel to the thin film stack of **PDPPF-TFPT** copolymer (right).

The electrical properties of **PDPPF-TFPT** were measured by using thin film of **PDPPF-TFPT** as channel semiconductors in bottom-gate, top-contact field effect transistor devices. Heavily *n*-doped silicon wafer as a gate with a layer of ~200 nm SiO₂ on the surface was used as a gate dielectric respectively. The Si/SiO₂ substrates were treated with OTS self-assembled monolayers (SAMs) prior to polymer thin film deposition. The polymer thin films were deposited from the chloroform solution on OTS treated substrates preannealed at 120, 160, 200 and 240 °C, respectively, for 20 min on a hot plate.

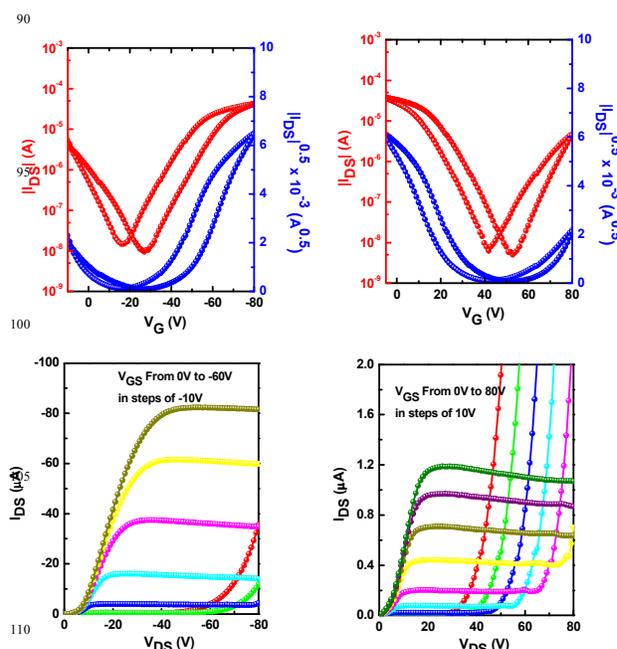


Fig. 4 Transfer and output characteristics in the hole and electron enhancement modes of **PDPPF-TFPT** based ambipolar OFET annealed at 240 °C on OTS treated *n*⁺-Si/SiO₂ substrate. The hole and electron transfer curves were derived at drain voltages (VD) of -80 V and +80V.

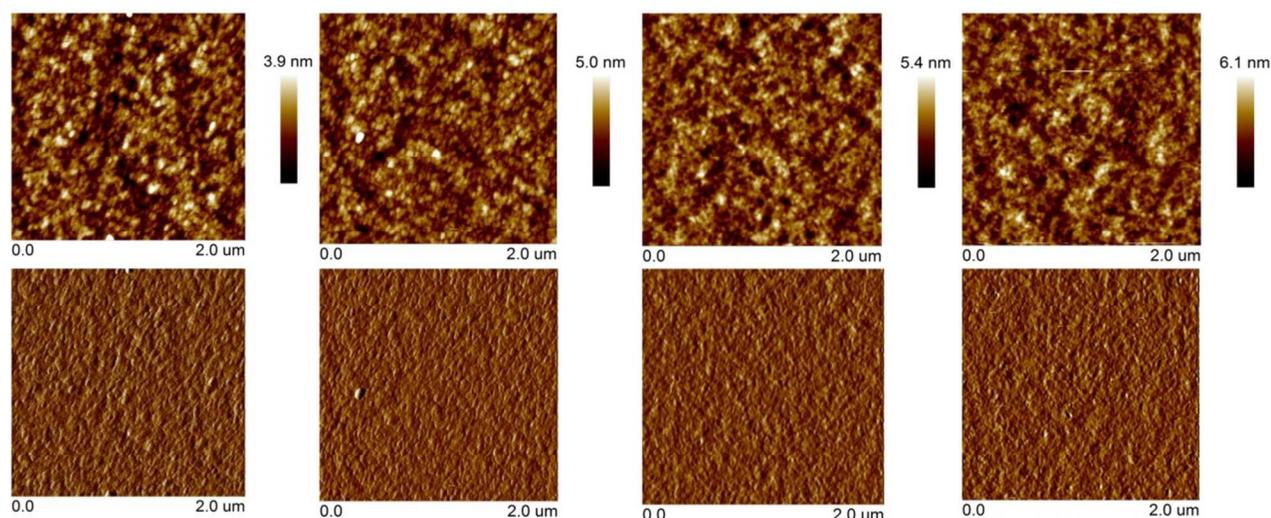
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Table 1. OFET device performance of **PDPPF-TFPT (P1)** thin films annealed at 120, 160, 200 and 240 °C on OTS treated n+-Si/SiO₂ substrates using bottom-gate, top-contact (BGTC) devices.

