



Star-shaped triazine–thiophene conjugated systems

Philippe Leriche^{a,*}, Flavia Piron^{a,b}, Emilie Ripaud^a, Pierre Frère^a, Magali Allain^a, Jean Roncali^a

^a University of Angers, CNRS, CIMA, Group Linear Conjugated Systems, 2 Bd Lavoisier 49045, Angers, France

^b Organic Chemistry Department and CCOCCAN, 'Babes-Bolyai' University, 11 Arany Janos str., 400028, Cluj-Napoca, Romania

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ABSTRACT

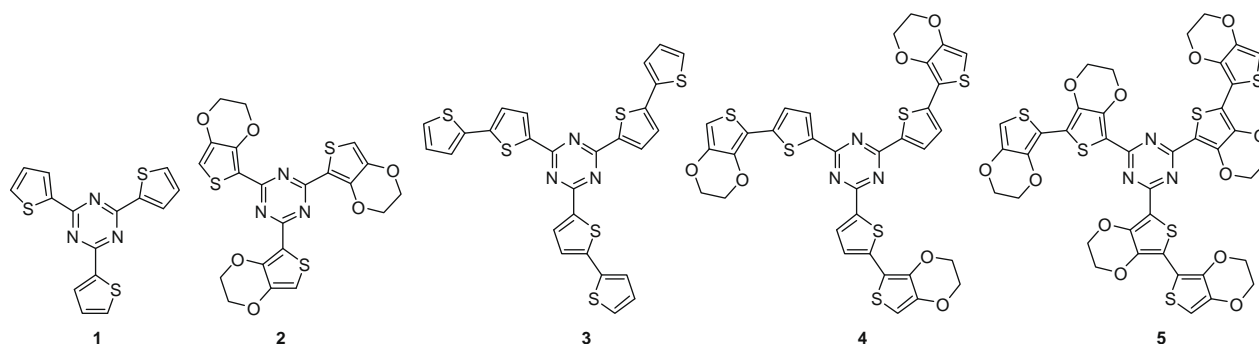
Star-shaped molecules consisting of short-chain oligothiophenes attached onto an electron acceptor triazine core have been synthesized. Results of the analysis of the electronic properties of these compounds by UV–vis spectroscopy and cyclic voltammetry are used to discuss the impact of the electron-withdrawing node on the properties of the compounds. The electrochemical oxidation of some of these systems into the corresponding electroactive polymers is briefly discussed.

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Star-shaped conjugated systems are subject to much current interest as basic unit for discotic liquid crystals¹ and as active materials for organic electronic devices such as field-effect transistors or solar cells.² On the other hand, star-shaped systems possessing donor–acceptor characters can present an intense internal charge transfer band at low energy and have found applications in organic solar cells.³ In this context, we present here the synthesis of a series of planar donor–acceptor systems **1–5** based on an electron-withdrawing triazine core substituted at the 2, 4 and 6 positions with various electron-donating bithiophene

branches (Scheme 1). Compounds **1–5** have been synthesized by Stille coupling reaction between the triazine core and various stannic derivatives. The syntheses as well as preliminary results on the characterization of the electronic properties of the compounds by UV–vis spectroscopy and cyclic voltammetry are presented.

Tris-2,4,6-thienyl-1,3,5-triazine **1** has been previously synthesized by Chérioux et al. by aromatic substitution of 2,4,6-trichloro-2,4,5-triazine namely cyanuric chloride⁴ with (bis)thienyllithium. Such compounds can also be synthesized by cyclotrimerization of thiophene-2-carbonitrile in trifluoromethylsulfonic acid.⁵ Recently,



Scheme 1. Structures of compounds **1–5**.

