# Using the nitro group to induce $\pi$ -stacking in terthiophenes

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Abstract: A new synthetic route to mononitrated oligothiophenes is described, as well as the preparation of halogenated derivatives (Br, I) thereof. An unusual deep red colour is observed and explained, with the aid of DFT calculations, as arising from a significant quinoidal contribution to the molecular structure. The crystal structures of two compounds,  $H(C_4H_2S)_3NO_2$  and  $Br(C_4H_2S)_3NO_2$ , are presented. Both compounds have planar sheets held together by intermolecular short contacts (hydrogen bonds and, for the latter, NO<sub>2</sub>...Br interactions); the sheets do not directly superimpose, so the effect of the  $\pi$ -stacking is not maximized. Solid-state fluorescence and extended-Hückel band-structure calculations are also presented for these materials.

Key words: oligothiophene, organic semiconductor, crystal structure, band structure, nitro-substitution.

Résumé : On décrit une nouvelle méthode générale de synthèse des oligothiophènes mononitrés ainsi que la préparation de leurs dérivés bromés et iodés. On a observé une couleur rouge foncé inhabituelle et, en se basant sur des calculs de la théorie de la fonctionnelle de la densité (TFD), on suggère qu'elle résulte d'une importante contribution quinonoïdale à la structure moléculaire. On a déterminé les structures cristallines des deux composés  $H(C_4H_2S)_3NO_2$  et  $Br(C_4H_2S)_3NO_2$ . Les deux composés se présentent sous la forme de feuillets plans maintenus en place par des contacts intermoléculaires courts (liaisons hydrogènes et, dans le deuxième cas, interactions NO<sub>2</sub>...Br); les feuillets ne sont pas directement superposés et il en résulte que l'effet de superposition  $\pi$  n'est pas maximisé. On rapporte aussi les résultats obtenus pour la fluorescence à l'état solide de ces matériaux ainsi que les calculs étendus de Hückel de leur structure de bande.

Mots-clés : oligothiophène, semiconducteur organique, structure cristalline, structure de bande, substitution par un groupe nitro.

[Traduit par la Rédaction]

# Introduction

Organic materials are carbon-based small molecules or polymers with interesting electronic properties. Two of the most studied organic semiconductors are the oligothiophenes<sup>1–3</sup> and the acenes.<sup>4</sup> The promise of organic materials is held in the ability of the compounds to undergo "tuning" of the electronic structures through molecular substitution. Thus, an overwhelming variety of oligomers have been made, from dendrimers to polymers to molecules substituted at every position.

Unsubstituted organic semiconductors are mostly *p*-type (where the charge is carried by positive charges, or holes). Attachment of electron-withdrawing groups can convert them to *n*-type conductors (negative charge carriers), e.g., dihexylsexithiophene is *p*-type while bis(perfluorohexyl)sexithiophene is n-type.<sup>5</sup> The lowering of the frontier orbitals upon attachment also increases environmental stability because reactivity with oxygen in the air is reduced. Molecules substituted with both an electronic acceptor and an electronic donor will contain an internal charge-transfer electronic transition that can be exploited for non-linear optical devices<sup>6,7</sup> or as light-emitting diode dyes.<sup>8</sup> These electronic consequences are well-documented; far less is known of the structural consequences. Perfluorination<sup>9</sup> and  $\alpha, \omega$ -cyanosubstitution,<sup>10,11</sup> for example, both lead to a greater degree of  $\pi$ -stacking in the single-crystal structure, which is fortunately a beneficial outcome as  $\pi$ -stacking has been shown to increase mobility in standard device configurations.<sup>12,13</sup>

The nitro group is a typical example of a strong electronwithdrawing group that has been attached to molecular materials.14-17 While the resultant materials have been wellstudied electronically, structural investigations into the consequences of nitro substitution are sparse. Therefore, we have undertaken the synthesis and crystal growth of structurally simple nitro-substituted oligothiophenes. We chose to limit ourselves to mono-nitrated derivatives because these species are of greater synthetic interest, potentially allowing

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<sup>1</sup>Corresponding author (e-mail: craig.mackinnon@lakeheadu.ca). <sup>2</sup>Present address: Department of Chemistry, University Science Laboratories, South Road, Durham DH1 3LE, United Kingdom. subsequent substitution to generate more complex molecules. The use of the letter "T" as an abbreviation for the 2,5-disubstituted thienyl ring is common in the oligothiophene literature (see Scheme 1). Using this abbreviation, we report herein the synthesis of several  $XT_nNO_2$  species, where X = H, Br, or I, and n = 2 (bithiophene) and 3 (terthiophene). We also present the crystal structures of HT<sub>3</sub>NO<sub>2</sub> and BrT<sub>3</sub>NO<sub>2</sub>.