	TA	Hole			Electron		
		[cm ² V ⁻¹ s ⁻¹]	V _T [V]	On/off	[cm ² V ⁻¹ s ⁻¹]	V _T [V]	On/off
P1	120	0.16-0.20	-40 - -43	4.9×10 ⁴	0.04-0.06	48 - 50	1.0×10 ⁴
P1	160	0.26-0.32	-36 - -38	1.3×10 ⁴	0.05-0.08	52-54	1.5×10 ³
P1	200	0.32-0.36	-27 - -30	7.3×10 ³	0.07-0.10	50-52	6.4×10 ²
P1	240	0.32-0.40	-29 - -32	8.1×10 ²	0.06-0.12	30-33	1.8×10 ²

**Fig. 5** AFM phase images of **PDPPF-TFPT** thin films annealed at 120, 160, 200 and 240 °C on OTS treated n+-Si/SiO₂ substrates.

PDPPF-TFPT based OFET devices exhibits ambipolar behavior in both hole and electron enhancement modes. Typical V-shaped transfer curves were observed in both modes (hole and electron enhancement) which is unique feature of ambipolar behavior. The hole and electron mobilities were calculated from the transfer curves using their respective saturation regime according to standard procedures and are summarized in Table 1. The hole and electron mobility of 0.20 cm²/Vs and 0.06 cm²/Vs was measured for 120 °C preannealed thin films. When the film was annealed at 160 °C, the hole mobility improved slightly to 0.32 cm²/Vs and the electron mobility improved to 0.08 cm²/Vs. Furthermore, when the annealing temperature was further increased to 200 °C, the hole mobility increased to 0.36 cm²/Vs whereas the electron mobility reached to 0.10 cm²/Vs. At the last, annealing was conducted at 240 °C and the hole mobility was reached maximum up to 0.40 cm²/Vs whereas electron mobility was recorded at 0.12 cm²/Vs. The mobility values measured at 240 °C annealing temperature is one of the highest among all annealed samples. Compared to the previously reported only n-type OFETs based

on tetrafluorophenylene and thiophene substituted DPP copolymer,²⁵ **PDPPF-TFPT** exhibits ambipolar nature which might be arising due to the incorporation of additional two electron donating thiophene and two furan flanked on DPP building blocks in the backbone balances hole transport. Atomic force microscopy (AFM) analysis was conducted to study the effect of various annealing temperatures on the charge carrier mobility. The AFM height and phase images of **PDPPF-TFPT** thin films annealed at 120, 160, 200 and 240 °C on OTS treated n+-Si/SiO₂ substrates are shown in Fig. 5. AFM was conducted to elucidate the effects of annealing on morphology. The AFM height images at 120 °C annealed polymer thin film exhibits fine grains with a surface roughness of 0.647 nm, as annealing temperature increased to 160 and 200 °C, the grain size becomes slightly bigger and surface roughness increase to 0.723 and 0.768 nm to some extent organized. As the annealing temperature was increased to 240 °C further, the morphology becomes more organized and exhibits well aligned grains with a surface roughness of 0.915 nm. The morphological observations studied

by AFM are also in a well agreement with the sharpening of the 2 θ peak with respect to annealing from lower to higher temperatures as shown in Fig. 2. As the annealing temperature increases, the amorphous nature of thin film becomes more semicrystalline and which is suitable for efficient charge carrier transport.

Conclusions

In summary, we have demonstrated that thiophene-tetrafluorophenyl-thiophene (D-A-D) is a potential conjugated building block for synthesizing high performance semiconducting polymer for use in ambipolar OFETs. By balancing the electron-withdrawing tetrafluorophenylene/DPP and electron-donating furan/thiophene building blocks in the conjugated backbone, the polymer **PDPPF-TFPT** displayed balanced hole and electron mobility in OFET devices. This polymer has shown high hole and electron mobility of 0.40 cm²/Vs and 0.12 cm²/Vs in a hole and electron enhancement modes, respectively, in a top-contact bottom-gate devices. The effect of annealing temperature on the thin films of **PDPPF-TFPT** clearly indicates the significant ordering of the grain size which is attributed with the enhancement of semicrystalline nature. Such a semi-crystalline nature is arising from the strong intermolecular interactions and lower π - π stacking distance between the polymeric chains. Such behavior is arising from the electronegative four fluorine atoms substituted at phenylene unit.

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Notes and references

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†Electronic Supplementary Information (ESI) available: NMR, MALDI-TOF MS, and DSC data of compounds **2** and **4** and **PDPPF-TFPT**. See DOI: 10.1039/b000000x/

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Thiophene-tetrafluorophenyl-thiophene donor-acceptor-donor building block was used in combination with furan substituted diketopyrrolopyrrole for synthesizing polymer PDPPF-TFPT. PDPPF-TFPT exhibits an ambipolar behaviour in organic thin-film transistors, with hole and electron mobilities as high as $0.40 \text{ cm}^2/\text{Vs}$ and $0.12 \text{ cm}^2/\text{Vs}$.