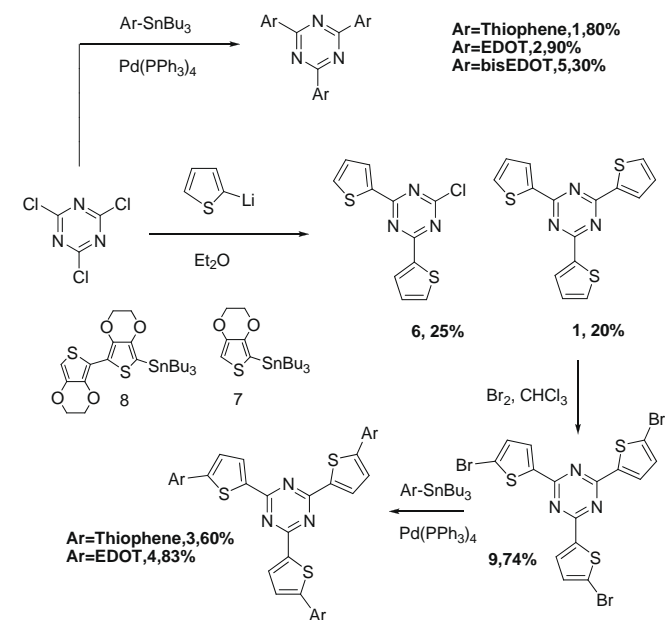
* Corresponding author. Tel.: +33 (0)2 41 73 50 10; fax: +33 (0)2 41 73 54 05.

E-mail address: philippe.leriche@univ-angers.fr (P. Leriche).

using the first method Avarvari et al. have synthesized TTF-triazine compounds⁵ and shown that the tris-functionalization of triazine by this route was not so straightforward.

We used the same method in a first attempt to synthesize compound **1**. The first mild synthetic pathway using lithiated thiophene and cyanuric chloride⁴ led to the target compound **1** in 20% yield together with 25% of the bis-derivatized compound **6**. In contrast, reaction of cyanuric chloride⁷ with 2-tributylstannylthiophene in the presence of Pd(PPh₃)₄ as catalyst led to the target compound **1** in 80% yield after recrystallization in petroleum ether. The same reaction starting from the stannic derivatives of EDOT **7** and bisEDOT **8** gave compounds **2** and **5** in 90% and 30% yield, respectively. The presence of the triazine electron-withdrawing moiety makes aromatic electrophilic substitution at the thiophene units of compound **1** difficult and attempts to brominate this compound using NBS remained unsuccessful. Bromination of **1** was achieved in the presence of 30 equiv of bromine in refluxing chloroform for 4 days. The tribromo compound **9** was isolated as single product in 74% yield after recrystallization in a mixture of methylene chloride and petroleum ether. Compound **9** was then reacted in a Stille reaction with the stannic derivative of thiophene or EDOT **7** leading to **3** and **4** in 60% and 83% yield, respectively. All compounds were satisfactorily characterized by NMR and mass spectrometry (Scheme 2).⁸

The crystallographic structure of compound **1** is presented in Figure 1. This compound crystallizes as two independent molecules in the orthorhombic *Pna*2₁ space group.⁹ The S1...S4 contacts at 3.512(2) Å and 3.534(2) Å are shorter than the sum of Van der Waals radii for two sulfur atoms (3.70 Å) suggesting intermolecular interactions (Fig. 1, top). For each molecule, positional disorder affects one of the three thiophene rings and both the sulfur atom and the carbon atom in 3-position of the thiophene ring are located at two positions. As shown in Figure 1 (bottom), the system is perfectly planar which is propitious for a good conjugation between the thiophene moieties and the triazine core. Moreover, the distances between two planar molecules are either 3.40 or 3.46 Å. The triazine core from one molecule stacks with a little shift to the thiophene ring of the other molecule.



Scheme 2. Syntheses of compounds 1–5.

