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Tricyanovinyl-Substituted Oligothiophenes

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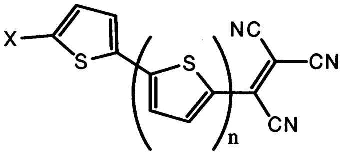
Organic materials endowed with electronic properties for applications such as light-emitting diodes (LEDs) and organic transistors have attracted increasing attention during the past several years.[1] The design of these materials and their electronic properties has benefited from theoretical studies,[2] an improved understanding of the principles governing the solid-state organization of molecular components in thin films and bulk crystals (i.e., crystal engineering),[3] and a recognition that the electronic properties (e.g., bandwidth and majority carrier) are governed by solid-state structure as well as molecular properties.[4] For example, the electronic transport properties of crystalline oligoacene and oligothiophene semiconductors are thought to depend strongly on whether the molecules adopt herringbone packing or π-stacked motifs. Generally, crystallinity and π-stacking are regarded as desirable structural characteristics for electron mobility.[5] The advancement of organic materials in field effect transistor configurations will benefit from new organic materials that can exhibit ambipolar behavior, that is, conduction of both n- and p-type carriers. The first step in achieving this property is the design of molecules with substituents that promote facile reduction and oxidation, which often can be deduced from electrochemical measurements, coupled with strategies for promoting desired crystal-packing motifs.

Structurally characterized oligothiophenes such as bithiophene, terthiophene, quaterthiophene, and sexithiophene crystallize in a herringbone motif.[6] However, examination of the Cambridge Crystal Structural Database reveals that π-stacking is observed frequently for thiophenes that possess one or more electron-withdrawing groups on the thiophene core.[7] Recently, a terthiophene derivative with dicyanomethine groups at opposite ends was reported to behave as an n-type semiconductor.[8] A related electron-withdrawing substituent, the tricyanovinyl group (TCV), can be attached readily to activated aromatic rings, an approach that has proven useful in the design of push−pull second-order nonlinear optical chromophores.[9] Herein, we describe the syntheses and electrochemical properties of four oligothiophene derivatives (**1**−**4**) with the TCV group, which facilitates reduction and promotes π-stacking, suggesting these materials may be suitable for n-type, and possibly ambipolar, transport.



(1) X = H, n = 1
(2) X = H, n = 2
(3) X = H, n = 3
(4) X = -C(CN)=C(CN)$_2$, n = 1

Compounds **1**−**4** were synthesized by adapting published procedures (details are provided as Supporting Information).[9a] Single-crystal X-ray diffraction reveals a nearly planar geometry for **1**, with the bithiophene core adopting a syn configuration (Figure 1).[10] Notably, density functional theory calculations at the B3LYP/6-

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(10) Formula: $C_{13}H_5N_3S_2$; formula weight: 267.32; color: red; dimensions (mm): 0.39, 0.36, 0.07; crystal system, orthorhombic; space group, Z: $Pna2_1$, 4; a, Å: 7.8613(10); b, Å: 24.495(3); c, Å: 6.1207(8); α, deg: 90; β, deg: 90; γ, deg: 90; V, Å^3: 1178.6(3); T, K: 173(2); d_{calcd}, g cm^{-3}: 1.507; $2\theta_{\max}$, deg: 56.00; R1, wR2 ($I > 2\sigma(I)$): 0.0303, 0.0691; GOF: 1.062.

