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Synthesis and electronic properties of terthienyls β-substituted by (thienyl)cyanovinylene groups

Dora Demeter [a,b], Magali Allain [a], Philippe Leriche [a,*], Ion Grosu [b], Jean Roncali [a,*]

[a] Group Linear Conjugated Systems, CNRS UMR 6200, MOLTECH, University of Angers, 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

Terthienyls functionalized at their two outer β,β′-positions by 2- and 3-(thienyl)cyanovinyl groups have been synthesized by basic condensation. The analysis of their electronic properties by UV–vis spectroscopy and cyclic voltammetry shows that the mode of derivatization affects essentially the LUMO level of the conjugated system.

The molecular engineering of functional thiophene-based π-conjugated systems has generated a huge research effort in synthetic chemistry for several decades.[1–4] During this period, the number of applications of molecules and materials derived from π-conjugated thiophene oligomers and polymers has considerably increased to include electrode materials, active materials for transistors and solar cells, chromophores for nonlinear optics and light-emitting devices, and molecular architectures for molecular electronics.[1–5]

All these applications impose specific prerequisites regarding the suitable electrochemical, optical, and electrical properties of π-conjugated systems. In particular the control of the energy levels of frontier orbitals determines to a large extent the optical properties of the conjugated system as well as the processes of charge-transfer between the active material and the metal electrodes.[2–4]

It is well known that the grafting of electron-withdrawing groups on the polythiophene backbone leads to a decrease of the HOMO and the LUMO levels.[2–10]Applications of this approach has led to the development of n-type organic semi-conductors[9] or to organic solar cells with large open-circuit voltage.[10]

Basic condensations represent a simple and convenient method to introduce electron-acceptor cyano groups on π-conjugated systems. Furthermore, depending on the structure of the reactive building blocks, this method can lead at the same time to an extension of the π-conjugated system. In fact basic condensations have been used to synthesize conjugated polymers and oligomers with reduced band gap and enhanced electron affinity.[11–19] Furthermore, these reactions often take place with high yield, in the absence of metal catalysts, and without the formation of by-products, which represents decisive advantages in the context of clean chemistry.

We have already described thiophene-based oligomers and polymers with high electron affinity synthesized by Knoevenagel condensation on conjugated systems bearing terminal carboxaldehyde groups.[16] Owing to their extended conjugation these compounds present a strong absorption in the visible region. However, for some specific applications such as electron injection and/or transporting layers for light-emitting devices,[2,4] it can be interesting to develop materials combining enhanced electron affinity with optical transparency in the visible region of the spectrum.

In an attempt to develop such materials in the above-exposed general context, we report here a series of compounds (**1**–**4**, Scheme 1) obtained by basic condensation from terthienyls-bearing aldehydes or cyanomethylene groups at their terminal 3,3″-positions. It was anticipated that the introduction of (thienyl)cyanovinyl substituents at these positions will have less impact on the HOMO–LUMO gap of the conjugated system than in the case of the fully linear conjugated chains. While all target compounds **1**–**4** are based on a terthienyl core, the structures differ from the position of the nitrile group on the vinyl linkage (inner for **1** and **3** or outer for **2** and **4**) and from the mode of linkage onto the end-thiophene ring namely α-positions for **1** and **2** and β-positions for **3** and **4**. Besides the use of different starting materials such differences can be expected to diversely affect the electronic properties of the π-conjugated system.

* Corresponding authors. Tel.: +33 0231735443; fax: +33 0241735405 (J.R.).
E-mail address: jeanroncali@gmail.com (J. Roncali).

