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PAPER

Incorporation of fused tetrathiafulvalene units in a DPP-terthiophene copolymer for air stable solution processable organic field effect transistors

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A new terthiophene–diketopyrrolopyrrole (DPP) copolymer has been synthesised in which the central thiophene ring within the terthiophene repeat unit is attached to a fused tetrathiafulvalene (TTF). The electrochemical and absorption data of the polymer, **p(DPP-TTF)**, are presented, and the multi-redox states are investigated by UV-vis spectroelectrochemistry. Bottom gate/bottom contact field effect transistors were fabricated from films of **p(DPP-TTF)** annealed at 200 °C. The material, which under these conditions forms a fibrous structure, exhibited hole mobilities of $4 \pm 2 \times 10^{-2}$ cm² V⁻¹ s⁻¹ with an on/off ratio of 1×10^4 . The transistors showed little sign of degradation over 15 days of exposure under ambient conditions, demonstrating excellent air-stability. This characteristic is attributed to the incorporation of the TTF unit into the polymer.

Introduction

Since the discovery of conjugated polymers in the late 70s,¹ plastic electronics have attracted vast interest due to their flexibility, light weight, ability to be produced on a large scale, ease of manufacture and relatively low cost. The development of better materials and new strategies in device fabrication methods have led these materials to be used in different applications such as organic photovoltaics (OPVs),² organic field-effect transistors (OFETs),³ organic light emitting diodes (OLEDs)⁴ and electrochromic devices.⁵ Several properties are desirable for candidate polymers in order for them to be considered for such applications, including a low band gap,⁶ specific levels for the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), broad absorption in the UV-vis and near-infrared, solution processability, planarity and crystallinity, superior film-forming ability and high stability.

Although OFETs have been mainly prepared by using (i) single-crystals,⁷ (ii) vacuum-deposited thin-films or (iii) solutionprocessed thin-films from small molecules (rubrene,⁸ acenes,⁹ perylenes,¹⁰ thiophene-fused aromatic compounds^{11,12} and tetrathiafulvalene-derivatives (TTFs)^{13,14}), conjugated polymers have also shown good device performances.^{15–18} In fact, these materials have already exceeded the benchmark of amorphous silicon (0.1–1 cm² V⁻¹ s⁻¹), which is the main active material in thin-film transistors. Among these materials, polymers based on diketopyrrolopyrrole (DPP, 1) have been widely studied in the last few years.¹⁹ The large intermolecular interactions, due to

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 π - π stacking between the chains of these polymers, favour supramolecular order and increased charge carrier mobilities (electrons and holes). The main advantage of DPP-containing polymers, such as 2,²⁰ is not only the good mobilities they present, but also their ambipolar characteristics.²⁰⁻²³

The combination of different electroactive units into one single material is a fascinating prospect as they can exhibit additional or even hybrid properties. In that sense, the incorporation of TTF into conjugated polymers has been particularly interesting.²⁴⁻²⁸ The aim of directly incorporating a TTF unit into a conjugated polymer led us to synthesise a fused dibromothieno-TTF derivative which was then polymerised using Yamamoto conditions (3).²⁹⁻³² Due to their outstanding donor properties, TTF and its derivatives have been widely used in charge-transfer complexes and organic radical salts that have shown metallic conductivity and superconductivity.^{33,34} Careful design of these materials leads to features such as (i) planarity, (ii) π – π stacking and (iii) chalcogen–chalcogen non-covalent bonding, which enhance interchain interactions. Therefore, such materials are promising candidates for use in OFETs.³⁵



Herein, we present the synthesis and characteristics of a new polymer, p(DPP-TTF), featuring a fused thieno-TTF unit that has been copolymerised with a dithieno-DPP derivative. We

demonstrate here that the spin-coated polymer produces fibrous structures on OTS treated substrates. The films exhibit good wettability and highly reproducible hole mobility in OFETs under open-air conditions.

