

Trithienylphenylamine – extended dithiafulvene hybrids as bifunctional electroactive species†

Emilie Ripaud, Philippe Leriche,* Nicolas Cocherel, Thomas Cauchy, Pierre Frère and Jean Roncali

Received 22nd July 2010, Accepted 29th October 2010

DOI: 10.1039/c0ob00471e

Extended hybrid conjugated systems based on a trithienylphenylamine core with 1, 2 and 3 peripheral dithiafulvenyl units have been synthesized and studied by cyclic voltammetry and UV-Vis. absorption spectroscopy. Theoretical calculations have also been undergone. The behaviour of these derivatives which depends on the number of dithiafulvene moieties grafted of the central core is cleared up. One polymer, obtained from derivative **3** presents polyelectrochromic properties.

Introduction

Triphenylamine systems substituted with (oligo)thiophene functionalities are in the focus of much interest.¹ Thus, these derivatives are interesting as active materials in organic electronic devices² and as block for electroactive polymers.³ In this trend, we have recently described a series of triphenylamine-dithiafulvene hybrid systems which have been incorporated in organic field effect transistors and in solar cells.⁴ These derivatives present a very rich electrochemistry and are potentially interesting as new electroactive materials.⁵ Therefore, in the continuation of our current work on hybrid systems associating TPA and dithiafulvene moieties, we have focused our interest on compounds **1–3** which bear 1 to 3 dithiafulvene groups separated from the triphenylamine node by one thiophene spacer (Chart 1). Their syntheses, electrochemical and spectroscopic properties are presented as well as those of corresponding polymers. Electrochemical and spectroscopic experiments on compounds and corresponding polymers provide a coherent picture of the behaviour of these derivatives.

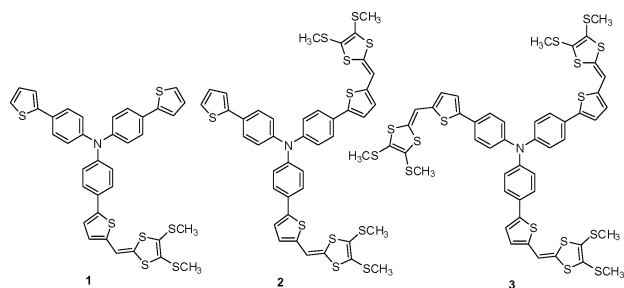


Chart 1

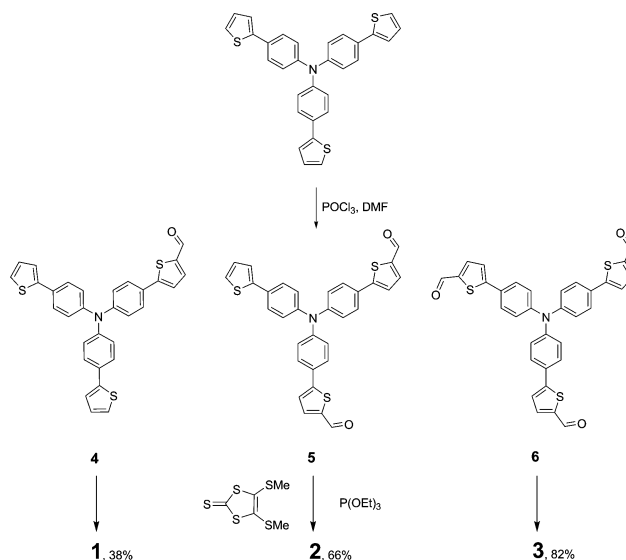
University of Angers, CNRS, MOLTECH-Anjou, 2 Bd Lavoisier, 49045, Angers, France. E-mail: philippe.leriche@univ-angers.fr; Fax: +33 (0)241735405; Tel: +33 (0)241735010

† Electronic supplementary information (ESI) available: UV-Vis spectra of compounds **1–3** – Deconvoluted CV of compound **1, 2, 9** – CV of **7**, molecular orbital diagrams of **1–3**, theoretical absorption spectrum of **1**, NMR spectra of compounds. See DOI: 10.1039/c0ob00471e

Results and discussion

Synthesis

Derivatives **1–3** have been synthesized by condensation of 4,5-dimethylthio-2-thioxo-1,3-dithiole on aldehydes **4–6** (Scheme 1).⁶ Trisaldehyde **6** was obtained in 90% yield by Vilsmeier reaction after treatment of the trithienylphenylamine with 4 equivalents of POCl_3/DMF .⁷ The use of 2 eq of POCl_3/DMF led to a mixture of derivatives **4, 5** and **6** in respectively 27, 25 and 20% yields. This reaction well reproducible can be envisioned in large scales and the purification of derivatives **4–6** is easy due to their important difference of polarity. After condensation of dithioles onto aldehyde functionalities in the presence of triethylphosphite, the target compounds **1–3** were isolated by precipitation at the end of the reaction by addition of petroleum ether or methanol in the reaction mixture. Derivatives were then purified by



Scheme 1 Synthesis of compounds **1–6**.