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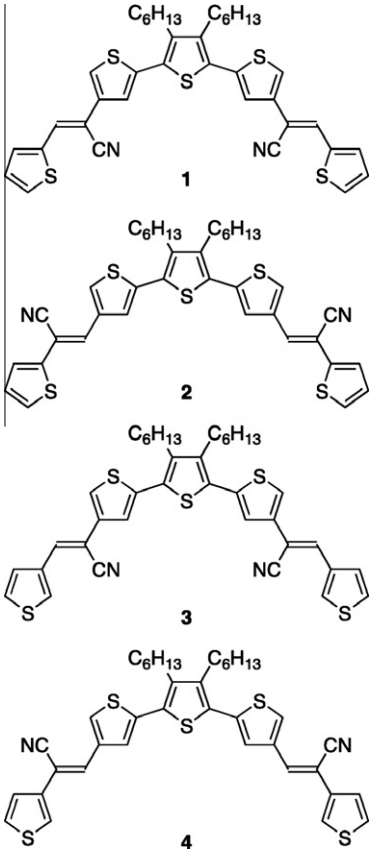
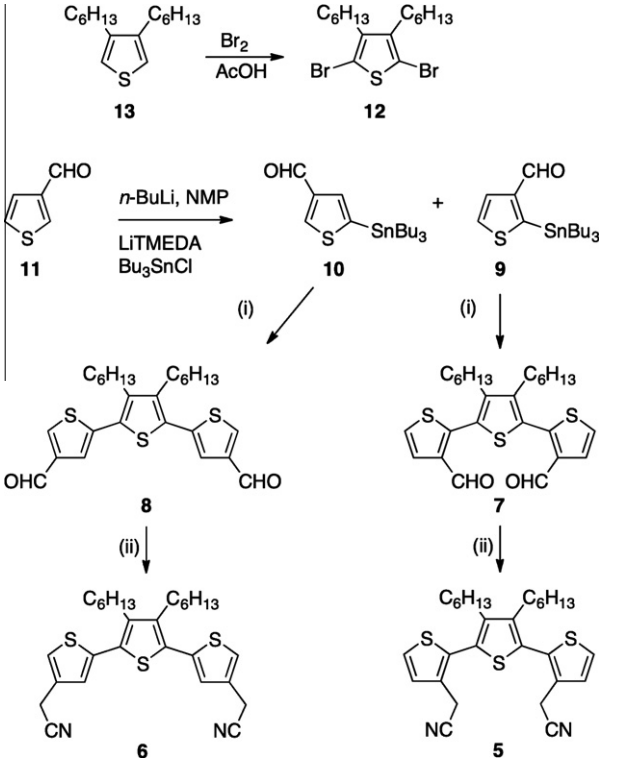


Scheme 1. Structure of the target compounds **1**–**4**.



Scheme 2. Synthesis of compounds **1**–**4**. Reagents: (i) $Pd(Ph_3)_4$, toluene reflux; (ii) TosMIC *t*-BuOK, THF.

The synthesis of the target compounds is depicted in Scheme 2. Bromination of 3,4-dihexylthiophene (**13**)[20] using bromine in acetic acid gave the corresponding 2,5-dibromo compound **12** in 81% yield. The Stille reagents **9** and **10** have been prepared from 3-thiophenecarboxaldehyde (**11**) using a one-pot protection/stannylation/deprotection procedure.[21,22] Addition of **11** to lithium 4-methylpyperazin-1-ide leads to a lithiated complex. Further addition of tetramethylethylenediamine (TMEDA), *n*-BuLi, and tributylstannylchloride leads to the Stille reagent **10** in 44% yield after hydrolysis. It is noteworthy that the intermediate complex not only acts at the same time as a protecting group but also contributes to orient the substitution at the desired 5-position due to steric hindrance. Nevertheless, compound **9** is also formed in 17% yield. However, after hydrolysis and deprotection of the aldehyde group, the two isomers can be easily separated by chromatography owing to their different polarity. These Stille reagents that present a limited stability are used shortly after synthesis.

A Stille cross-coupling reaction between 3,4-dihexyl-2,5-dibromothiophene **12** and the Stille reagent **10** gave compound **8** in 35% yield. Similarly, the coupling of **9** with **12** gives compound **7** in 14% yield. Finally, treatment of compounds **7** and **8** with *t*-BuOK and toluenesulfonylmethyl isocyanide (TosMIC) gave compounds **5** and **6** in 68% and 54% yields, respectively.[23,24] The target compounds **2** and **4** have been obtained in 11% and 42% yields, respectively, by condensation of dialdehyde **8** with 2-thienyl-acetonitrile and 3-thienylacetonitrile, respectively, in the presence of 3 equiv of *t*-BuOK in a 3:1 refluxing mixture of *t*-BuOH/THF. Reaction of compound **6** with 2- and 3-thiophenecarboxaldehyde under the same conditions gave compounds **1** and **3** in 15% and 35% yield, respectively.[26] It should be underlined that even in the most favorable case of the external coupling, the yields are inferior to those obtained with thiophenic reagents functionalized at the α-positions.