10.1021/cm025628i CCC: $25.00

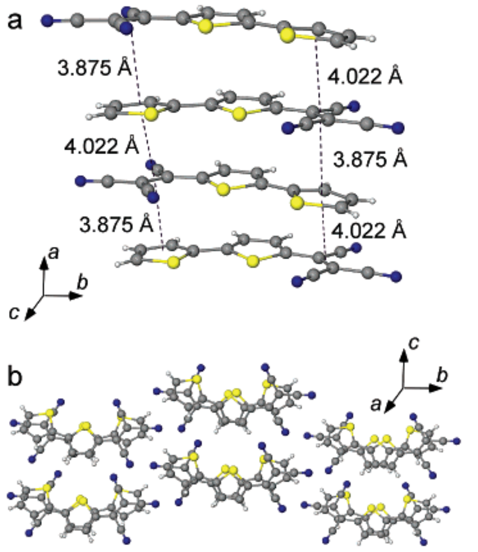

Figure 1. Molecular packing in **1** as determined by single-crystal X-ray diffraction, illustrating (a) the syn conformation of molecules, which form π-stacks along the *a* axis and (b) the noncentrosymmetric organization of the stacks. The close contacts between the centroids of the TCV double bonds and the thiophene rings are depicted.

31G* level suggest that **1** is nearly planar[11] and that the anti conformation is 1.0 kcal/mol lower in energy than the syn conformer. The observation of the syn conformer in the solid state indicates that crystal-packing forces override the preference for the anti conformer, consistent with previous theoretical studies that suggest comparable energies for the two forms.[12] Although in the minority, the syn conformation has been observed in a few other oligothiophenes. [13]

Furthermore, the thiophene rings are oriented identically along the *c* axis, resulting in polar symmetry (noncentrosymmetric $Pna2_1$ space group). The molecules alternate orientation in π-stacks along the *a* axis with the centroids of the TCV double bonds overlapping the terminal thiophene rings in adjacent molecules (average distances of 3.875 and 4.022 Å). This motif suggests a donor(thiophene)−acceptor(TCV) interaction, similar to the mixed-stack motifs observed in two-component systems based on oligothiophenes and tetracyanoquinodimethane acceptors.[14] Other short contacts include S...N contacts of 3.404 Å between adjacent molecules within the π-stacks and C−H···NC distances between stacks along the *b* and *c* axes of $d_{\mathrm{H\cdots N}} = 2.704$ Å and $d_{\mathrm{H...N}} = 2.638$ Å, respectively.

In contrast to **1**, the single-crystal structure of **2** reveals an all-anti configuration for the thiophene core (Figure 2).[15] The molecules form centrosymmetric π-stacked dimers, with these organized as highly canted π-stacks along the *b* axis. The closest contact between adjacent molecules within the stack is 3.76 Å. The π-stacks organize as pairs in the *bc* plane, alternating their orientation along the *c* axis. Unlike **2**, the TCV groups do not overlap the thiophene rings. Instead, the TCV groups exhibit very close contacts between the terminal nitrogen atoms of the TCV group and the TCV carbon atom attached to the thiophene core. These contacts alternate along the *c*-axis as $d_{\mathrm{N\cdots C}} = 3.106$ Å and $d_{\mathrm{N\cdots C}} = 3.213$, which are considerably less than the sum of the van der Waals radii. The overlap between these TCV atoms can be explained as a local donor−acceptor interaction, which is supported by the HOMO and LUMO calculated for the optimized structure of **2**.