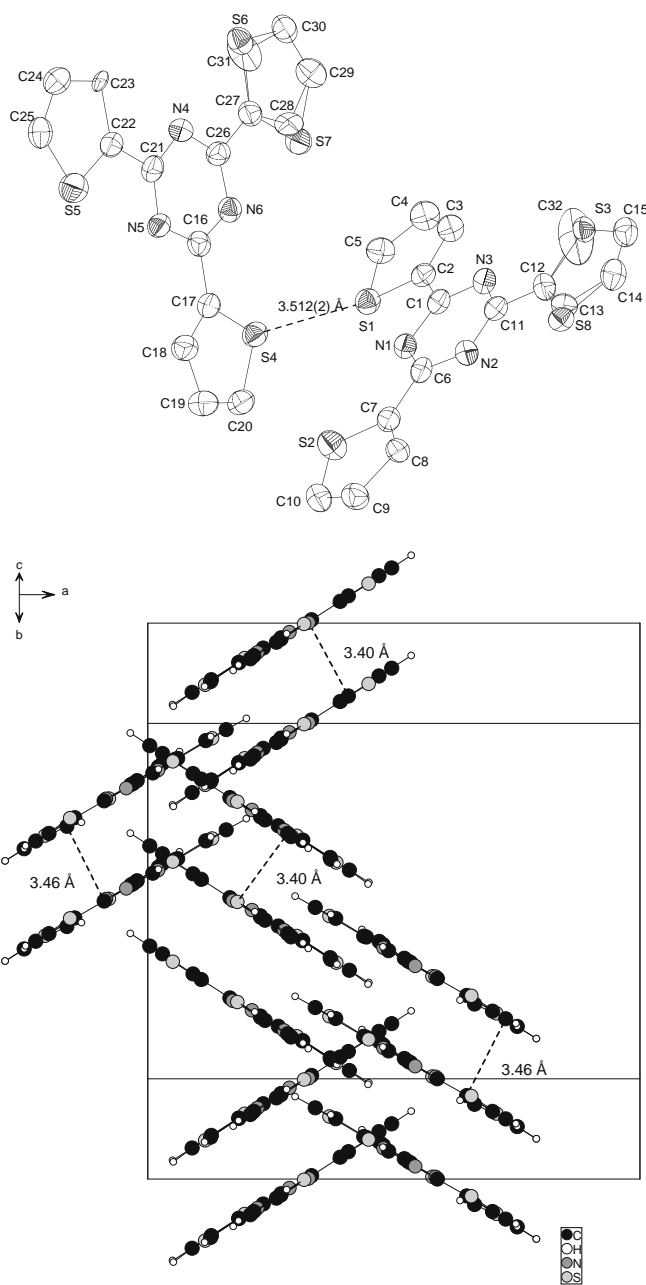


Figure 1. Top. Ortep view of derivative **1**, ellipsoids drawn at 50% probability level. Bottom. Part of the packing diagram in the unit cell.

Cyclic voltammetric and UV–vis spectroscopic data of compounds **1–5** are gathered in Table 1. All compounds present a large π – π^* absorption band with a λ_{max} which depends on the length and composition of the side arms. Thus, extending the branches by one thiophene ring (**1** and **3**) produces a red shift, of λ_{max} from 316 to 390 nm. On the other hand, the replacement of thiophene by EDOT also produces a bathochromic shift of λ_{max} (Fig. 2.). Note that the absorption maxima of compounds **3–5** are bathochromically shifted compared to those of the respective branches namely bithiophene, thienyl-EDOT and bis-EDOT,¹⁰ an effect attributed to the presence of the electron-withdrawing triazine core. For compound **4** a weakly intense absorption tail is observed around 500 nm (Fig. 2). The dependence of the position of this band on solvent polarity is consistent with a charge-transfer origin.

Table 1
Electrochemical and UV-vis spectroscopic data of compounds **1–5** and related polymers

Entry	λ_{\max}^a (nm)	Eox ₁ ^b	Eox ₂ ^b
1	316	—	—
2	323	1.93	—
3	390	1.38	1.65
4	423	0.98	1.17
5	438	0.80	1.10
Poly(3)	—	1.27	1.6
Poly(4)	—	0.79	1.26
Poly(5)	—	0.54	0.94

^a In CH₂Cl₂ 10⁻⁵ M.

^b Versus SCE, 100 mV/s.

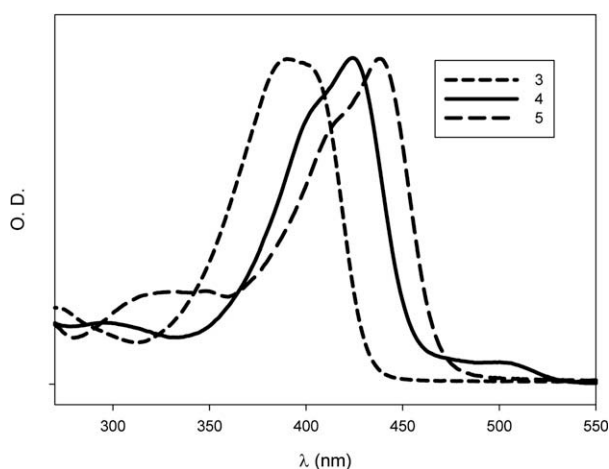


Figure 2. UV-vis spectra of compounds **3–5** in methylenechloride (normalized).