Table 1 Theoretical, spectroscopic and electrochemical data for derivatives **1–3**

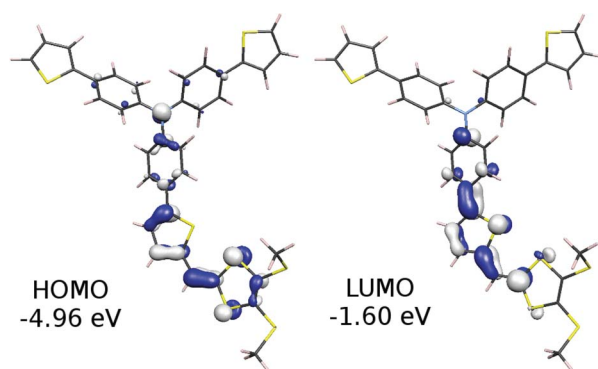
Cpnd	λ_{\max}^a /nm	E_{pa1}^b	E_{pa2}^b	HOMO	LUMO	GAP
1	422	0.56	0.71	-4.96	-1.60	3.36
2	423	0.54–0.60	0.87	-4.85	-1.62	3.20
3	436	0.54	0.89	-4.78	-1.62	3.16

^a 10^{-5} M in CH_2Cl_2 ; ^b oxidation peak vs. SCE measured from cyclic voltammetry, $<10^{-4}$ M of compounds in CH_2Cl_2 with 0.1 M Bu_4NPF_6 as supporting electrolyte, $v = 100 \text{ mV s}^{-1}$

precipitation in mixtures of solvents or when necessary carefully flash-chromatographed on neutral alumina gel in mixtures of methylenechloride/hexane with 1% of triethylamine in order to avoid oxidation. They all were satisfactorily characterized by NMR and mass spectrometry.

Theoretical calculations, spectroscopic and electrochemical measurements

The electronic properties of compounds **1–3** have been analyzed by *ab initio* theoretical calculations, UV-Vis absorption spectroscopy and cyclic voltammetry; the corresponding data are listed in Table 1. The geometries of compounds **1–3** have been optimized with DFT calculations (see exp. Part). The HOMO and LUMO of compound **1** are shown on Fig. 1 (More complete orbital diagrams of the three compounds are presented on ESI†).

**Fig. 1** Frontier orbitals of compound **1**.

As generally observed for TPA derivatives, the three N–C bonds of compounds are coplanar what is characteristic of enamines. Steric hindrances between the phenyl rings grafted on the central nitrogen atom generate the typical propeller shape of the molecules.

The HOMO and LUMO levels of compound **1** (Fig. 1) are mostly located on the arm which bears the dithiolenyl ring with very little contributions of nude thiophene rings. Note that the LUMO of **1** is strongly quinoïdic. HOMO and LUMO localizations on compounds **2** and **3** are analogous. Depending on the number of dithiolenyl rings (2 or 3), different combinations of the same HOMO or LUMO than that of **1** form the frontier orbitals of compounds **2** and **3** (ESI†). TD-DFT calculations have been undergone for derivative **1** and show unambiguously that the low lying energy transition is centered on the arm which bears the dithiafulvene group (ESI†).

Table 1 lists the calculated HOMO and LUMO energies for compounds **1–3**. As the localizations of these later are analogous, their energetic levels are very close together to leaving predict similar electronic, spectroscopic and electrochemical measurements. Nevertheless, passage from **1** to **3** leads to a slight increase of the HOMO level accompanied with a gap decrease.

Thus, in UV-vis spectroscopy, all compounds present a broad π – π^* absorption band with a λ_{\max} which shows a slight red shift from 422 to 436 nm when the number of dithiolenyl rings grafted on the trithienylphenylamine node increases from **1** to **3**.

Cyclic voltammetry was performed in methylene chloride in the presence of 0.10 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. The CV of compounds **1–3** show at least two series of oxidation processes with anodic peak potentials E_{pa}^1 and E_{pa}^2 in the 0.50–0.60 and 0.70–0.90 V regions. As shown in Table 1, E_{pa}^1 is roughly independent of the number of dithiolenyl rings on the molecule, in contrast to E_{pa}^2 which shifts positively from 0.71 V for **1** to 0.89 V for **3**. The number of electrons involved in each redox process and the eventual formation of new compounds upon oxidation depend on the number of dithiolenyl rings grafted on the trithienylphenylamine core.

CV of compounds **1–3** are shown on Fig. 2, deconvoluted CV of **1–2** are shown on ESI.† In diluted solution ($<10^{-4}$ M) derivative **1** undergoes two 1 electron reversible oxidation processes at 0.56 and 0.71 V respectively (Table 1, Fig. 1, ESI†) leading to stable radical cation and dication. Derivative **2** undergoes two series of reversible oxidation waves. The first one, close to that of **1**, corresponds to two quasicoescent 1 electron processes respectively at 0.54 and 0.60 V. The second one at 0.87 V corresponds at one electron as demonstrated on deconvoluted CV (ESI†). Thus, the two first processes at 0.54 and 0.60 V correspond to the oxidation of the dithiolenyl moieties as the last one at higher potential can be attributed to the trithienylphenylamine core. Fig. 1 (bottom) shows the first and third scans of the CV of derivative **3**. Since compound **3** undergoes polymerization in the first cycle, it is difficult to attribute the different waves to monomer or polymer. However, by comparison with the CV of Poly(**3**), (Fig. 5, bottom), the waves at 0.54, 0.89 V and 1.3 V can be attributed to **3**.

Note that the first oxidation waves of **1–3** are very close together oscillating between 0.54 and 0.56 V what is in accordance with theoretical calculations and shows that the processes are similar in all cases. Moreover the relative intensities of the two redox processes are correlated with the number of dithiolenyl rings grafted on the core; compound **1** presents two 1 electron processes, derivative **2**, two very close 1 electron processes followed by one single electron process at higher potential. For **3**, the relative intensities are more difficult to determine as this derivative does not undergo reversible processes. Nevertheless, the two processes at 0.54 and 0.89 V can be attributed to 3 and 1 electrons respectively. Thus, for each compound **1–3**, the first process(es) around 0.55 V correspond(s) to the oxidation of the peripheral dithiolenyl ring(s) as the second one, at higher potential, is attributable to the central trithienylphenylamine core. Moreover, the second oxidation potential increases with the number of dithiolenyl rings grafted on the TPA core passing from 0.71 V for **1** to 0.89 V for **3**. This behavior can be explained by the intramolecular coulombic repulsions which are higher in the tetracation 3^{4+} than in the radical trication 2^{3+} and dication 1^{2+} . Thus, in dilute conditions **1** and **2** lead to