Experimental

¹H and ¹³C NMR spectra were recorded, unless stated otherwise, at room temperature on a Bruker DRX500 at 500 and 125 MHz or a Bruker Avance 400 instrument at 400 and 100 MHz; chemical shifts are given in ppm and all J values are in Hz. Elemental analyses were conducted on a Perkin Elmer 2400. MALDI-TOF spectra were run on a Shimadzu Axima-CFR spectrometer (mass range 1-150 000 Da). Cyclic voltammetry measurements were performed on a CH Instruments 660A Electrochemical Workstation with iR compensation, using anhydrous dichloromethane as the solvent. Absorption spectra were recorded on a UNICAM UV 300 instrument in dichloromethane solution. IR spectra were recorded on an ATR Microlab PAL spectrometer. Column chromatography was carried out on silica gel Zeoprep 60 Hyd (40-63 µm mesh). Alfa Aesar supplied the filter aid Celite Hyflo Super-cel (dioxosilane) used for purification. Solvents were removed using a rotary evaporator (vacuum supplied by low vacuum pump) and, where necessary, a high vacuum pump was used to remove residual solvent. All distillations were performed on a Kugelrohr Z24 with a high vacuum pump. Dry solvents were collected through a purification system. Unless stated otherwise, all reagents used were obtained commercially from Sigma Aldrich or Lancaster and used without any purification.

OFETs were characterised by bottom gate and bottom contact source and drain method. n-Doped Si wafers were used as substrates with thermally grown SiO₂ (~200 nm). The wafers had a capacitance of 17.25 nF cm⁻² and incorporated prefabricated interdigitated gold electrodes with a channel length of 2.5 mm and width of 1 cm. These prefabricated substrates were ultrasonically cleaned with organic solvents such as acetone, isopropyl alcohol and methanol, followed by nitrogen blow-dry and 2 minutes of oxygen plasma cleaning. Cleaned substrates were then treated with 10 mM of PFBT in ethanol for 15 minutes followed by treatment of 10 mM of OTS in toluene for 5 minutes. Thin films were deposited onto these substrates from 12 mg ml⁻¹ solutions of p(DPP-TTF) in chloroform via spin-coating, and each was subsequently annealed at 200 °C for 20 min in an inert atmosphere glove box. Current-voltage characteristics were recorded using a Keithley 4200 semiconductor parameter analyser under ambient atmosphere. The surface morphology was investigated by tapping mode atomic force microscopy (AFM), Dimension 3100.

Synthesis of 9

To a mixture of **8** (0.25 g, 1.1 mmol) and **6** (0.26 g, 0.8 mmol), triethylphosphite (5 ml) was added and the reaction was stirred under nitrogen at 120 °C for 2 h. The reaction mixture was diluted in dichloromethane (200 ml) and filtered. The solvent was removed under vacuum and the residue was dissolved in dichloromethane and precipitated in methanol. The precipitate was washed with cold methanol and dried at low pressure to give

an orange powder (250 mg, 63%). ¹H-NMR (CDCl₃): 2.44 (6H, s); ¹³C-NMR (100 MHz, CDCl₃): 136.5, 126.5, 116.2, 111.6, 96.5, 18.3; MS: *m*/*z*, MALDI, M⁺ 509.42; IR ν_{max} (cm⁻¹): 2993, 2923, 1526, 1495, 1418, 1288, 1032, 967, 896, 762. Elemental analysis: C₁₀H₆Br₂S₇ C, 23.53; H, 1.18; S, 43.97%; found: C, 23.12; H, 0.98; S, 43.50%. M.p.: 170–172 °C.

