ELECTRONIC SUPPLEMENTARY INFORMATION

SYNTHESIS AND CHARACTERISATIONS OF FLUORENONE-THIOPHENE BASED DONOR-ACCEPTOR OLIGOMERS: ROLE OF MOIETY SEQUENCE ONTO PACKING AND OPTO-ELECTRONIC PROPERTIES

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1-Characterization of T2FT2

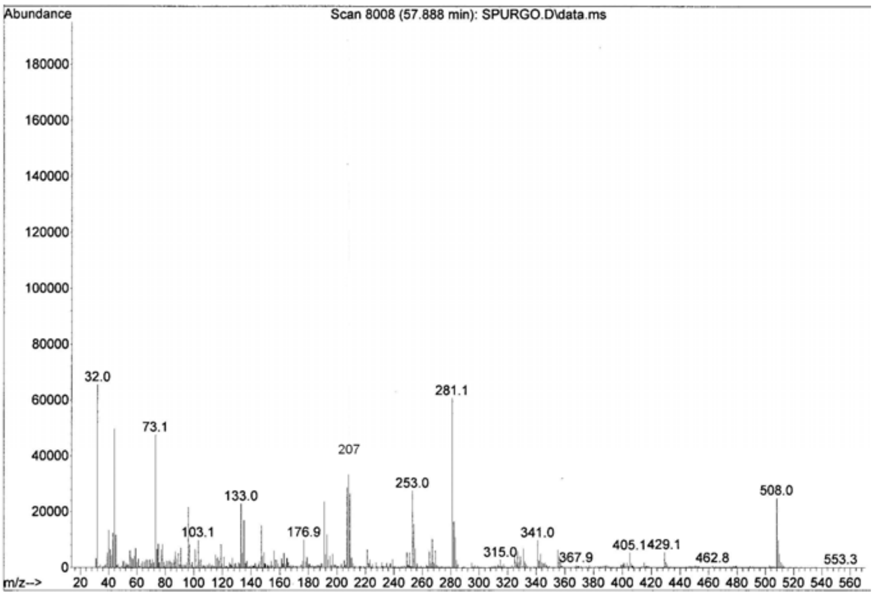


Fig 1 Mass Fragmentation of 2,7-Bis(2,2'-Bithiophene-5'-yl)-fluoren-9-one. (T2FT2)

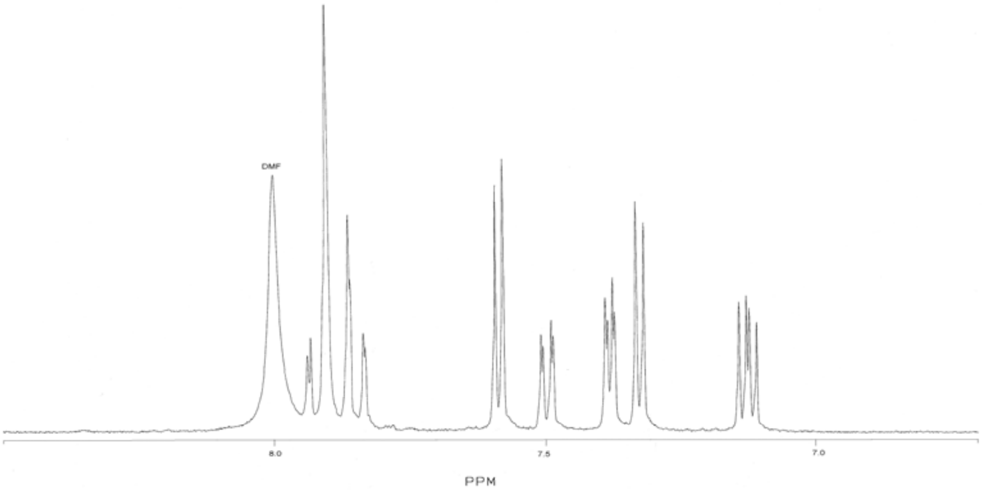


Fig. 2. ^{1}H NMR in d^{7-}DMF at 120°C of **T2FT2** molecule.

2-Electrochemistry of the individual molecules

TFT and H2TFT

H2TFT is the T-F-T monomer with hexylsubstitution at the internal 3-positions of the two thiophene rings. Thus this monomer may be compared with its analogue dioctylsubstituted at the external 4 positions FDOBT [1] (or O2TFT by using the acronym corresponding to those in present work) which shows larger conjugation hence an irreversible oxidation peak at 0.6V [4]. The cyclic voltammogram CV of TFT and H2TFT shows irreversible oxidation with production of polymer **(**degradation occurs if higher potentials are used) at 0.95V and 0.99V respectively and a reversible reduction processes at -1.42V an-1.50V respectively.