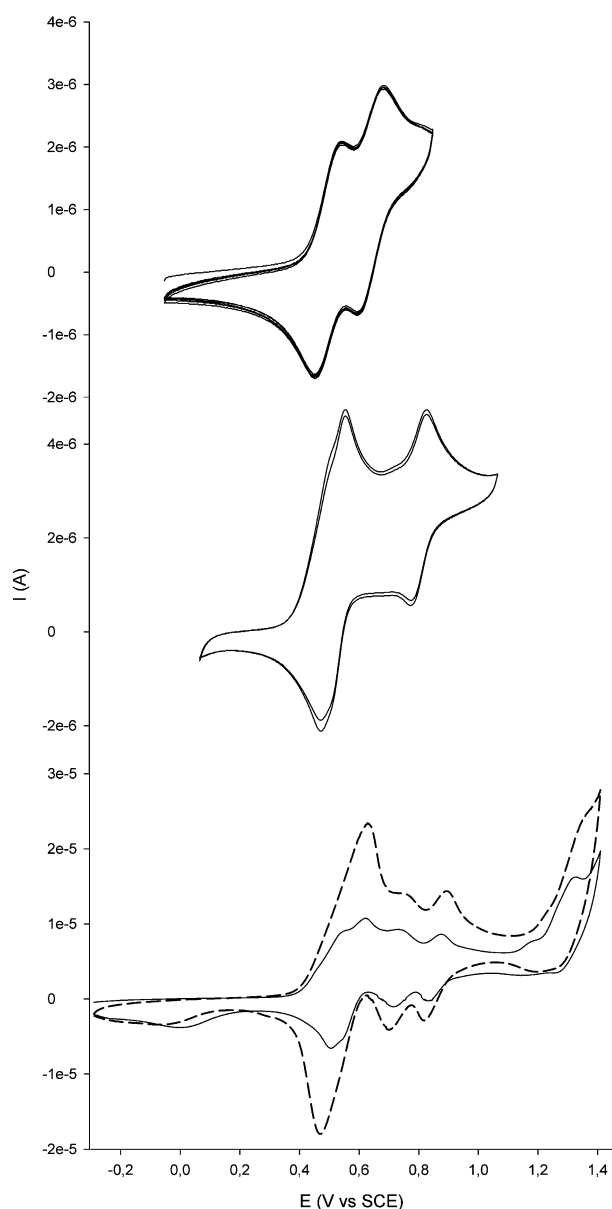
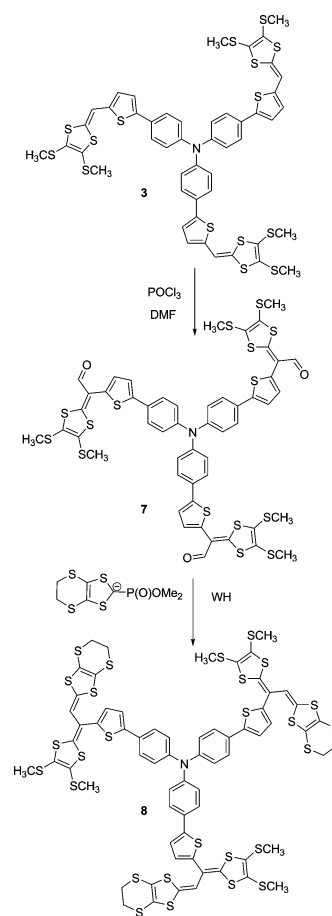


Fig. 2 CV of **1** (top), **2** (middle) and **3** (back, line 1st scan, dotted line 3rd scan), CH_2Cl_2 TBAPF₆ 0.1 M 100 mV s^{-1} .

stable oxidized species as **3** polymerizes. In more concentrated conditions (around 10^{-3} M), the first oxidation process of **1** appears less reversible and a blue coloration appears in solution around the electrode what is characteristic of the formation of a new species near the electrode. Considering the structures of molecules and previous works based on thienylfulvalene systems,^{5,8} it is strongly probable that a coupling reaction occurs at the vinyl linkage connecting the dithiafulvene and the thienyl moieties. In the case of **1**, this coupling may lead to a sterically constrained extended TTF while in that of **3** a polymeric system is expected.

In order to confirm this supposition and to eliminate an hypothetical electrodeposition of the compound **3**,⁹ we have blocked the incriminate positions (Scheme 2). For this purpose derivative **7** with 3 aldehyde functionalities has been synthesized by Viels-Meyer reaction starting from **3**.¹⁰ This later, engaged in a WH reaction with the Akiba's reagent of EDT-dithiole led



Scheme 2

to the extended analogue of TTF¹¹ **8**. This slightly stable compound presents a trithienylphenylamine core substituted by three extended analogues of TTF. Upon oxidation, this derivative does not undergo polymerization but presents 3 reversible processes at **3**, **3** and **1** electrons at 0.45, 0.63 and 1.13 V respectively (Fig. 3, ESI†). The two first processes are attributable to the oxidation of the lateral extended TTFs in radical cations and dications; the last single electron wave corresponds to the oxidation of the central node. The blocking of the dithiafulvenyle positions

