Reduced Band Gap Dithieno[3,2-*b*:2′,3′-*d*]pyrroles: New n-Type Organic Materials via Unexpected Reactivity

Ted M. Pappenfus,*,† **Bethany J. Hermanson,†** **Tyler J. Helland,†**
Garett G. W. Lee,† **Steven M. Drew,#** **Kent R. Mann,§** **Kari A. McGee,§ and**
Seth C. Rasmussen*,‡

Division of Science and Mathematics, University of Minnesota,
Morris, Minnesota 56267, Department of Chemistry, University of Minnesota,
Minneapolis, Minnesota 55455, Department of Chemistry and Molecular Biology,
North Dakota State University, Fargo, North Dakota 58105

pappe001@morris.umn.edu; seth.rasmussen@ndsu.edu

ABSTRACT

BTCV-DTP   DTP-Q
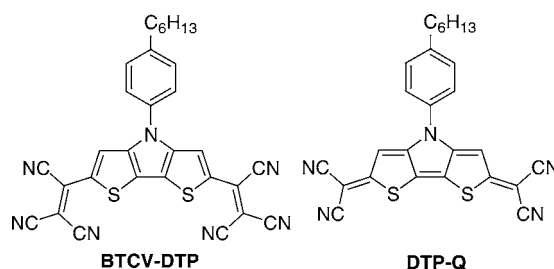
Direct addition of tetracyanoethylene to *N*-(*p*-hexylphenyl)dithieno[3,2-*b*:2′,3′-*d*]pyrrole yields not only the aromatic mono- and bis-tricyanovinyl-substituted products but also a quinoidal product with dicyanomethylene groups. The analogous reaction with dithieno[3,2-*b*:2′,3′-*d*]thiophene yields exclusively the aromatic mono-tricyanovinyl product. The aromatic and quinoidal products possess red-shifted absorptions, increased electron affinities, and favorable π-stacking motifs in comparison to the unsubstituted oligomers.

Dithieno[3,2-*b*:2′,3′-*d*]thiophene (DTT, Figure 1) is an important building block for a wide variety of functional organic materials. In particular, DTT has been employed in materials acting as the active layer in organic thin-film transistors (OTFTs).[1] The fused structure of DTT can promote π-stacking[1d,2] which is predicted to be a favorable motif for high charge transport in devices.[3] Far less investigated are the related dithieno[3,2-*b*:2′,3′-*d*]pyrroles (DTPs, Figure 1)[4] which are emerging as a useful structure for both molecular[4] and polymeric[5] materials. Functionalization of DTPs with electron-withdrawing groups is intriguing with
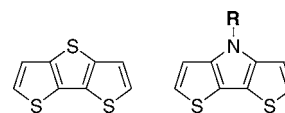
Figure 1. Structures of dithieno[3,2-*b*:2′,3′-*d*]thiophene (left) and dithieno[3,2-*b*:2′,3′-*d*]pyrroles (right).

regards to the development of reduced band gap materials given the fact that they possess lower oxidation potentials than DTTs.[4a] This approach can help create molecular materials with low-energy electronic transitions based on donor−acceptor interactions.[6]

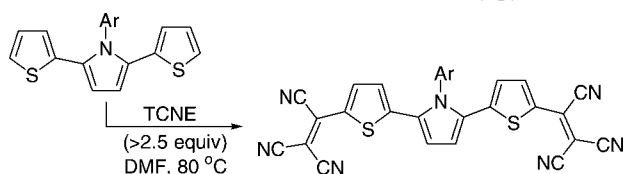† University of Minnesota, Morris
‡ North Dakota State University
§ University of Minnesota
# Department of Chemistry, Carleton College, Northfield, MN 55057.