Synthesis of 11

A solution of 10 (0.86 g, 1.0 mmol) and 2-isopropoxy-4,4,5, 5-tetramethyl-1,3,2-dioxaborolane (0.61 ml, 0.56 g, 3.0 mmol) in dry THF (10 ml) was cooled to -25 °C and lithium diisopropylamide (1.43 ml, 1.6 M in tetrahydrofuran, 2.3 mmol) was added drop-wise. The reaction was stirred under nitrogen at 0 °C for 1 h. A solution of HCl (0.1 M, 10 ml) was added and the product was extracted with dichloromethane $(3 \times 25 \text{ ml})$, dried over MgSO₄ and the solvent evaporated. The crude mixture was dissolved in dichloromethane and poured into cold acetone. After filtration, the filtrate was washed with cold acetone and dried under low vacuum to give a dark pink powder (0.84 g, 75%). ¹H-NMR (CDCl₃): 8.91 (2H, d, *J* = 3.9), 7.71 (2H, d, *J* = 3.9), 4.05 (4H, d, J = 7.7), 1.89 (2H, br), 1.37 (24H, s), 1.30–1.17 (64H, m) and 0.86 (12H, m); ¹³C-NMR (CDCl₃): 161.25, 140.02, 137.14, 135.61, 135.17, 108.24, 84.07, 45.78, 37.28, 31.41, 31.37, 30.79, 29.51, 29.12, 29.07, 29.04, 29.01, 28.84, 28.77, 25.83, 24.27, 22.17 and 22.15; MS: m/z, MALDI, M⁺ 1112.51; IR ν_{max} (cm⁻¹): 2926, 2854, 1661, 1560, 1515, 1454, 1400, 1362, 1340, 1308, 1243, 1167, 1103, 1077, 1014, 852. Elemental analysis: C, 71.20; H, 9.96; N, 2.52; S, 5.76; found: C, 71.60; H, 9.52; N, 2.43; S, 5.81%. M.p.: 166-168 °C.

Synthesis of p(DPP-TTF)

Compound 11 (760 mg, 0.7 mmol), compound 9 (350 mg, 0.7 mmol), tris[dibenzylideneacetone]dipalladium(0) (50 mg) and tri-tert-butyl phosphonium tetrafluoroborate (60 mg) were dissolved in dry tetrahydrofuran (20 ml) and tripotassium phosphate (0.22 g, 1.0 mmol) dissolved in water (3 ml) was added to the solution. The reaction was stirred at 80 °C under nitrogen for 48 h and 2-bromothiophene (0.01 ml, 16 mg, 0.1 mmol) added after this time. The reaction was stirred at the same temperature for 6 h and 2-thienylboronic acid (19 mg, 0.15 mmol) was then added. At this point, the reaction was stirred for another 6 h before it was poured into methanol (500 ml) and filtered. The solids were purified by Soxhlet extractions with methanol, acetone and chloroform. The chloroform fractions were redissolved in chloroform and precipitated in methanol to give 620 mg of a dark green-black powder (73% yield). ¹H-NMR (CDCl₃): 8.87-9.50 (2H, br), 7.40-6.80 (2H, br), 4.50-3.62 (4H, br), 2.73-2.40 (6H, br), 2.12-1.85 (2H, br), 1.49-1.10 (64H, br) and 0.94–0.80 (12H, br); $M_{\rm n} = 9.6$ kDa (P.I. = 3.0).

Results and discussion

Synthesis of monomers and polymerisation

The synthesis of the fused thieno-TTF monomer was carried out following a previously published procedure for an analogous compound with thiohexyl chains instead of thiomethyl substituents.^{31,32} Transchalcogenation of **4** using $Hg(OAc)_2$ gave

compound **5**, with subsequent bromination using bromine in dichloromethane to afford the first half-unit of the TTF monomer, **6**. Since the yield of unsymmetrical TTFs is enhanced by coupling a carbonyl derivative with a corresponding thione derivative,³⁶ the thione version of the bismethylthio half unit of the TTF was synthesised. Compound **8**³⁷ was obtained after reacting the zincate complex³⁸ **7** with methyl iodide. Whereas for polymer **3**, long alkyl chains were required to give solubility to the polymer, in this case we avoided them as X-ray crystallographic studies showed that the two hexyl chains of the monomer of polymer **3** are almost orthogonal to the remainder of the molecule (85.2°).³² This could be detrimental towards close interchain interactions and the film-forming properties of the polymer. Triethyl phosphite-mediated coupling of **6** and **8** gave the orange TTF derivative **9** in 63% yield (Scheme 1).