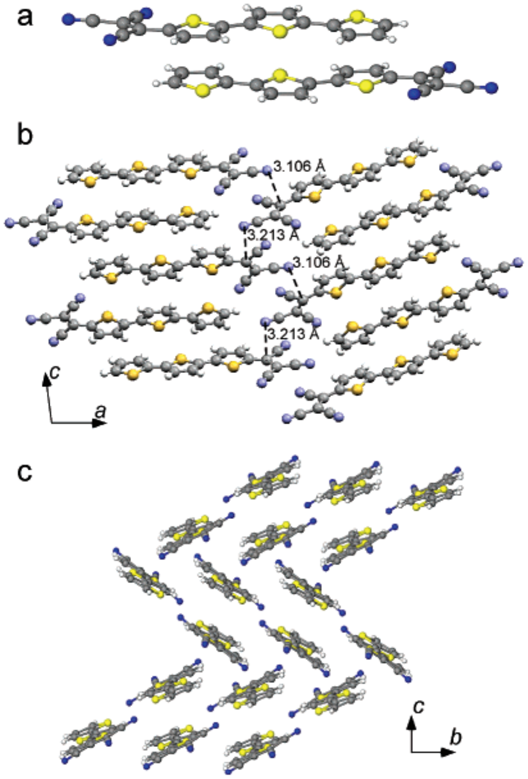

Figure 2. Molecular packing in **2** as determined by single-crystal X-ray diffraction, illustrating (a) the centrosymmetric π-stacked dimers with the terthiophene core exhibiting the anti conformation, (b) the *ac* plane illustrating the close contacts of the TCV groups along the *c* axis, and (c) the π-stacking of the oligothiophene cores along the *b* axis.

Single crystals suitable for X-ray diffraction analysis have not yet been obtained for compounds **3** and **4**. Calculations at the B3LYP/6-31G* level revealed that both compounds favor the all-anti conformation. Unlike **1** and **2**, the optimized geometry for **3** exhibits considerable conformational twisting within the quaterthiophene core, with S−C−C−C dihedral angles of 1.90°, −11.44°, and 20.10°. In contrast, these calculations afford a nearly planar and nearly centrosymmetric geometry for **4**.

The oxidation and reduction peak potentials ($E_{\mathrm{p,ox}}$ and $E_{\mathrm{p,red}}$, respectively) of **1**−**4** were determined by cyclic voltammetry 0.1 M n-$Bu_4N^+ClO_4^-/CH_3CN$ and com-

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(11) Titan: Wavefunction Inc. and Schrodinger Inc., 1999.

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(15) Formula: $C_{17}H_7N_3S_3$; formula weight: 349.44; color: red; dimensions (mm): 0.50 × 0.17 × 0.08; crystal system: monoclinic; space group, *Z*: $P2_1/c$, 8; *a*, Å: 35.473(8); *b*, Å: 5.8036(13); *c*, Å: 15.078(3); α, deg: 90; β, deg: 102.271(3); γ, deg: 90; *V*, Å^3: 3033.2(1); *T*, K: 173(2); d_{calcd}, g cm^{-3}: 1.530; $2\theta_{\mathrm{max}}$, deg: 56.08; R1, wR2 ($I > 2\sigma(I)$): 0.1768, 0.4720; GOF: 1.714.

pared with the corresponding unsubstituted oligothiophenes and tetracyanoethylene (Table 1). Compounds **1**−**4** exhibited chemically irreversible oxidations at potentials more anodic than those of their corresponding oligothiophenes, revealing the electron-withdrawing character of the TCV group. The oxidation potential also decreases with an increasing number of thiophene units, in parallel with the behavior of the unsubstituted oligothiophenes. The extent of this decrease (ca. 0.12 V per thiophene ring) is somewhat less than that of the oligothiophenes (ca. 0.25 V per thiophene ring).

Table 1. Cyclic Voltammetry and Spectroscopic Data for 1−4, Unsubstituted Oligothiophenes, and Tetracyanoethylene[a]

compound	E_p (ox)	E_p (red)	ΔE_p	λ_{max} (nm) (acetonitrile)
1	1.71	−0.41 (rev) −0.94	2.12	485.5
2	1.62[b]	−0.37 (rev) −1.01	1.99	546.0
3	1.48[c]	−0.34 (rev) −1.00	1.82	564.5
4	2.12	−0.08 (rev) −0.37 (rev) −0.81 −1.47	2.20	504.0
bithiophene[d]	1.25	−2.41 −3.10	3.66	303.5
terthiophene[d]	0.95	−2.07 −2.47	3.02	353.5
quaterthiophene[d]	0.80	−1.91 −2.21 −3.25	2.71	386[f]
tetracyanoethylene	not measurable	0.12[e] −0.54[e]		