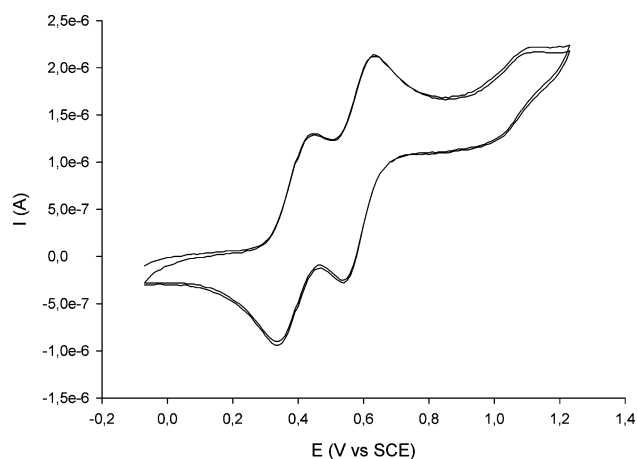
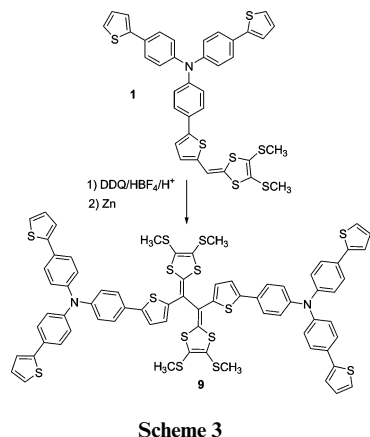


Fig. 3 CV of **8**, CH_2Cl_2 TBAPF₆ 0.1 M 100 mV s^{-1} .

thus prevents the duplication of compounds what confirms the localization of the coupling process.

This observation is sustained by chemical oxidation of **1** with DDQ and HBF₄.¹² After reduction with zinc, compound **9**, which results from a coupling at the vinylic linkage is isolated in 30% yield together with a large part of the starting material (Scheme 3).



The UV-vis. spectrum of **9** shows two maxima at 374 and 417 nm at higher energies than that of **1** at 422 nm. This behaviour already observed for extended TTF is due to a lack of conjugation consecutive to steric hindrances between the aromatic rings.⁸ For the same reason, compound **9** presents two first reversible redox processes at higher potentials than **1** at 0.70 and 0.86 V respectively (ESI†).

At the higher potential of 1.5 V, compound **9** presents a third non reversible peak. Recurrent oxidation until this later leads to the difficult formation of a polymeric film on the surface of the electrode. The polymer which results from thiophene-thiophene couplings upon oxidation has been studied in a free monomer electrolytic solution. Poly(**9**) shows a main intense process between 0.5 and 1 V with a maximum at 0.9 V followed by a less important one centered on 1.1 V (Fig. 4).

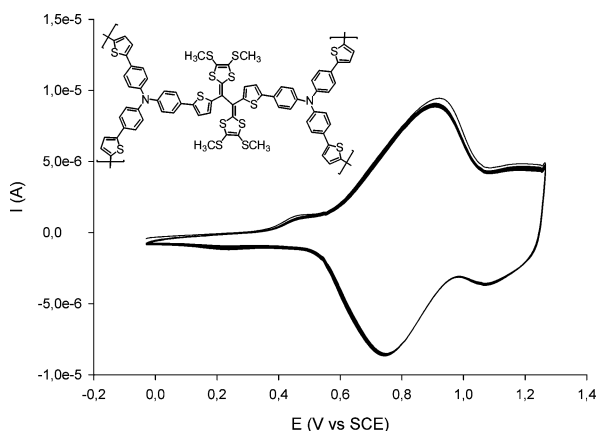


Fig. 4 CV of poly(**9**) deposited on Pt, CH₃CN Bu₄NPF₆ 0.1 M 100 mV s⁻¹.

As already mentioned, derivative **3** polymerizes at its first oxidation state which leads to the trication radical **3³⁺**. Nevertheless, the electropolymerization in potentiodynamic conditions at its second

oxidation potential is easier and leads to thicker films (Fig. 5, top). Poly(**3**), studied in a free monomer electrolytic solution presents two well discriminated processes with relative intensities of 3 and 1 at 0.6 and 0.74–0.8 V respectively (Fig. 5, bottom). These redox processes very close to those of **3** are well reversible and cycling up to the second redox process for an hundred cycles led the film unchanged. Thus, poly(**3**) presents two reversible and well disjointed redox processes.

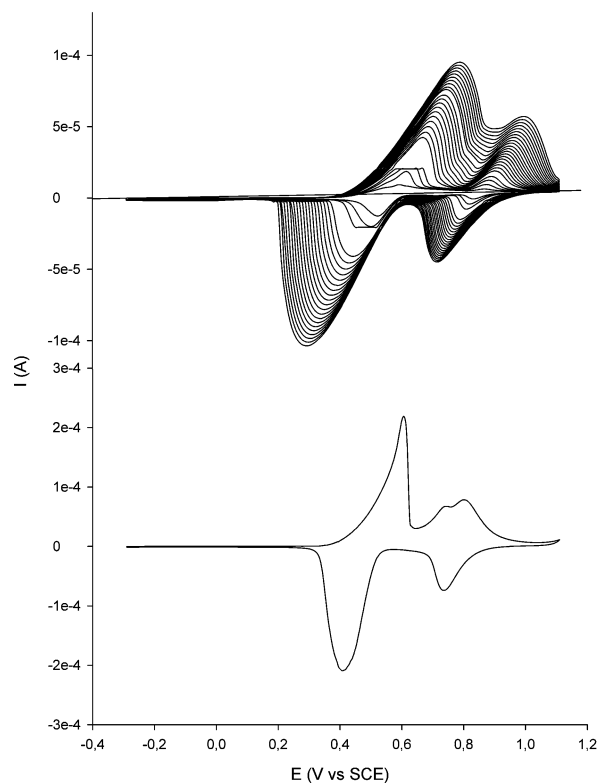


Fig. 5 (top) Electropolymerization of **3**, CH₂Cl₂ TBAPF₆ 0.1 M 100 mV s⁻¹ (bottom) CV trace of poly(**3**) deposited on Pt in CH₃CN Bu₄NPF₆ 0.1 M 100 mV s⁻¹.