# **Results and discussion**

#### Synthesis

The compounds HT<sub>3</sub>NO<sub>2</sub> and BrT<sub>3</sub>NO<sub>2</sub> have been previously reported, but experimental details are scanty.<sup>18</sup> Further, we found the reported conditions to be excessively harsh, resulting in loss of regiochemical control, multiple nitrations, or oxidation of the thiophene ring.<sup>19</sup> Therefore, we report a new, milder synthesis of these species. We also report synthesis of the new species BrT<sub>2</sub>NO<sub>2</sub> and IT<sub>3</sub>NO<sub>2</sub>, which can be made the same way (although synthesis of  $BrT_2NO_2$  by the route  $T_2 \rightarrow BrT_2H \rightarrow BrT_2NO_2$  proved to have higher yield and purity). The reaction Scheme summarizes the syntheses. Nitration using nitric acid in acetic anhydride gave the best results, allowing us to heavily favour nitration at one (and only one) of the  $\alpha$ -sites on H<sub>2</sub>T<sub>2</sub> and H<sub>2</sub>T<sub>3</sub>. Unfortunately, this could not be extended to longer oligomers (the lack of solubility of T<sub>4</sub>, for example, required heating the nitration step, leading to inseparable mixtures of regioisomers). Suzuki coupling<sup>20-22</sup> of HT<sub>2</sub>B(OH)<sub>2</sub> and  $BrT_2NO_2$  seemed to be a reasonable alternate route, but the low solubility of the product HT<sub>4</sub>NO<sub>2</sub> prevented purification by recrystallization or chromatography. Sublimation afforded some material but it was always accompanied by a significant amount of H<sub>2</sub>T<sub>4</sub> and unidentified decomposition product(s) (probably due to polymerization). The insolubility of HT<sub>4</sub>NO<sub>2</sub> also prevented the regioselective synthesis of halogenated derivatives. Stille coupling<sup>23-26</sup> was even less useful because it had the same problems as the Suzuki method, with the additional difficulty of stannyl contamination.

#### Spectroscopic and computational studies

1A



2

1Q

NO



ized in Table 1. It is obvious from these data that the nitro group has an effect on  $\lambda_{MAX}$  that is larger than it should be based on a simple particle-in-a-box argument, i.e., the NO<sub>2</sub> group should extend the molecule by only two bonds, the same as the nitrile group. Instead, the  $\lambda_{MAX}$  of HT<sub>3</sub>NO<sub>2</sub> is closest to that of H<sub>2</sub>T<sub>5</sub> (extending the conjugation by eight bonds). We conclude that the NO<sub>2</sub> substituent helps rigidify the backbone by introducing a quinoidal resonance structure 1Q to the molecule. This restricts the free rotation (it has a very small energy barrier<sup>35,36</sup>) about the C5-C2' and the C5'-C2' (ring-ring) bonds in the aromatic form 1A. This rotation disrupts the extended conjugation of the oligomer and shortens the  $\lambda_{MAX}$ , so the restricted rotation in 1Q increases the effective average conjugation length. Addition of a second nitro group (e.g., compound 2) does not have the same effect, presumably because the quinoidalization has already occurred with the first NO<sub>2</sub> group.