The DPP core 1 (R = thienyl) was N-alkylated with long branched chains in DMF to give 10.22 The boronic ester 11 was prepared following a procedure reported in the literature for a similar compound by reacting 10 with LDA and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxoborolane.³⁹ The polymer p(DPP-TTF) was synthesised by a modified Suzuki-Miyaura crosscoupling method using Pd₂(dba)₃ as a catalyst and potassium phosphate as a base. Soxhlet extractions with methanol, acetone and chloroform were carried out to give a dark-greenish polymer. The solids obtained from the chloroform fractions were used for characterisation of the polymer and for the preparation of OFET devices. The degree of polymerisation was studied by gel permeation chromatography in chlorobenzene giving a molecular weight of $M_n = 9.6$ kDa (P.I. = 3.0). The ¹H-NMR of p(DPP-TTF) (see Fig. 1) also shows broad peaks indicating that a high degree of polymerisation had been obtained.

Thermal properties

Thermogravimetric analysis (TGA) was carried out in order to study the thermal stability of **p(DPP-TTF)**. The polymer showed



Fig. 1 ¹H-NMR of p(DPP-TTF) in deuterated chloroform.

good stability up to 300 °C. This temperature is high enough to treat the polymer thermally and obtain ordered morphologies without damaging the polymer during the preparation of devices. Differential scanning calorimetry (DSC) of **p(DPP-TTF)** showed evidence of a crystallisation point occurring at around 175 °C.

Electrochemistry and electronic absorption studies

Cyclic voltammetry of the polymer both in solution (0.1 mM of **p(DPP-TTF)** based on the repeat unit) and solid-state, as a dropcast film, was carried out to study its redox behaviour (Fig. 2 and Table 1). The electrochemistry of the polymer in solution was carried out in dichloromethane using tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) (0.1 M) as the supporting electrolyte. The solid-state electrochemistry was carried out by drop-casting a solution of **p(DPP-TTF)** in dichloromethane, onto a glassy carbon disk working electrode and the studies were developed in acetonitrile using Bu₄NPF₆ (0.1 M) as the



Scheme 1 Synthetic route to p(DPP-TTF). (a) 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, LDA, dry THF.



Fig. 2 Cyclic voltammetry of **p(DPP-TTF)** in solution (continuous line) and thin-film (dot-dashed line). The experiments in solution were carried out in dichloromethane (0.1 mM) using a glassy carbon electrode. A film was deposited from a solution of **p(DPP-TTF)** in dichloromethane on a glassy carbon electrode and experiments were carried out in acetoni-trile. In both cases, a Ag wire reference electrode and a Pt counter-electrode, in the presence of Bu_4NPF_6 (0.1 M), were used.

supporting electrolyte. All the values are quoted *versus* the redox potential of the ferrocene/ferrocenium couple.

In solution, **p(DPP-TTF)** shows several oxidation processes, beginning with a well-defined wave at +0.33 V, followed by peaks at +0.56, +0.71 V and +0.85 V. Based on our previous studies, the first reversible oxidation peak can be attributed to the bis-(thioether)-substituted half-unit, whereas the next reversible process is ascribed to the dithiole half-unit fused to the thiophene of the polymer backbone.^{29,30,32} This accounts for the classical reversible double oxidation process of the TTF unit. Accurately assigning the remaining peaks in the voltammogram is speculative due to the complexity of the structure, but oxidation of the terthiophene unit will certainly be taking place.⁴⁰ The polymer shows a quasi-reversible reduction wave at -1.45 V which is assigned to the DPP repeat unit.

Interestingly, the redox behaviour of **p(DPP-TTF)** in the solidstate differs significantly from its behaviour in solution. The polymer shows two quasi-reversible peaks at +0.45 and +0.68 V and two reduction peaks at -1.41 and -1.76 V, respectively. The latter could well be due to the reduction of the terthiophene component of the polymer, which is less reversible than the redox wave associated with the DPP unit. The first oxidation in the solid state occurs at a considerably higher potential value compared to the same process in solution. This difference in the first oxidation potential of the polymer in solution and in the solid might be attributed to partial charge transfer between the TTF and DPP units in the solid state.