[a] All TCV oligothiophene potentials measured with cyclic voltammetry (1 mM solutions) in 0.1 M n-$Bu_4N^+ClO_4^-/CH_3CN$ at 100 mV/s (vs Ag/AgCl). [b] Peak intensity gradually diminishes upon prolonged cycling, suggesting anodic polymerization and formation of a nonconducting product. [c] Measured at 20 mV/s. [d] Literature values for oxidation peaks measured in 0.1 M n-$Bu_4N^+PF_6^-/CH_2Cl_2$; reduction peaks measured in 0.1 M n-$Bu_4N^+Br^-$/dimethylamine (Meerholz, K.; Heinze, J. *Electrochim. Acta* **1996**, *41*, 1839). [e] $E_{1/2}$ values. [f] Measured in n-hexane. DiCesare, N.; Belletete, M.; Donat-Bouillud, A.; Leclerc, M.; Durocher, G. *Macromolecules* **1998**, *31*, 6289.

Compared to the unsubstituted oligothiophenes, however, reduction of **1**−**4** was facile and reversible, the TCV group shifting the potential of the first reduction anodically by nearly 2 V. The reduction potentials for **1**−**3**, each endowed with one TCV group, were nearly identical. This indicates that reduction of these compounds is dominated by the TCV group and relatively unaffected by the addition of thiophene rings. This is supported by calculations (B3LYP/6-31G* level) (Figure 3) of the unpaired spin density distributions of the radical anions of **1**−**3**, which indicate negligible spin density on the thiophene rings beyond the one attached to the TCV group. The introduction of the second TCV group in **4**, however, affords a symmetrical spin density with substantial contributions on the bithiophene core. The effect of two TCV groups is reflected by the more facile first reduction, at −0.08 V vs SCE, and a second rerversible reduction at −0.37 V, essentially identical to the first reduction potentials of **1**−**3** and substantially lower than the irreversible second reduction potentials for **1**−**3**.

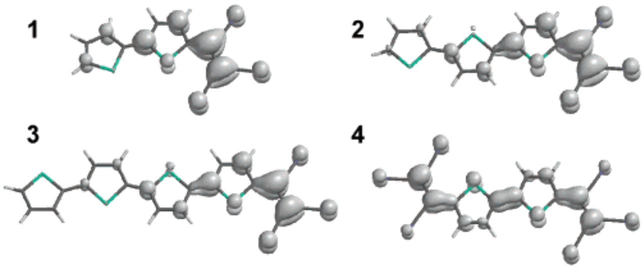

Figure 3. Calculated (B3LYP/6-31G*) unpaired spin density surfaces for the optimized structures of the monoanions of **1**−**4**.

The introduction of the TCV groups affords bathochromic shifts in the λ_{max} values compared with the respective unsubstituted oligothiophenes (see Table 1). Like the unsubstituted versions, the λ_{max} values of the TCV-substituted compounds increase with the number of thiophene rings. These optical transition energies therefore decrease in parallel with the ΔE_p values, which may be expected because both effectively are measures of the HOMO−LUMO gap in these compounds. Similar trends are observed for the unsubstituted oligothiophenes. These data, coupled with the π-stacking observed in **1** and **2** and the likelihood of π-stacking in **3** and **4**, suggest these compounds are candidates for n-type semiconductors in field effect transistor configurations. The electrochemical data also reveal that the difference between the oxidation and reduction potentials, ΔE_p, for **1**−**4** is significantly smaller than the corresponding values for the unsubstituted oligothiophenes. This suggests that these compounds are more likely to exhibit ambipolar transport. The observations here suggest that this can be made even more likely by adding electronic-donating groups to the thiophene cores. Synthesis, crystal growth, and FET device performance of these and related molecules are currently in progress.

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Supporting Information Available: X-ray experimental details (CIF files) for compounds **1**−**2** and the synthetic procedures and characterization data for **1**−**4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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