As a first evaluation of its electrochromic properties, derivative **3** has been electropolymerized on ITO. The film is stable in its neutral state and can be stored several hours in ambient conditions without degradation or oxidation. The maximum of absorption of the yellow polymer in its neutral state is close to that of **3** at 437 nm. In CV, the film of poly(**3**) always presents two well disjointed reversible redox processes thus allowing to study the two oxidation states by spectroelectrochemistry (Fig. 6).¹³ The first process leads to a blue film with 2 maxima respectively at 403 nm and 703 nm. Oxidation until the second process leads to a stable grey-violet film which strongly absorbs in the IR region. During each oxidation process the presence of isobestic points on the spectroscopic trace confirms the stability of oxidized species.

Conclusion

During this work we have synthesized three new hybrids incorporating a trithienylphenylamine core and one to three dithiafulvenyle moieties. Electrooxidation of these compounds, cleared up by chemical oxidation of **1** as well as by blocking of incriminate

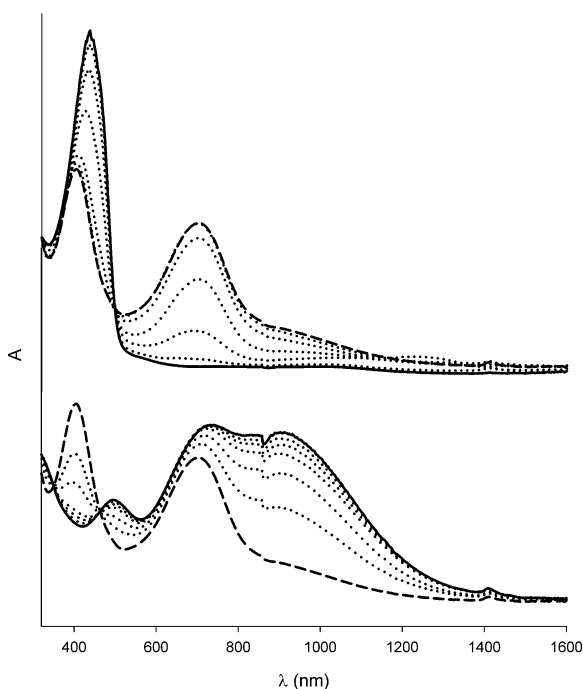


Fig. 6 Electronic absorption spectra of a film of poly(3) on ITO electrode in CH_3CN Bu_4NPF_6 0.1 M; (Top) from its reduced form at 0 V to 0.6 V; (bottom) from 0.6 V to its fully oxidized form at 1 V. line (neutral and fully oxidized states) – short dash (partially oxidized state at 0.6 V) – dotted lines (intermediate states).

positions in **8**, leads to dimerization or polymerization products at the vinylic linkage between the thiophene and the dithiole rings. Poly(3) allows the observation of two well resolved and reversible redox processes. This polymer, electrogenerated on an ITO plate, presents three coloured stable redox states and can be considered as a first example of polychrome mixed TPA-TTF system. Efforts are now in due course in order to get soluble and processable polymers in this family.

Experimental

General experimental

Solvents were purified and dried using standard protocols. ^1H -NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE DRX 300 spectrometer; δ are given in ppm (relative to TMS) and coupling constants (J) in Hz. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded by a Bruker Biflex-III, equipped with a N_2 laser (337 nm). For the matrix, dithranol in CH_2Cl_2 was used. High resolution mass spectra were recorded under FAB mode on a Jeol JMS 700 spectrometer. UV-visible optical data were recorded with a Perkin-Elmer lambda 19 spectrophotometer. For cyclic voltammetry (scan rate 100 mV cm^{-1}), the electrochemical apparatus consisted of a potentiostat EG&G PAR 273A and of a standard three-electrode cell. As the working and counter electrodes, a platinum foil and a platinum wire were used, respectively, while a SCE electrode served as reference. Electrochemical experiments were carried out in methylene chloride or acetonitrile (spectro grade) containing 0.10 M tetrabutylammonium hexafluorophosphate (Fluka puriss, used as received). Spectroelectrochemical exper-

iments were carried out with a home-made cell on polymers grown on ITO. Trithienylphenylamine was prepared from tris-4-bromophenylamine as described in literature.¹⁴

Computational details

The molecular orbitals have been calculated for the optimized geometries of compound **1–3**. A full geometry optimization for **1** and **2**, and a constrained optimization (restricted to a C_3 symmetry point group) for **3** have been carried out using Density Functional Theory (DFT) methods. All calculations were performed with the hybrid adaptation of the PBE functional^{15–16} (usually referred as PBE0) as implemented on the Gaussian09 program.¹⁷ A triple- ζ quality basis set proposed by Weigend *et al.* has been used with polarization functions for all atoms (TZVPP).¹⁸ Then the first mono-electronic excitations (10 firsts) were computed using a Time Dependent Density Functional Theory (TD-DFT) procedure with the same program, functional and basis set as the optimization step (see ESI†).

Compounds 4–5

To 500 mg (1 mmol) of tris[4-(2-thienyl)phenyl]amine dissolved in 30 mL of 1,2-dichloroethane, 0.12 mL of dimethylformamide (1.5 mmol) and 0.14 mL of phosphorus oxychloride (1.5 mmol) are added. The mixture is heated to reflux under nitrogen and kept stirred overnight. After cooling, 50 mL of methylene chloride and 100 mL of saturated sodium acetate solution are added and stirred 1 h. Then, the mixture is poured into water and extracted with methylene chloride. The organic phase is separated, washed with water and dried with magnesium sulfate. After evaporation of solvent, the residue is purified by silica column chromatography (methylene chloride as eluent) to give 140 mg of [mono[4-(2-thienylformyl)phenyl]bis[4-(2-thienyl)phenyl] amine **4** (yield: 27%) and 140 mg of [bis[4-(2-thienylformyl)phenyl]mono[4-(2-thienyl)phenyl]amine **5** (yield: 25%). Compound **6** was also obtained in 20% yield.