UV-vis spectroelectrochemical measurements were carried out on a thin film of the drop-cast polymer on an ITO slide. The film was dedoped in an acetonitrile solution in the presence of Bu₄NPF₆ (0.1 M), by repetitive cycling between the first oxidation and the first reduction waves, which covers the neutral state of the polymer. The results are shown in Fig. 3. Previous spectroelectrochemical studies of TTF derivatives show that when the first oxidation of the TTF derivative occurs two new absorption bands are observed at 430 and 580 nm.^{29,30} These bands are sometimes accompanied by an extra absorption band at around 800 nm, which is assigned to intermolecular charge transfer processes between TTF radical cations or as an additional absorption band associated to the radical cation. The second oxidation leads to the dication and the disappearance of the previous absorption bands, whilst another band at around 390 nm develops (for the TTF dication). Using a pseudo-silver wire reference electrode, the potentials at which the peaks at 390



Fig. 3 UV-vis spectroelectrochemical plot upon p-doping **p(DPP-TTF)**, deposited on ITO glass, using a Ag wire reference electrode and Pt counter-electrode. Experiments were run in monomer-free acetonitrile solution and in the presence of Bu_4NPF_6 (0.1 M).

 Table 1
 Data of electrochemistry and electronic studies

	Cyclic voltammetry						UV-vis absorption	
	Solution			Film			Solution	Film
	$E_{\rm ox}/{\rm V}$	$E_{\rm red}/{\rm V}$	HOMO/ LUMO [gap]/eV	$E_{\rm ox}/V$	$E_{\rm red}/{\rm V}$	HOMO/ LUMO [gap]/eV	$\lambda(\max)/nm$ [E_g/eV]	$\lambda(\max)/nm$ [E_g/eV]
p(DPP-TTF)	$+0.37/0.29^{a},$ $+0.56^{b}, +0.76/$ $0.67^{a}, +0.85^{b}$	-1.45 ^c	-4.95/ $-3.55 [1.40]^d$	+0.45 ^c , +0.68 ^c	$-1.41^{a}, -1.76^{b}$	-5.13/ -3.49 [1.64] ^d	769 [1.32] ^c	786 [1.26] ^e

^{*a*} Reversible peaks. ^{*b*} Irreversible peaks. ^{*c*} Quasi-reversible peaks. ^{*d*} Electrochemical HOMO–LUMO gap was calculated from the onset of the first oxidation and reduction processes and referred to ferrocene (-4.8 eV). ^{*e*} Optical band gap was calculated from the onset of the longest wavelength absorption peak.

and 600 nm appeared are around ± 1.0 V. These bands are assigned to the radical cations of the TTF derivatives that are produced upon oxidation. Interestingly, **p(DPP-TTF)** reveals an additional broad band that extends from around 890 nm to 1100 nm. The nature of this band is overlapped by the large absorption band of the polymer backbone, but it can be assigned to the charge transfer process that occurs from the TTF part of the polymer to the conjugated backbone when the TTF unit is oxidised.

Fig. 4 shows the electronic absorption spectra of copolymer p(DPP-TTF) in a dichloromethane solution and as a film dropcast on indium tin oxide (ITO). The polymer has a broad absorption band in both states from around 500 nm to 1000 nm. Due to interactions between polymer chains in the solid state, the values of the absorption maximum and the onset of the longest wavelength absorption band are bathochromically shifted compared to the solution state spectrum. In solution, the maximum absorption occurs at 769 nm, whereas in the solid state it is shifted by 17 nm. The onset of the optical absorption of the polymer film lies at around 1000 nm, which gives an optical band gap of 1.26 eV.

In conjugated polymers, the difference between the onset of the first oxidation and the onset of the first reduction corresponds to the electrochemical band gap.6 As we have stated, the first oxidation peak of p(DPP-TTF) does not belong to a removal of an electron from the polymeric backbone, but from the bis-(thioether)-substituted half-unit of the TTF. Therefore, the band gap we can obtain from the difference of oxidation and reduction onsets cannot be illustrative of the optical band gap of the polymer, which is inferred from the onset of the π - π * band in the absorption spectrum. The electrochemical studies carried out in solution give a HOMO-LUMO gap of 1.40 eV, whereas the gap obtained for the solid state is 1.64 eV. On the other hand, the optical values are 1.32 eV and 1.26 eV for studies carried out in solution and in the solid state. As expected, the optical band gap in the solid state is lower than that obtained in solution due to interchain interactions.⁶ If we compare these two values with the ones obtained by electrochemistry, we see that whereas the gap in solution is similar and within the same values, the gap in the solid state differs by more than 0.30 eV. This is not uncommon in conjugated polymers and is attributed to the structural differences in the thin film or to the exciton binding energy for conjugated polymers.⁴¹ As stated above, stronger donor-



Fig. 4 UV-vis absorption spectra of **p(DPP-TTF)** in a dichloromethane solution (continuous line) and in the solid state (dot-dashed line).

acceptor interactions between the TTF and DPP units will arise in the solid state and this will affect the redox potentials of these two components.