Figure 1 shows the crystallographic structure of compound **3**. The molecule crystallizes in the centrosymmetric monoclinic space group $P2_1/c$. One of the two terminal thiophene units presents a conformational disorder with two forms co-existing with 64% and 36% probability.

The terthiophene unit is non coplanar and shows a 31° dihedral angle between C11 and C12. The two coplanar thiophene units are in *syn* conformation. This unusual structure may be explained by strong S···S intermolecular interactions (d(S4···S4′) = 3.440(7) Å). These interactions associated with other S···S and S···N contacts (d(S1···S5) = 3.68(3) Å, d(S5···N1) = 3.22(4) Å, d(S6···N1) = 3.14(2) Å) lead to a global structure in which the ribbon of molecules are separated by slabs of hexyl chains.

Table 1 lists the UV–vis absorption maxima and oxidation potentials determined by cyclic voltammetry. Comparison of the absorption maxima of compounds **1**–**4** shows that π-electron delocalization is larger when the end-thiophene rings are linked at their α-position and when the cyano groups are at the outer positions of the vinyl linkages. These combined effects result in a 32 nm red shift of λ_{max} between compounds **3** and **2**, which corresponds to a 0.36 eV decrease of the HOMO–LUMO gap ΔE.

On the other hand, comparison of the λ_{max} for compounds **7** and **8** and **5** and **6** shows that the position of the aldehyde or cyanomethyl substituent strongly affects the absorption spectrum with a 20 nm red shift between the inner and outer positions in the case of the aldehyde groups and 37 nm between **5** and **6** for the more bulky cyanomethyl groups. These effects can be explained by the distortion of the terthienyl structure by steric interactions.

Cyclic voltammetry was carried out with 10^{-3} M solutions of substrate in 0.10 M Bu_4NPF_6/CH_3CN. The CV of all compounds shows an irreversible oxidation process. All target compounds **1**–**4** present an anodic peak potential (E_{pa}) at 1.13–1.15 V. This *quasi*-invariance of E_{pa} which contrasts with the differences observed among ΔE values indicates that the electronic effects associated with the structure of the (thienyl)cyanovinyl end blocks essentially