Compound **4**: NMR ^1H (CDCl_3): 9.87 (s, 1H)- 7.72 (d, 1H, $^3J = 4 \text{ Hz}$)- 7.55 (m, 6H)- 7.33 (d, 1H, $^3J = 4 \text{ Hz}$)- 7.27 (m, 4H)- 7.15 (m, 6H)- 7.08 (dd, 2H, $^3J = 3.5 \text{ Hz}$, $^3J = 5 \text{ Hz}$); NMR ^{13}C (CDCl_3): 182.6; 154.3; 148.4; 145.9; 143.8; 141.5; 137.7; 130.0; 128.1; 127.4; 127.0; 126.8; 125.0; 124.5; 123.2; 123.1; 122.7; IR ($\text{C}=\text{O}$) 1647 cm^{-1} ; SM (Malditof) $\text{C}_{31}\text{H}_{21}\text{NOS}_3$; ms M^+ : 519.1, theo: 519.08; HRMS M^+ (calcd) (519.07798) 519.0780.

Compound **5**: NMR ^1H (CDCl_3): 9.87 (s, 2H)- 7.73 (d, 2H, $^3J = 4 \text{ Hz}$)- 7.58 (m, 6H)- 7.34 (d, 2H, $^3J = 4 \text{ Hz}$), 7.28 (m, 2H)- 7.17 (m, 6H)- 7.09 (dd, 1H, $^3J = 3.5 \text{ Hz}$, $^3J = 10 \text{ Hz}$); NMR ^{13}C (CDCl_3): 182.7; 153.9; 147.9; 145.5; 143.6; 141.7; 137.7; 130.6; 128.1; 127.676; 127.5; 127.1; 125.6; 124.7; 123.9; 123.3; 122.9; IR ($\text{C}=\text{O}$) 1655 cm^{-1} ; SM (Malditof) $\text{C}_{32}\text{H}_{21}\text{NO}_2\text{S}_3$; ms M^+ : 547.1, theo: 547.078; HRMS $\text{M}+\text{Na}^+$ (calcd) (570.0627) 570.0629

[4-((4,5-bis(methylthio)-1,3-dithiol-2-ylidene)methyl)thienylphenyl]dithienylphenylamine **1**

100 mg (0.19 mmol) of [4-(5-formyl-2-thienyl)phenyl]-bis[4-(2-thienyl)phenyl]amine **4** and 87 mg (2 eq) de 4,5-bis(methylthio)-2-thioxo-1,3-dithioleare dissolved in 2 mL of boiling toluene after what 2 mL of dry triethylphosphite are added. The mixture is refluxed 4 h under nitrogen atmosphere. After cooling and

addition of methylenechloride, the mixture is washed with brine and dried on magnesium sulfate. After evaporation of solvent the residue is washed with methanol affording 220 mg of a pure rusty solid.

yield: 38%; Decomp=95 °C; R_f 0.39 (EP/CH₂Cl₂ 2:1); NMR ¹H (CDCl₃): 7.52 (d, 4H, ³J = 8.5 Hz)- 7.50 (d, 2H, ³J = 8.5 Hz)- 7.25 (m, 4H)- 7.19 (d, 1H, ³J = 4 Hz)- 7.14 (d, 4H, ³J = 9 Hz)- 7.14 (d, 2H, ³J = 8.5 Hz)- 7.08 (dd, 2H, ³J = 4 Hz et ³J = 5 Hz)-6.82 (d, 1H, ³J = 4 Hz)- 6.66 (s, 1H)- 2.47 (s, 3H)- 2.45 (s, 3H); NMR ¹³C (CDCl₃): 146.4- 146.3- 144.0- 142.5 139.3- 130.1- 129.3- 129.1- 128.1- 128.0- 126.9- 126.4- 125.3- 125.2- 125.1- 124.4- 124.3- 122.8- 122.5- 108.5- 19.2- 19.0; MS (Malditof) C₄₂H₃₃NS₉; ms M⁺: 902.8, theo: 902.9; SM (Malditof) C₃₆H₂₇NS₇; ms M⁺: 696.9, theo: 697.0; HRMS M⁺ (calcd) (697.0188) 697.0201

Bis-[4-((4,5-bis(methylthio)-1,3-dithiol-2-ylidene)methyl)thienyl-phenyl]thienylphenylamine 2

50 mg of dialdehyde **5** and 100 mg de 4,5-dimethoxy-2-thioxo-1,3-dithiole are dissolved in 5 mL of boiling toluene after what 1 mL of dry triethylphosphite is added. The mixture is refluxed 1 h 30 min under nitrogen atmosphere. After cooling 30 mL of petroleum ether are added in the flask and the mixture is stirred one hour. The pure yellow powder is then filtered, washed with petroleum ether and dried. Yield: 70%; R_f 0.7 (CH₂Cl₂/EP); Tcomp≈107 °C; NMR ¹H (CDCl₃): 7.51 (d, 2H, ³J = 8.5 Hz)- 7.50 (d, 4H, ³J = 8.5 Hz)- 7.25 (m, 2H)- 7.19 (d, 2H, ³J = 4 Hz)- 7.13 (d, 2H, ³J = 8.5 Hz)- 7.12 (d, 4H, ³J = 8.5 Hz)- 7.07 (d*d, 1H, ³J = 5 Hz ³J = 3.5 Hz)- 6.82 (d, 2H, ³J = 4 Hz)- 6.66 (s, 2H)- 2.47 (s, 6H)- 2.45 (s, 6H); NMR ¹³C (CD₂Cl₂): 147.0- 146.9- 144.5- 143.0- 138.8- 130.8- 129.8- 129.6- 128.8- 128.6- 127.3- 126.8- 125.8- 125.6- 125.0- 124.9- 124.8- 123.4- 123.0- 108.8- 19.5- 19.3; HRMS M⁺ (calcd) (902.95353) 902.95279