The redox processes of the polymer are reversible. The charge stored for H2TFT polymerization corresponds to ca 3% of that used for deposition, the scarce yield being due to dissolution of oligomers in solution. The bulk polymer is in fact soluble (see below) and only the insoluble fraction deposits on the electrode.

It is interesting to note that poly(H2TFT) is reversibly oxidized at ca 0.95 V whereas its analogue poly(FDOBT) is oxidized at ca 0.46 V [37]. This high difference in redox potentials may be related to the different substitution pattern, as it appears from the optical spectrum of poly(H2TFT) (maximum at 365nm) hypsochromically shifted compared with that of poly(FDOBT). (maximum at 389nm)

Electrosynthesis of poly(H2TFT)

Bulk polymer has been produced by electrolysis (2 F mol^{-1}) at 1.1 V of 32 mg H2TFT in 25 ml CH_2Cl_2 + 0.1 M Bu_4NClO_4. The resulting dark suspension of the oxidized product has been reduced with a few drops of ammonia to red-orange. The solvent was evaporated, electrolyte and non reacted monomer washed out with acetonitrile and the orange solid dissolved in CHCl3 and dried (24 mg crude product, 75% yield).

T2FT2

The cyclic voltammogram CV of T2FT2 in chlorobenzene + 0.1 M Bu_4NClO_4 shows an irreversible oxidation process with polymerization on the electrode.

The redox processes of the polymer deposit are reversible and centered at E_0 = 0.50 and 0.80 V (twin process) for the oxidation and at E_0 = –1.65 V for reduction (fig.1b). The charge stored in oxidation $Q_r$ox is twice the reversible charge in reduction $Q_r$red, which corresponds to the one-electron reduction of the fluorenone moiey. Thus it is established that the two oxidation processes are the subsequent formation of the one-electron and two-electron oxidized forms of the T4 moieties.

The polymer is insoluble in all solvents included boiling tetrachloroethane.

H4T3FT3

Oxidation of this T3-F-T3 monomer produces polymer deposition. This is clearly evidence by CV (fig.5) showing the progressive growth of the polymer.

The redox processes are reversible and centered at E_0 = 0.3 and 0.6 V (twin process) for the oxidation and at E_0 = –1.6 V for the reduction (fig.1c in the text). The charge stored in oxidation $Q_r$ox corresponds to ca 30% of that used for deposition.

The charge stored in reduction $Q_r$red is a fraction of $Q_r$ox which increases as the thickness is decreased. This indicates that only a fraction of the polymer, close to the electrode, is involved in the reduction process due to charge localization and consequent slow transport. For the lower thicknesses $Q_r$ox is twice $Q_r$red, so that the two oxidation processes are also in this case the subsequent formation of polarons and bipolarons. The polymer is insoluble in all solvents included boiling tetrachloroethane.

3-FTIR spectroscopy of polymers

Infrared spectroscopy is a useful technique in the characterization of polythiophenes since it gives important information on the regularity of the polymer chain with respect to the bonding sites.

The FTIR spectrum of the investigated polymers is dominated by a band at 1720 cm^{-1} (carbonyl stretching), by the CH out-of-plane deformation band of 2,5-coupled thiophene rings at 795 cm^{-1} [10] and, in the case of hexylsubstitution, by bands at 2930 and 2860 cm^{-1} due to the methylene antisymmetrical and symmetrical stretching modes.

The band at 690 cm^{-1}, present in the monomer and due to the terminal 2-coupled thiophene rings, has almost disappeared in the polymer.

Similar behaviour is seen in the high-frequency region, where the $C\beta$-H aromatic stretching mode appears at 3060 cm^{-1}, while the band at 3100 cm^{-1} is due to the $C\alpha$-H stretch [R. M. Souto Maior, K. Hinkelmann, H. Eckert, F. Wudl, *Macromolecules* **1990,23,** 1268].

The latter band, which is clearly shown in the spectrum of the monomer, is almost absent in the spectrum of the polymer. The other bands are in practice unchanged. All these results indicate that the material is the expected α-coupled polymer.

FTIR provides an extimation of the degree of polymerization DP of the polymer through the ratio of absorbance R1 = A_{790}/A_{690} of inner over terminal hydrogen atoms (the bands are of the same relative intensity [Akimoto, M.; Furukawa, Y.; Takeuchi, Y.; Harada, I.; *Synth.Met*. **1986,***15,*353].We can also compare the band of the terminal rings with that of the carbonyl moiety. The intensity ratio R2 = A_{1720}/A_{690}, related to that of the monomer, gives directly DP of the polymer. In the case of poly(TFT) R2, and hence DP, is ca 13. In poly(T2FT2) and poly(H4T3FT3) R1 = 25-30. Since in both cases R1 = 2DP-1, DP = 13-15. The results indicate relatively long polymer chains, much longer than usually encountered in polythiophene from its oligomers.