Field effect transistor properties and surface morphology

Fig. 5 (top) shows the output characteristics of p(DPP-TTF) devices recorded at different source and drain voltages up to -80V at intervals of 1 V, with a gate bias voltage between -10 V and -90 V at intervals of -20 V. Though these devices exhibit some hysteresis, they all have clear linear and saturation regions. Fig. 5 (bottom) shows transfer characteristics recorded at a V_{DS} of -90 V for 15 days, and for clarity, data recorded on the 1st, 8th and 15th days are shown. A saturation mobility of 4 \pm 2 \times 10^{-2} cm² V⁻¹ s⁻¹ was calculated by fitting a straight line to V_{GS} vs. $(I_{\rm DS})^{1/2}$ in the saturation region. An on/off ratio of 1×10^4 is also deduced from Fig. 5 (bottom). This hole mobility is similar to that of non-TTF analogues of DPP polymers already reported.^{20–23} Fig. 6 shows a topographic image recorded by tapping mode AFM. The representative picture was taken from the same devices used for mobility measurements. It is seen here that annealed p(DPP-TTF) films on octadecyltrichlorosilane (OTS) treated Si/SiO₂ substrates produce fibre-like structures upon annealing (200 °C for 20 min). Notably, DPP analogues reported to date are semi-crystalline.20-23

Non-uniform distribution and orientation of these fibre-like structures may lead to a slightly lower mobility (of the order of $\sim 3 \times 10^{-2}$ cm² V⁻¹ s⁻¹) as opposed to DPP polymer analogues



Fig. 5 Output characteristics (top) measured at intervals of -20 V and (bottom) transfer characteristics with $V_{\rm DS} = -90$ V of **p(DPP-TTF)** measured in an ambient lab atmosphere over 15 days. For clarity, the data shown here are measured on the 1st, 8th and 15th days. Hole mobility of $4 \pm 2 \times 10^{-2}$ cm² V⁻¹ s⁻¹ is calculated by fitting a straight line to $V_{\rm GS}$ vs. $(I_{\rm DS})^{1/2}$ in the saturation region.



Fig. 6 Tapping mode AFM height images of **p(DPP-TTF)** on OTS treated SiO₂ surfaces after annealing at 200 °C for 20 min.

that do not contain the TTF unit but have thiophene units (highest mobility of ~1 cm² V⁻¹ s⁻¹).²⁰⁻²³ Further optimisation of processing conditions for device fabrication such as the spinning process, solution concentration, and OTS treatment of SiO₂ substrates might produce higher mobilities similar to other DPPcontaining polymers. These device characteristics are highly reproducible under ambient laboratory conditions as shown in Fig. 5 (bottom). The stability of these devices under ambient atmospheric conditions has been attributed to the aforementioned partial charge transfer interactions between the TTF and DPP units in **p**(**DPP-TTF**), which define a stable morphology and propensity of the materials to withstand the effects of an ambient environment. Moreover, the stability of the TTF unit towards oxidation is extremely well known.

Summary

We have reported the synthesis, properties and device characteristics of **p(DPP-TTF)**, an air stable and solution processable polymer containing TTF and DPP units within the conjugated chain, that exhibits a field effect mobility of $\sim 4 \times 10^{-2}$ cm² V⁻¹ s⁻¹ and an on/off ratio of $\sim 10^4$. Air stability is due to the presence of TTF–DPP interactions in the bulk of the solid film and the inherent stabilisation of the TTF structure towards p-doping. Additionally, uniform wettability (even on OTS treated SiO₂) over 2 cm \times 2 cm substrates by spin-coating means that this polymer can be efficiently used in any solution processing methods such as inkjet printing, spin-coating or roll-to-roll processing for organic device applications.

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