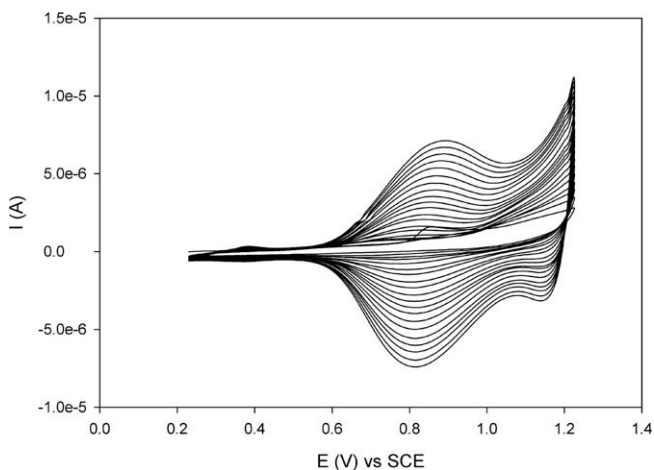


Figure 3. Potentiodynamic polymerization of **5**, <1 mM in 0.1 M Bu₄NPF₆/DCM, scan rate 100 mV/s.

All compounds are sparingly soluble and therefore electrochemical experiments were carried out with saturated solutions of **1–5** ($C < 10^{-3}$ mol L⁻¹) in methylene chloride (spectro grade) containing 0.10 M tetrabutylammonium hexafluorophosphate (Fluka puriss, used as received) as electrolyte.

Because of the presence of the electron-withdrawing triazine moiety, oxidation of **1** was not observed in the potential range accessible with the used electrolytic medium. Compound **2** with three EDOT units is more easily oxidized and presents an irreversible oxidation wave at 1.93 V namely 0.50 V more positive than

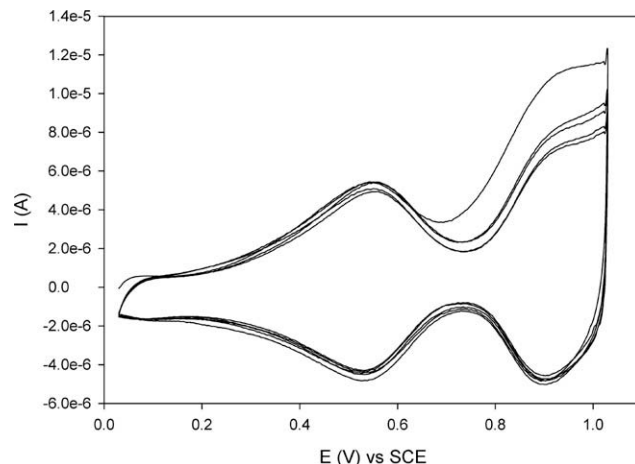


Figure 4. CV trace of poly(**5**) in 0.1 M Bu₄NPF₆/ACN, scan rate 100 mV/s.

EDOT, which confirms the electron-withdrawing effect of the triazine core.

As expected the increase in the EDOT content of the branches from **3** to **5** leads to a decrease in the oxidation potential of the molecule. The CV of the most easily oxidized compounds **4** and **5** present their two successive oxidation waves at 0.98 and 1.17 V for **4** and 0.80 V and 1.10 V for **5**. Application of recurrent potential scans to electrolytic solutions of compounds **3–5** leads to the progressive grow of a reversible broad redox system corresponding to the electrodeposition of an electroactive material on the electrode surface (Fig. 3). Electrodeposition was found less efficient for compound **3** than for compounds **4** and **5** that both possess a terminal EDOT unit well known to facilitate electropolymerization.¹¹ The most efficient polymerization process was observed for compound **4** probably because the density of unpaired electron is maximal on the terminal EDOT whereas it is more delocalized in the case of compound **5**. As these polymers form highly cross-linked networks, their solubility is too low to envision structural characterization in solution.

As for the precursor molecules, the oxidation potential of the polymers decreases with the increase in the number of EDOTs.¹² The CV of poly(**3**) presents a single quasi-reversible broad oxidation wave peaking at 1.27 V the intensity of which rapidly decreases upon cycling. The CV of poly(**4**) presents two redox processes at 0.79 and 1.26 V, respectively. The first redox process is reversible but cycling up to the second oxidation potential leads to a rapid decrease of electroactivity. Finally, poly(**5**) presents two reversible redox waves at 0.54 and 0.94 V (Fig. 4). Upon scanning in the negative potential region an irreversible reduction wave is observed at ca. -2.0 V for poly(**5**) while poly(**4**) presents a quasi-reversible reduction wave at -1.8 V assigned to the reduction of the triazine core.