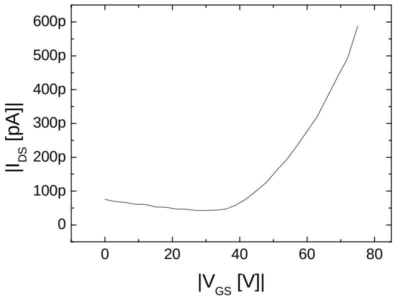
4- Optical investigations

Table 1. Optical data of the series of compounds .

compound	solution		Solid-state	
	Abs	PL	Abs	PL
TFT	288; 352;	610	310; 356; 463	547; 578
T2F	274; 327; 360; 475	600	323; 363; 443	569
H2TFT	299; 343; 460	580	295; 343; 447	580
FT2F	387; 478; 511	580; 630	407; 540	/
T2FT2	325; 394	656	394; 485	625
c-H2T2FT2	272; 318; 390;	650; 695	325; 398; 500	675
H4FT6F	354; 464; 546	663	358; 438	551; 598
H4T3FT3	345; 413; 524	662	401; 503	700

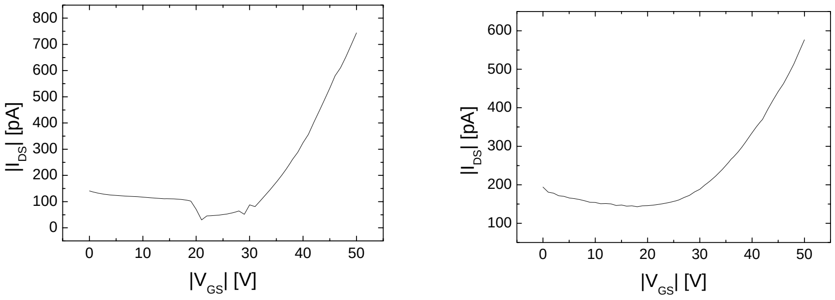
5- Curves of FET devices

TFT L=6micron |VDS|=70V



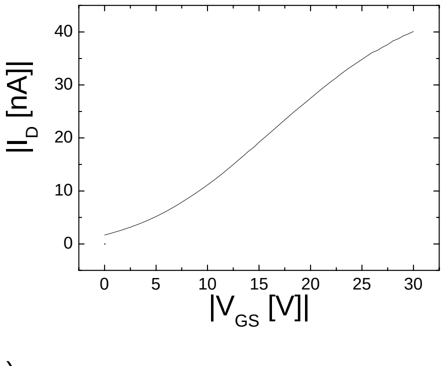
a)

FT2F L=3micron |VDS|=50V



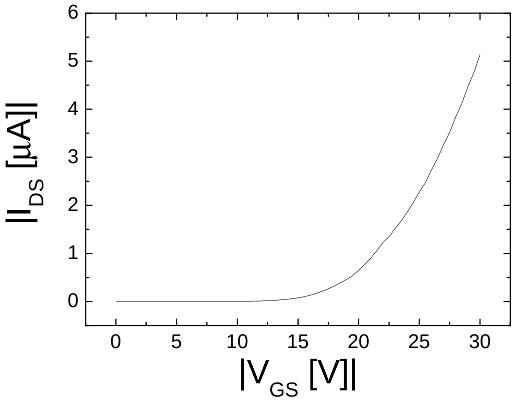
b)

T2F L=6micron |VDS|=30V



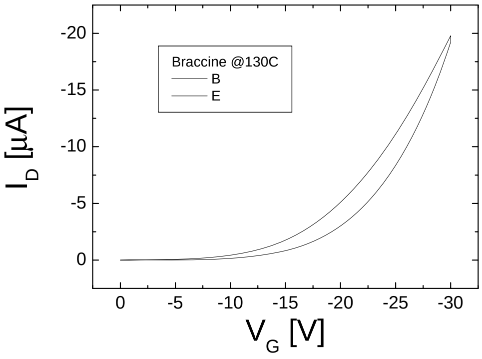
c)

T2FT2 L= 3micron |VDS|=30V



d)

c-H2T2FT2 L=6micron |VDS|=30V



e)

Fig. 3. I-V curves of OFET devices a) **TFT,** b) **FT2F,** c) **T2F,** d) **T2FT2**, e) **c-H2T2FT2 .**

5. Bulk hetero-junction solar cell

Details

Composition 1:1 **H4FT6F**:PBCM by weight

Concentration: 2.12mg + 2.12mg in 212 µL of Chlorobenzene

Contacts: LiF=0.8nm + Al= 100nm

Layers spin coating: 1000 r.p.m. x60s
1500 r.p.m. x60s

Film thickness : 100 nm for film deposited at 1000 r.p.m.; 80 nm for film deposited at 1500 r.p.m.