Tris-[4-((4,5-bis(methylthio)-1,3-dithiol-2-ylidene)methyl)thienyl-phenyl]amine 3

200 mg of Tris[4-(5-formyl-2-thienyl)phenyl]amine 6(3.5 10⁻⁴ mol) and **6** eq. de 4,5-dimethoxy-2-thioxo-1,3-dithiole (470 mg) are dissolved in 8 mL of boiling toluene after what 2 mL of dry triethylphosphite are added. The mixture is refluxed 1 h under nitrogen atmosphere. After cooling, 30 mL of petroleum ether are added in the flask and the mixture is stirred one hour. The yellow powder is then filtered, washed with petroleum ether and dissolved in methylenechloride. The organic phase is washed with water and dried on magnesium sulfate. After evaporation of the solvent, the residue is dissolved in the minimum of methylenechloride and chromatographed on silica gel using EP/CH₂Cl₂ 1/1 then 1/2 and then CH₂Cl₂ as eluent. 300 mg of the target are isolated (elution with EP/CH₂Cl₂ 1/1). Yield: 82%; Decomp≈189 °C; R_f 0.6 (EP/CH₂Cl₂ 1/1); NMR ¹H (CDCl₃): 7.49 (d, 6H, ³J = 8.5 Hz)- 7.18 (d, 3H, ³J = 3.5 Hz)- 7.01 (d, 6H, ³J = 8.5 Hz)- 6.81 (d, 3H, ³J = 3.5 Hz)- 6.65 (s, 3H)- 2.46 (s, 9H)- 2.44 (s, 9H); NMR ¹³C (CDCl₃): 146.2- 142.4- 139.2- 130.0- 129.1- 128.0- 126.3- 125.2- 125.1- 124.3- 122.8- 108.5- 19.1- 19.0; HRMS M⁺ (calcd): (1108.8893) 1108.8893.

Derivative 7

0.2 mL of phosphorus oxychloride and 0.3 mL of dry DMF are added at 0 °C under nitrogen atmosphere in 30 mL of methylenechloride. 50 mg of derivative **3** (4.5 10⁻⁵ mol) are then added and the mixture is refluxed overnight. After cooling, 50 mL of an aqueous solution of sodium acetate 4 M are added and the mixture is stirred 2 h. The organic phase is then washed with water and dried on magnesium sulfate. After evaporation of the solvent, the residue is chromatographed on silica gel using methylenechloride as eluent. 30 mg of trisaldehyde **8** are isolated as a red glassy solid. Yield: 56%; NMR ¹H (CDCl₃): 9.53 (s, 3H)- 7.54 (d, 6H, ³J = 8.5 Hz)- 7.26 (d, 3H, ³J = 4.5 Hz)- 7.15 (d, 6H, ³J = 8.5 Hz)- 7.13 (d, 3H, ³J = 3.5 Hz)- 2.56 (s, 9H) 2.46 (s, 9H). NMR ¹³C (CDCl₃): 183.3- 161.3- 146.5- 143.9- 136.9- 134.2- 128.8- 127.4- 126.8- 126.4- 124.4- 122.8- 115.5- 19.3- 18.8; HRMS M⁺ (calcd): 1192.8755 (1192.8735)

Derivative 8

18 mg of derivative **7** (1.5 10⁻⁵ mol) and 60 mg (1.9 10⁻⁴ mol) of the phosphonate of ethylenedithiodithiole are dissolved in 5 mL of dry THF under nitrogen atmosphere. 1.5 10⁻⁴ mol of *t*-BuOK (solution 1 M) are then added and a yellow powder immediately appears. The mixture is stirred 1 h and 5 mL of methanol are added. After 1 h of flocculation, the powder is filtered, washed with methanol. 23 mg of derivative are isolated as a yellow powder. Yield: 89%; R_f (CH₂Cl₂/EP 1/1): 0.4 – oxidation on the plate; NMR ¹H (CD₂Cl₂): 7.55 (d, 6H, ³J = 8.5 Hz)-7.26 (d, 3H, ³J = 4 Hz)- 7.14 (d, 6H, ³J = 8.5 Hz)- 6.94 (d, 3H, ³J = 3.5 Hz)- 5.20 (s, 3H)- 3.25 (m, 12H)- 2.44 (s, 9H) 2.38 (s, 9H); MS (Malditof)(calcd): (M+H, 1721.6) 1721.9

Derivative 9

50 mg of **1** (7.2 10⁻⁵ mmol) are dissolved in 50 mL of dry diethyl ether. Then 30 mg of DDQ, 0.4 mL of HBF₄·H₂O and two drops of concentrated hydrochloric acid are added. The yellow solution turns deep green and is stirred one hour at room temperature. After addition of 50 mL dry diethyl ether the very thin powder is filtered on celite (the filtrate is mostly composed by starting unoxidized derivative). The green precipitate is dissolved in acetonitrile, an excess of zinc is added and the mixture is stirred 45 min at room temperature. After filtration of zinc, the solvent is evaporated and the residue dissolved in methylenechloride; the organic phase is washed with water and then dried on magnesium sulfate. After evaporation of the solvent, the residue is chromatographed on silica gel using EP/CH₂Cl₂ 1/2 as eluent affording 15 mg (30%) of a yellow glassy solid. NMR ¹H (CDCl₃): 7.52 (d, 8H, ³J = 8.5 Hz)- 7.50 (d, 4H, ³J = 8.5 Hz)- 7.25 (m, 10H thiophene)- 7.19 (d, 2H, ³J = 4 Hz)- 7.14 (d, 8H, ³J = 8.5 Hz)- 7.12 (d, 4H, ³J = 8.5 Hz)- 7.01 (d*d, 4H, ³J = 5 Hz ³J = 4 Hz)- 2.49 (s, 6H)- 2.45 (s, 6H).