We and others have found that the tricyanovinyl (TCV) functionality is a good acceptor group for creating reduced band gap materials of oligothiophenes.[7] The resulting materials display intriguing nonlinear optical properties, as well as favorable electron transport in OTFTs.[6,8] One approach to introduce TCV functionality in conjugated oligomers involves the formation of organolithium species followed by quenching with tetracyanoethylene (TCNE).[7,9] For activated aromatic rings, a more convenient method is to add TCNE directly to the molecule in a polar solvent.[10] This method has been applied to a variety of systems ranging from bithiophenes[11] to ferrocene.[12] Our present study was influenced by the investigation of Ogura et al. which reports the direct addition of TCNE to 1-aryl-2,5-di(2-thienyl)pyrroles (Scheme 1).[13] The reactivity toward bis-TCV products in this

Scheme 1. Addition of TCNE to Dithienylpyrroles

case is in contrast to other reports where mono-TCV products prevail. The bis-TCV products are reported as high-melting-point materials with metallic appearance. In this communication, we report the reactivity of DTPs under similar reaction

conditions in an effort to further tailor their electronic and redox properties.

In order to best match the pyrrole substitution in the work of Ogura and co-workers,[13] a known aryl-functionalized DTP, *N*-(*p*-hexylphenyl)dithieno[3,2-*b*:2′,3′-*d*]pyrrole[4a] (**DTP**, **1**) was chosen for this study. The reactivity of **DTP** with TCNE, however, is unique in comparison to previous studies. As shown in Scheme 2, addition of TCNE to **DTP** resulted in the formation of three products. All products were separable

Scheme 2. Addition of TCNE to **DTP**
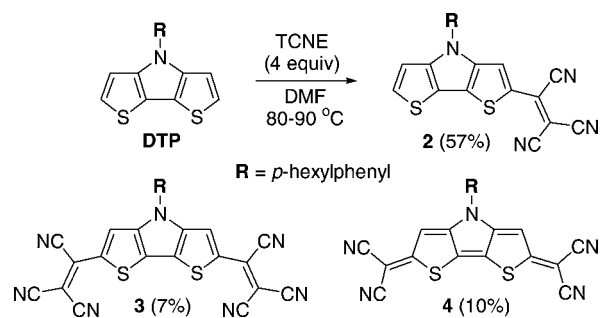
by column chromatography, and the first two products were quickly identified as the mono- and bis-TCV-substituted products, **TCV-DTP** (**2**) and **BTCV-DTP** (**3**), with **2** being the major product. The low production of the bis-TCV product **3** can be rationalized by deactivation of the remaining α-carbon upon TCV substitution due to the more strongly coupled π-system of the fused ring structure.

The identity of the last product **DTP-Q** (**4**) was established using NMR, combustion analysis, and X-ray crystallography (vide infra). This product was unexpected since dicyanomethylene-capped quinoidal species are typically prepared from bis-halo precursors using either Pd-catalyzed methods or TCNE oxide.[14] To our knowledge, preparation of quinoidal systems by direct TCNE addition to unsubstituted oligomers is unprecedented.

Although no precedent could be found for this reactivity in the literature, further investigation of its potential scope was of interest. As a result, DTT (**5**)[15] was treated with TCNE under the same conditions as DTP (Scheme 3). The reaction, however, yielded only one product, which was confirmed to be the mono-TCV product **6**. Prolonged reaction times yielded identical results, and no additional products were observed.

To further investigate this unique reactivity and confirm the lack of multiple product formation in the previous work

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Scheme 3. Addition of TCNE to DTT

of Ogura,[13] 1-(*p*-hexylphenyl)-2,5-di(2-thienyl)pyrrole[16] was prepared and treated with TCNE. In agreement with Ogura, the reaction yielded a single product which was confirmed by ^{1}H NMR, HRMS, and combustion analysis to be the bis-TCV product.

From the studies above, it is clear that the reactivity of DTP with TCNE is unique. When scaling up the reaction, it has been confirmed that this process is reproducible in affording products **2**, **3**, and **4**. In attempts to improve the reaction yields, the treatment of dilithiated DTPs with TCNE was investigated. Contrary to expectations, however, this gave poor results, giving even lower yields and no production of **4**.

Typical reactivity of π systems with TCNE to produce TCV products is thought to occur via an electron-transfer mechanism,[12] which would account for the formation of **2**, **3**, and **6**. However, while much less common, cycloaddition processes have also been reported,[17] and it is proposed that such processes could be responsible for the formation of the quinodal product **4** (see Supporting Information for proposed mechanism). This would be consistent with both the increased reactivity of DTPs[4,5] and the lack of product **4** from the dilithiated DTP.