Thermal treatment: post-annealing 70°C x5min

6-Crystal structure of TFT .

Crystal data

a = 14.8615(0.0020) alpha= 90.

b = 5.8880(0.0020) beta = 93.09(1)

c = 18.0997(0.0030) gamma= 90.

V = 1581.50(0.63) cubic-Angstrom

Niggli reduced cell: 5.888 14.861 18.100 93.09 90.00 90.00

Niggli matrix: 34.6685 220.8642 327.5992

-14.4997 0.0000 0.0000

Transformation matrix: 0.00 1.00 0.00

1.00 0.00 0.00

0.00 0.00 1.00

S 2 , O 1, C 21, H 12.

M = 344.43 (Atomic weights 1977)

Z = 4

D(calc.)= 1.4466 Mg/m**3

F(000) = 712.0

mu = 3.403 cm**-1 (Int.Tab. Vol.C, Table 4.2.4.2, p.193)

Lambda = 0.7107300 Angstrom

Number of atoms: 36

R1 = 0.0564 for 1457 Fo > 4.sigma(Fo) and 0.2127 for all 3442 data

wR2 = 0.1853, GooF = S = 0.956, Restrained GooF = 0.956 for all data

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GooF = S = 0.956; Restrained GooF = 0.956 for 0 restraints

Weight = 1 / [sigma^2(Fo^2) + (0.0828 * P)^2 + 0.54 * P] where P = (Max (Fo^2, 0) + 2 * Fc^2) / 3

Possible hydrogen bonds

Donor-H	Donor...Acceptor	H...Acceptor	Donor-H......Acceptor	
C4 -H4	C4 ...O (1)	H4 ...O (1)	C4 -H4 ...O (1)	
0.930	3.353(5)	2.47(5)	158	
1.080		2.34	156	(**)
C11 -H11	C11 ...O (1)	H11 ...O (1)	C11 -H11 ...O (1)	
0.930	3.366(5)	2.454(5)	167	
1.080		2.31	166	(**)

Number of possible hydrogen bonds 2

(**) Values normalized following G.A.Jeffrey & L.Lewis, Carbohydr.Res. (1978).60,179; R.Taylor, O.Kennard, Acta Cryst.(1983).B39,133.

Equivalent positions:

(1) -x+1,-y-1,-z+1

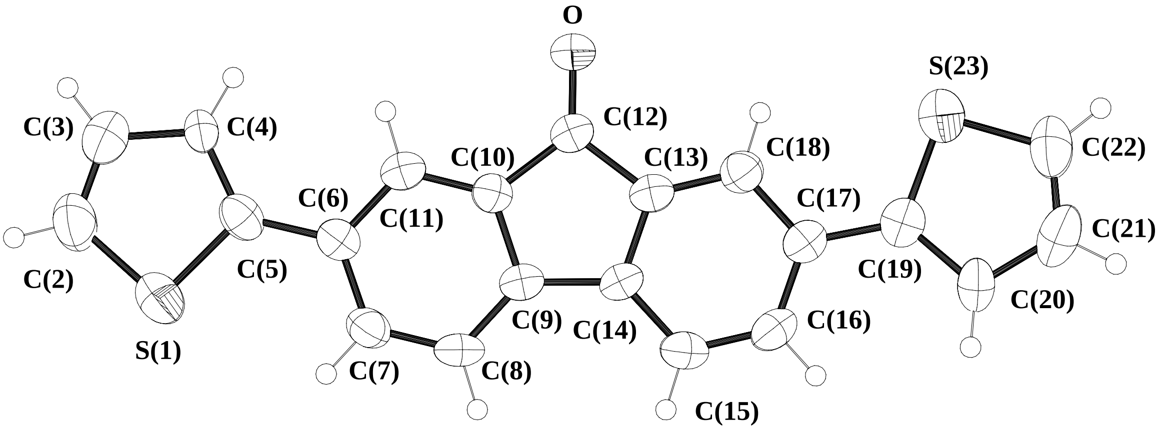

Fig.4. ORTEP drawing of **TFT** molecule. The ellipsoid probability is 50%.