For verification, we turned to DFT calculations. If the resonance form 1Q is significant, it should lead to a greater degree of  $\pi$ -bonding between C2 and C3 than is present in the aromatic form 1A. The bonds C1-C2 and C3-C4 should also lengthen. The results are shown in Table 2, along with experimental bond lengths from crystal structures when available (HT<sub>3</sub>NO<sub>2</sub> and BrT<sub>3</sub>NO<sub>2</sub> are reported below for the first time, while the other species have been previously reported). Unfortunately, the ratio derived from the crystal structures is unconvincing, partly due to the fact that the ratio (C2-C3/C1-C2) can vary widely due to crystal packing effects, and partly because the errors in the calculated ratios are within the statistical errors arising from the atomic ESDs. The computational results are more convincing, and may anyway be more representative of the structure in solution (i.e., in the absence of packing effects). For the computed structures, the C2-C3 bond decreases in length by 0.012 Å on changing from an H to an NO<sub>2</sub>. The C1–C2 bond lengths also increase slightly, verifying that the resonance structure 1Q does, in fact, have some influence on the structure of these molecules.

This change is essentially identical no matter what is happening at the other end of the molecule (independent of R<sup>2</sup>). This is somewhat counterintuitive because the quinoidal form **1Q** should be stabilized by lone pairs on R<sup>2</sup>, which could occur when R<sup>2</sup> = Br but not when R<sup>2</sup> = H. We would conclude that the nitro group is such a strong electron-withdrawing substituent that a donor group at the other end is Sears et al.

Compound	UV-vis absorption	Fluorescence (solution) <sup>a</sup>	Fluorescence (solid) <sup>a</sup>	HOMO–LUMO gap <sup>b</sup>
H <sub>2</sub> T <sub>3</sub>	[354]	428, 420 [411, 433]	480, 505, 455 [471, 455, 505] <sup>32</sup>	318
$H_2T_4$	[390]	440, 465 [454, 484]	528, 552 [555, 526] <sup>33</sup>	
$H_2T_5$	417 [418, C <sub>6</sub> H <sub>6</sub> ] <sup>29</sup>	496, 516 [482, 514, dioxane] <sup>30</sup>	669	
BrT <sub>2</sub> NO <sub>2</sub>	401	504	575 <sup>c</sup>	332
HT <sub>3</sub> NO <sub>2</sub>	[440]	581 [610]	643	379
BrT <sub>3</sub> NO <sub>2</sub>	[430]	581 [590]	669	383
IT <sub>3</sub> NO <sub>2</sub>	442	585	670	
Compound 2	[444] <sup>31</sup>			
BrT <sub>3</sub> CN	381	426	438	

**Table 1.** Absorption and fluorescence data for  $XT_nNO_2$  compounds. Solutions of  $CH_2Cl_2$  were used,  $\lambda_{MAX}$  values are reported in nm units. Literature values are in brackets.

Note: Literature values are also in CH<sub>2</sub>Cl<sub>2</sub> from ref. 18, unless otherwise stated.

"Italicized peaks are shoulders, peaks are listed in order of decreasing intensity.

<sup>b</sup>Using the PBE0/6-311++G(2df,pd) basis set, energy converted to equivalent wavelength in nm.

 $^{\textit{c}}\textsc{Transition}$  overlaps with a Raman scattering peak, which might alter the  $\lambda_{MAX}$  slightly.

**Table 2.** Selected bond lengths for  $H_2T_3$ ,  $HT_3NO_2$ ,  $BrT_3NO_2$ , compound **2**, and  $T_3CN_2$ ; calculated values are at the PBE0/6–311++G(2df,pd) level, distances in Å.