Acknowledgements

Authors thank the PIAM of Angers for analytical experiments and the french government for granting E. Ripaud.

Notes and references

- 1 Y. Shirota, *J. Mater. Chem.*, 2005, **15**, 75 and references cited therein.
- 2 J. Roncali, P. Leriche and A. Cravino, *Adv. Mater.*, 2007, **19**, 2045; J. Roncali, *Acc. Chem. Res.*, 2009, **42**, 1719; J. L. Delgado, P.-A. Bouilt, S.

- Filippone, M. A. Herranz and N. Martin, *Chem. Commun.*, 2010, **46**, 4853; A. Cravino, S. Roquet, O. Alévêque, P. Leriche, P. Frère and J. Roncali, *Chem. Mater.*, 2006, **18**, 2584; P. Leriche, P. Frère, A. Cravino, O. Alévêque and J. Roncali, *J. Org. Chem.*, 2007, **72**, 8332; S. Roquet, R. De Bettignies, P. Leriche, A. Cravino and J. Roncali, *J. Mater. Chem.*, 2006, **16**, 3040; C. He, Q. He, X. Yang, G. Wu, C. Yang, F. Bai, Z. Shuai, L. Wang and T. Li, *J. Phys. Chem. C*, 2007, **111**, 8661; H. Kageyama, H. Ohishi, M. Tanaka, Y. Ohmori and Y. Shirota, *Appl. Phys. Lett.*, 2009, **94**, 063304; G. Wu, G. Zhao, C. He, J. Zhang, Q. He, X. Chen and Y. Li, *Sol. En. Mat. Solar Cells*, 2009, **93**, 109; G. Quian, Z. Zhong, M. Luo, D. Yu, Z. Zhang, Z. Y. Wang and D. Ma, *Adv. Mater.*, 2009, **21**, 111; J. Kwon, W. Lee, J.-Y. Kim, S. Noh, C. Lee and J.-I. Hong, *New J. Chem.*, 2010, **34**, 744.
- 3 for example see: S.-H. Cheng, S.-H. Hsiao, T.-H. Su and G.-S. Liou, *Polymer*, 2005, **46**, 5939; G.-S. Liou, H.-W. Chang, K.-H. Lin and Y. O. Su, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 2118.
- 4 O. Alévêque, P. Leriche, N. Cocherel, P. Frère, A. Cravino and J. Roncali, *Sol. Energy Mater. Sol. Cells*, 2008, **92**, 1170.
- 5 N. Cocherel, P. Leriche, E. Ripaud, N. Gallégo-Planas, P. Frère and J. Roncali, *New J. Chem.*, 2009, **33**, 801.
- 6 P. Leriche, S. Roquet, N. Pillere, G. Mabon and P. Frère, P., *Tetrahedron Letters*, 2004, **44**, 1523.
- 7 S. Roquet, A. Cravino, P. Leriche, O. Alévêque, P. Frère and J. Roncali, *J. Am. Chem. Soc.*, 2006, **128**, 3459.
- 8 M. Fourmigué, I. Johannsen, K. Boubekeur, C. Nelson and P. Batail, *J. Am. Chem. Soc.*, 1993, **115**, 3752; A. Benahmed-Gasmi, P. Frère, J. Roncali, E. Elandaloussi, J. Orduna, J. Garin, M. Jubault and A. Gorgues, *Tetrahedron Lett.*, 1995, **36**, 2983; S. Gonzalez, N. Martin, L. Sanchez, J. L. Segura, C. Seoane, I. Fonseca, F. H. Cano, J. Sedo, J. Vidal-Gancedo and C. Rovira, *J. Org. Chem.*, 1999, **64**, 3498; D. Lorcy, L. Mattiello, C. Poriel and J. Rault-Berthelot, *J. Electroanal. Chem.*, 2002, **530**, 33; M. Guerro, R. Carlier, K. Boubekeur, D. Lorcy and P. Hapiot, *J. Am. Chem. Soc.*, 2003, **125**, 3159; R. Berridge, P. J. Skabara, R. Andreu, J. Garin, J. Orduna and M. Torra, *Tetrahedron Lett.*, 2005, **46**, 7871; J. Massue, J. Ghilane, N. Bellec, D. Lorcy and P. Hapiot, *Electrochem. Commun.*, 2007, **9**, 677; P. Frère and P. J. Skabara, *Chem. Soc. Rev.*, 2005, **34**, 69.
- 9 A. Kanibolotsky, S. Roquet, M. Cariou, P. Leriche, C.-O. Turrin, R. de Bettignies, A.-M. Caminade, J.-P. Majoral, V. Khodorkovsky and A. Gorgues, *Org. Lett.*, 2004, **13**, 2109.
- 10 M. R. Bryce, M. A. Coffin, P. J. Skabara, A. J. Moore, A. S. Batsanov and J. A. K. Howard, *Chem.-Eur. J.*, 2000, **6**, 1955.
- 11 A. Gorgues, P. Hudhomme and M. Sallé, *Chem. Rev.*, 2004, **104**, 5151; J. L. Segura and N. Martin, *Angew. Chem., Int. Ed.*, 2001, **40**, 1372; M. Bendikov, F. Wudl and D. F. Perepichka, *Chem. Rev.*, 2004, **104**, 4891.
- 12 R. Mayer and H. Kröber, *J. Prakt. Chem.*, 1974, **316**, 907.
- 13 C. Wang, A. S. Batsanov and M. R. Bryce, *Chem. Commun.*, 2004, 578; S. Inagi, K. Naka and Y. Chujo, *J. Mater. Chem.*, 2007, **17**, 4122.
- 14 K. Yamamoto, M. Higushi, K. Ushida and Y. Kojima, *Macromolecules*, 2002, **35**, 5782.
- 15 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865B.
- 16 C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158b.
- 17 *Gaussian 09, Revision A.02*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- 18 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297.