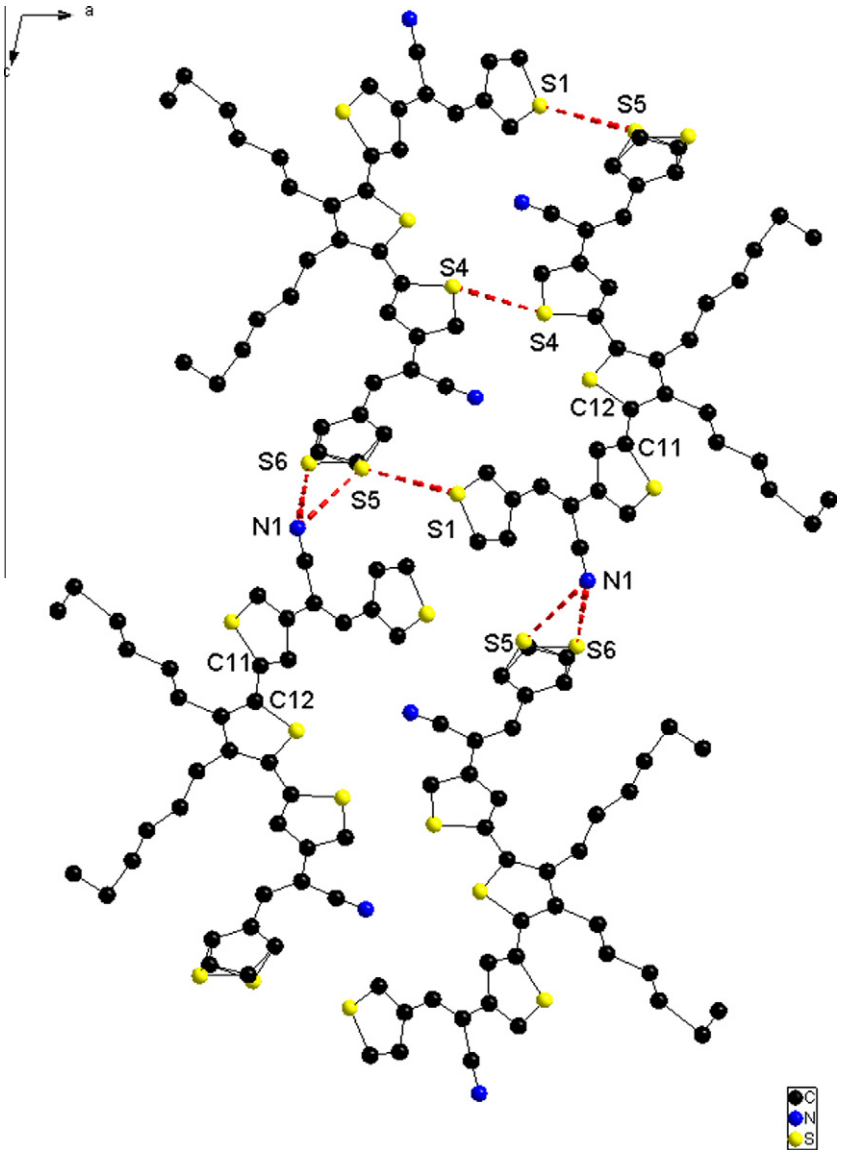


Figure 1. Crystallographic structure of compound **3**.[25]

Table 1
UV–vis absorption maxima and oxidation potentials of compounds **1**–**8**

Compd	λ_{max} (nm)	ΔE (eV)	E_{pa} (V) vs SCE
1	346	3.58	1.13
2	352	3.52	1.15
3	320	3.88	1.14
4	332	3.74	1.13
5	288		1.64
6	325		1.11
7	317		1.61
8	337		1.28

affects the LUMO level while the HOMO which is essentially localized on the terthienyl core is practically unaffected by these structural variations. Unfortunately it was not possible to experimentally confirm this conclusion by recording the reduction potentials of the compounds that are expected in a strongly negative potential range (−2.40 to −2.80 V).

To summarize terthienyls functionalized at their two outer β,β′-positions by various (thienyl)cyanovinyl groups have been synthesized by basic condensation. Preliminary analysis of the relationships between the molecular structure and the electronic properties shows that the nature and mode of linkage of the (thienyl)cyanovinyl group affects essentially the LUMO level of conjugated system.