To summarize, a series of star-shaped molecules based on a triazine core substituted with short-chain oligothiophene has been synthesized. The UV-vis and cyclic voltammetric data of these compounds show, in agreement with expectations, that the increase in the number of EDOTs in the branches leads to a red shift of the absorption spectrum and to a decrease in the oxidation potential. On the other hand, compounds with a terminal EDOT unit can be electropolymerized to produce electroactive materials.

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Supplementary data

Potentiodynamic polymerizations of derivatives **3** and **4** and CV traces of corresponding polymers. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.07.126.

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8. *Examples of procedures and spectroscopic data. Compound 2.* Hundred milligrams of 2,4,6-trichloro-2,4,5-triazine are suspended in 30 mL of dry toluene. Four equivalents of the stannic derivative of EDOT are added and the mixture is degassed with nitrogen. Then, Pd(PPh₃)₄ (5%) is added and the mixture is refluxed for 5 h under nitrogen atmosphere. After cooling, 100 mL of petroleum ether is added. After flocculation and filtration of the precipitate, it is dissolved in methylenechloride and filtered on silica gel leading to 540 mg (90% yield) of compound **2** as a white powder. ¹H NMR (CDCl₃): 6.65 (s, 1H); 4.51 (m, 2H); 4.29 (m, 2H) ¹³C NMR (CDCl₃): 166.6; 145.2; 142.3; 115.9; 107.2; 65.7; –64.0–MS–Malditoff (calcd), (501.0) 502.0 (M+H)⁺–MP > °C. *Compound 7.* Hundred milligrams of compound **1** are dissolved in 10 mL of a 1/1 mixture of chloroform and acetic acid. Then, 30 equiv of bromine is added and the mixture is refluxed for 4 days. The reaction is monitored by TLC and stopped when only one spot is observed. After cooling, the organic phase is washed thrice with sodium sulfite, twice with sodium hydrogenocarbonate and once with water, and dried on magnesium sulfate. After evaporation of toluene, the residue is dissolved in hot methylenechloride and precipitated by addition of petroleum ether and cooling at 0 °C yielding 127 mg (74%) of creamy powder. ¹H NMR (CDCl₃): 7.96 (d, 1H, ³J = 4 Hz); 7.17 (d, 1H, ³J = 4 Hz)–¹³C NMR (CDCl₃): 166.7; 142.1; 132.0; 131.6; 120.8–MS–EI (calcd), (562.7; 564.7), 562.5; 564.6 (100%)–MP: 250 °C (decomp).
9. Data collections were performed at 150K on a STOE IPDS diffractometer equipped with a graphite monochromator utilizing MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods using SIR92 (Altomare et al., 1993) and refined on F² by full-matrix least-squares method, using SHELXL97 (G. M. Sheldrick, 1998). Non-hydrogen atoms were refined anisotropically and absorption was corrected by gaussian technique. All hydrogen atoms were treated with a riding model. The refinement reveals a positional disorder for one thiophene ring on each independent molecule. The treatment of disorder leads to define two cycles for the thiophene, the component being, after refinement, in a 65% majority for the first independent molecule and equal to 50% for the second. C₁₅H₉N₃S₃, Mw = 327.43, crystal size 0.38 × 0.27 × 0.08 mm³, orthorhombic, Pna2₁, a = 19.537(1) Å, b = 5.0744(3) Å, c = 29.532(2) Å, V = 2927.8(3) Å³, Z = 8, $\rho_{\text{calc}} = 1.486 \text{ g/cm}^3$, 15,842 reflections collected in the 2–26° θ range, 5128 independent reflections ($R_{\text{int}} = 0.09$), $R_1 = 0.0540$ and $wR_2 = 0.1429$ using 4204 reflections with $I > 2\sigma(I)$, $R_1 = 0.0664$ and $wR_2 = 0.1564$ using all data, absolute structure parameter 0.2(1), GOF = 1.047, $-0.475 < \Delta\rho < 0.607 \text{ e \AA}^{-3}$.
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