UV−vis absorption and cyclic voltammetry (CV) data of the various DTP and DTT species are summarized in Table 1. Consistent with previous TCV oligomers, red-shifts in the electronic spectra are observed with increasing TCV substitution.[6,7] For example, the lowest energy $\lambda_{\max}$ values increase across the **DTP/2/3** series: $300 \rightarrow 538 \rightarrow 577$ nm. Compounds **4** ($\lambda_{\max} = 545$ nm) and **6** ($\lambda_{\max} = 499$ nm) also display red-shifts in comparison to **DTP** and DTT, respectively. This general trend has been previously attributed to the large stabilization of the LUMO by the electron-withdrawing groups in both aromatic[18] and quinoidal[19] systems. Density functional theory (DFT) calculations at the B3LYP/6-31G(d, p) level were performed for the DTP series to illustrate this point (Figure 2). Although the HOMO levels are also stabilized in these molecules, the magnitude of the LUMO stabilization is much greater, resulting in a net reduction in HOMO−LUMO energy upon TCV substitution.

The redox properties of the DTP and DTT series were investigated by CV (Table 1). Both DTT and **DTP** display

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Table 1. Spectroscopic and Electrochemical Data of the DTP and DTT Molecules

molecule	$\lambda_{\max}$, nm ($\log \epsilon$)[a]	$\lambda_{\max}$ (film) nm[b]	band gap (eV)[c]	$E°_{\text{ox}}$, V[d] (ΔE, mV)	$E°_{\text{red}}$, V[d] (ΔE, mV)
DTP (1)	300 (4.4)	318	3.56	1.07[f]	[g]
	262 (4.0)				
TCV-DTP (2)	538 (4.7)	440	1.88	1.51[f]	−0.54 (87)
	285 (4.2)				−1.20 (118)
BTCV-DTP (3)	577 (5.0)	606	1.72	1.88 (78)	−0.12 (80)
	540[e] (4.9)				−0.41 (82)
	380 (4.1)				−1.46 (150)
	363[e] (4.0)				
	269 (4.3)				
DTP-Q (4)	545 (5.0)	465	1.74	1.76 (101)	−0.23 (90)
	510 (4.9)				−0.53 (93)
	477[e] (4.6)				
	312 (3.9)				
	270 (4.0)				
DTT (5)	291 (4.5)	[h]	[h]	1.44[f]	[g]
TCV-DTT (6)	499 (4.6)	[h]	[h]	1.78[f]	−0.47 (94)
	275 (4.1)				−1.13 (108)

[a] Measured in dry CH_2Cl_2. [b] Solvent cast film. [c] Optical. [d] Potentials vs Ag/AgCl in 0.1 M $TBAPF_6/CH_2Cl_2$ solution. [e] Shoulder. [f] Irreversible process; E_{pa} value provided. [g] No observable reduction processes. [h] Not measured due to poor film formation.

irreversible oxidations with no observable reductions under the experimental conditions. Upon TCV substitution, however, reductions are observed at decreasing potentials with increased TCV substitution. To a lessor degree, increased TCV substitution results in the oxidations shifting to higher potentials. The DFT calculations accurately reflect both redox trends for the DTP series as predicted by Koopmans' theorem, which suggests that the HOMO/LUMO energies relate, respectively, to the first oxidation/redution potentials. For example, here the DFT calculations accurately predict that **3** should be the easiest to reduce (i.e., lowest energy LUMO) and **DTP** should be the easiest to oxidize (i.e., highest energy HOMO).

The solid-state structures of the DTP series were examined via X-ray crystallography, and selected bond lengths are given in Table 2. The crystal structure of **DTP** has been
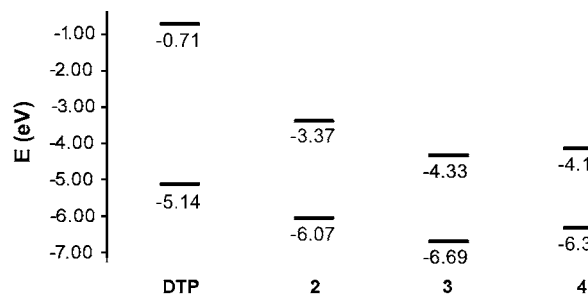
Figure 2. Calculated HOMO and LUMO levels for **DTP**, **TCV-DTP (2)**, **BTCV-DTP (3)**, and **DTP-Q (4)**.