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25. X-ray single-crystal diffraction data for **3** were collected at 293 K on a BRUKER-NONIUS KappaCCD diffractometer, equipped with a graphite monochromator utilizing MoKα radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined on F^2 by full-matrix least-squares method, using SHELX97 package (G.M. Sheldrick, 1998). S atoms were refined anisotropically and C, N atoms isotropically. Absorption was corrected by gaussian technique and the H atoms were included in the calculation without refinement. Crystallographic data for **3** : $C_{38}H_{38}N_2S_5$, M = 683.00, yellow needle, 0.25 × 0.04 × 0.02 mm^3, monoclinic, space group $P2_1/c$, a = 20.97(2) Å, b = 5.128(2) Å, c = 34.40(2) Å, β = 102.17(6)°, V = 3616(4) Å^3, Z = 4, ρ_{calc} = 1.255 g/cm^3, μ(MoKα) = 0.350 mm^{-1}, F(0 0 0) = 1440, θ_{min} = 2.42°, θ_{max} = 20.02°, 16,367 reflections collected, 3338 unique (R_{int} = 0.30), parameters/restraints = 220/5, R_1 = 0.1182 and wR_2 = 0.2534 using 1234 reflections with $I > 2\sigma(I)$, R_1 = 0.2827 and wR_2 = 0.3367 using all data, GOF = 1.010, $-0.337 < \Delta\rho < 0.336$ e Å^{-3}. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 775755. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ UK. E-mail: deposit@ccdc.cam.ac.uk.
Compound **1**. Under inert atmosphere 3 equiv of CsOH are added to a solution of **6** (100 mg) in 50 mL of 3:1 *t*-BuOH/THF. After 15 min stirring at rt 2-thiophenecarboxyaldehyde (45.5 mg) is added. The mixture is refluxed for 1.5 h. After concentration the residue is diluted with CH_2CL_2 and washed with water. The aqueous solution is extracted with CH_2CL_2. The organic phase is washed with water, dried over $MgSO_4$, and concentrated. Chromatography on silica gel, eluting with 1:1 petroleum ether/CH_2CL_2 gives 22 mg (15%) of a yellow powder. ^{1}H NMR ($CDCl_3$): 7.64 (d, 2H); 7.57 (s, 2H); 7.55 (d, 2H); 7.53 (d, 2H); 7.33 (d, 2H); 7.15 (dd, 2H); 2.72 (t, 4H); 1.57–1.55 (m, 4H); 1.43–1.32 (m, 12H); 0.90 (t, 6H); ^{13}C NMR ($CDCl_3$): 141.0; 137.9; 137.6; 135.9; 132.8; 132.0; 129.9; 129.3; 127.9; 123;1; 122.3; 117.8; 103.4, 31.4; 30.7;29.5; 28.1; 22.6; 14.0; −64.0; MS IE m/z (I%) 682 [M]$^+$ (100); mp 138 °C; IR (KBr, cm^{-1}): 2229.
26. Compound **5**. Under inert atmosphere CsOH (165 mg) in 10 mL of dry THF is added dropwise at −30 °C to a solution of TosMIC (170 mg) in 10 mL of dry THF. After 30 min stirring at 30 °C a solution of **7** (164 mg) in dry THF is added. After 30 min stirring 10 ml of methanol is added. The mixture is refluxed for 15 min and concentrated. The residue is diluted with 9 mL of water and 0.4 mL of acetic acid and extracted with CH_2CL_2. The organic phase is washed with aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated. Chromatography on silica gel eluting with CH_2CL_2 gives 100 mg (54%) of yellowish oil. ^{1}H NMR ($CDCl_3$): 7.44 (d, 2H); 7.17 (d, 2H); 3.63 (s, 4H); 2.48 (t, 4H); 1.45–1.37 (m, 4H); 1.27–1.22 (m, 12H); 0.84 (t, 6H); ^{13}C NMR ($CDCl_3$): 143.6; 131.9; 128.9; 127.9; 127.9; 127.2; 117.4; 31.3; 30.7; 29.4; 28.0; 22.5; 17.7; 14.0; MS MALDI 494.1 [M]$^+$.
Compound **7**. A mixture of **9** (200 mg), **12** (500 mg) and $Pd(PPh_3)_4$ (570 mg, 5 mol %) in 100 mL of anhydrous toluene is refluxed for 12 h under nitrogen. After concentration, the residue is taken in CH_2CL_2, the organic phase is washed twice with aqueous $NaHCO_3$ and then with water. After drying over $MgSO_4$ and solvent removal, chromatography on silica gel with CH_2CL_2 as eluent gives 120 mg (15%) of a yellow powder. mp 62 °C; ^{1}H NMR ($CDCl_3$): 9.83 (s, 2H); 7.57 (d, 2H); 7.40 (d, 2H); 2.85 (t, 4H); 1.46–1.38 (m, 4H), 1.24–1.20 (m, 12H), 0.83 (t, 6H); ^{13}C NMR ($CDCl_3$): 185.2; 145.9; 144.1; 139.6; 127.5; 127.0; 126.0; 31.3; 30.6; 29.3; 28.0; 22.5; 14.0; MS MALDI 472.0 [M]$^+$.