Table 2. Select Bond Lengths (Å) for the DTP Series

bond	DTP[a]	BTCV-DTP (**3**)	DTP-Q (**4**)
C1−C2	1.348	1.381	1.438
C2−C3	1.416	1.395	1.356
C3−C4	1.377	1.397	1.446
C4−C5	1.422	1.409	1.360
C5−C6	1.379	1.401	1.452
C6−C7	1.421	1.388	1.353
C7−C8	1.352	1.385	1.422

[a] Reference 4a.

reported previously,[4a] and exhibits no π-stacking as p-hexylphenyl groups occupy the space between the DTP units. The crystal packing of **3** and **4**, however, each contain π-stacking, a property typical of thiophene-based oligomers with electron-withdrawing substituents.[7,20]

Molecules of **3**, co-crystallized with toluene, are very flat with a mean deviation from planarity of 0.0114 Å. Infinite π-stacks of 3.252 Å are present where the molecules are slipped along the long molecular axis such that little more than the TCV groups overlap to give a stairstep-type stack (Figure 3). The toluene molecules interact with the molecular
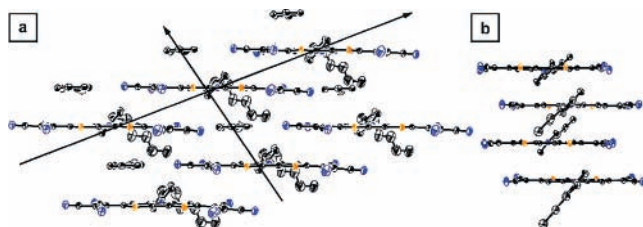
Figure 3. π-Stacking of **3** (a) and **4** (b).

core of the DTP with "π-stacking" interactions less than the van der Waals radii, resulting in a second type of π-stack via alternating DTP and toluene molecules. The π-stacking occurs in layers so that the hexyl substituents of the side chains aggregate together giving alternating layers of hexyl chains and π-stacking molecules. Several additional short intermolecular interactions occur between adjacent molecules (Table S3) but will not be discussed here.

Similar to **3**, the core of **4** is very flat with a mean deviation from planarity of 0.0076 Å. Molecules of **4** pack

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to give stacks of π-dimers with two short stacking distances: an intradimer distance of 3.423 Å and an interdimer distance of 3.439 Å. Columns of π-stacking molecules arrange so that hexyl chains of the p-hexylphenyl groups aggregate together giving layers of side chains and π-stacks. This organization appears to be driven by the tendency of the nitriles of the dicyanomethylene substituents to interact with atoms in adjacent molecules. Several additional short intermolecular interactions occur (Table S4) but will not be discussed here.

The structural data of the DTP series can shed light on the aromatic and quinoidal character of each molecule. Bond-by-bond data analysis shows that the C−C bond lengths change so that the "long" and "short" bonds of **DTP** become the "short" and "long" bonds of **4**. Compound **3** represents an intermediate case for all selected bonds. An alternative analysis is to treat each C−C bond as a variable and analyze using principal component analysis (PCA) as described previously.[20c] The two scores that contain most of the variance are plotted by projecting the data set (3 × 7 total variables) onto the PC1−PC2 plane (Figure S30). In this analysis, 99% of the variance lies within PC1 which means 99% of the changes in C−C bonds can be described by a single variable relating to the quinoidal character of the DTP core in each molecule.

In summary, the addition of TCNE to **DTP** affords two unique types of functional organic materials: TCV−aromatic and dicyanomethylene−quinoidal DTPs. Both types exhibit reduced band gaps in comparison to **DTP**. These properties, in conjuction with favorable redox and solid-state properties, make the materials attractive for electronic device applications. Further efforts will focus on more efficient syntheses of these materials, as well as device construction and evaluation.

Supporting Information Available: Experimental procedures, characterization data, crystallographic CIF files, and plots of physical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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