Compound		C1C2	C2-C3	C3–C4	C4–C5	Ratio <sup>a</sup>
H <sub>2</sub> T <sub>3</sub>	Crystal structure <sup>b</sup> Calculated	1.374(13) 1.359(13) 1.385(12) 1.3282(14) [1.375 (avg)] 1.362	1.458(12) 1.412(13) 1.431(11) 1.407(13) [1.427 (avg)] 1.412	1.422(11) 1.398(12) 1.426(11) 1.442(11) [1.422 (avg)] 1.373	1.450(12) 1.439(13) 1.460(13) 1.447(12) [1.449 (avg)] 1.442	1.038 1.032
	Calculated <sup>c,d</sup>	1.368	1.423	1.380	1.457	1.040
HT <sub>3</sub> NO <sub>2</sub>	Crystal structure Calculated	1.354(3) 1.366	1.405(2) 1.400	1.369(2) 1.382	1.450(2) 1.437	1.038 1.025
BrT <sub>3</sub> NO <sub>2</sub>	Crystal structure Calculated Calculated <sup>c,d</sup>	1.391(9) 1.366 1.373	1.404(9) 1.400 1.409	1.371(10) 1.382 1.392	1.464(9) 1.437 1.450	1.009 1.025 1.026
Compound 2	Crystal structure <sup>e 31</sup> Calculated <sup>c</sup>	1.363(3) 1.359(3) [1.361 (avg)] 1.373	1.404(3) 1.402(3) [1.403 (avg)] 1.410	1.377(3) 1.379(3) [1.378 (avg)] 1.391	1.461(3) 1.451(3) [1.456 (avg)] 1.452	1.031 1.027
T <sub>3</sub> (CN) <sub>2</sub>	Crystal structure <sup>f 10</sup>	1.367(15) 1.362(14) 1.302(17) 1.350(16) 1.341(16) [1.344 (avg)]	1.389(16) 1.424(13) 1.376(16) 1.417(14) 1.384(14) [1.398 (avg)]	1.367(15) 1.370(14) 1.345(16) 1.346(14) 1.353(15) [1.356 (avg)]	1.461(14) 1.362(14) 1.447(14) 1.450(14) 1.469(14) [1.438 (avg)]	1.040

<sup>a</sup>The ratio of the bond lengths (C2–C3)/(C1–C2).

<sup>b</sup>There are two crystallographically independent  $H_2T_3$  molecules, neither of which have  $C_{2\nu}$  symmetry.

<sup>c</sup>At the B3LYP/631G\*\* level, from ref. 34.

<sup>*d*</sup>Calculated for the mononitrated equivalent of 2 (H or Br in place of one  $NO_2$ ).

<sup>e</sup>The molecule does not have  $C_{2\nu}$  symmetry in the crystal structure.

<sup>f</sup>There are 2.5 molecules in the asymmetric unit.

essentially irrelevant (or, put another way, the far thiophene ring acts as the donor group).

#### Solid-state structures

Since we wished to determine the solid-state influence of the nitro group, crystals of both  $HT_3NO_2$  and  $BrT_3NO_2$  were grown, the former by sublimation and the latter from solution. The pertinent refinement data are given in Table 3. Unfortunately, the crystals for  $BrT_3NO_2$  were of low quality. Because of its low solubility, conversion from  $HT_3NO_2$  to  $BrT_3NO_2$  required heating and a long reaction time, which created a mixture of brominated products. Purification by repeated recrystallization did not fully separate these substances, so consequently a small amount of disubstituted material remained, which was modeled using partial occupancies as shown in Fig. 1 (the atoms labeled "H/Br2" and "H/Br3" are the partially occupied sites). Repeated sublimation of the product did lead to pure  $BrT_3NO_2$  by combustion

Compound	HT <sub>3</sub> NO <sub>2</sub>	BrT <sub>3</sub> NO <sub>2</sub>
Empirical formula	$C_{12}H_7NO_2S_3$	C <sub>12</sub> H <sub>6</sub> BrNO <sub>2</sub> S <sub>3</sub>
Formula weight	293.37	476.53
Crystal system	Triclinic	Triclinic
Space group	$P\overline{1}$	PĪ
a (Å)	6.3225(3)	7.3587(6)
b (Å)	7.6385(4)	7.8832(7)
<i>c</i> (Å)	13.2640(6)	13.7617(12)
α (°)	74.5191(10)	97.595(2)
β (°)	83.4360(10)	96.644(2)
γ (°)	87.3150(10)	113.5590(10)
V (Å <sup>3</sup> )	613.20(5)	712.77(11)
Formula units $(Z)$	2	2
$\rho_{\text{calcd.}}$ (g cm <sup>-3</sup> )	1.589	2.222
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.595	7.063
Crystal dimensions (mm)	$0.40 \times 0.24 \times 0.14$	$0.22 \times 0.08 \times 0.04$
F(000)	300	457
$\theta$ range (°)	$3.21 < \theta < 26.50$	$2.98 < \theta < 25.99$
Reflections collected	7285	8090
Unique reflections	2532	2795
$R_1 \left[ I > 2\sigma(I) \right]$	0.0315	0.0537
$wR_2$ (all data)	0.0881	0.1084
Goodness of fit on $F^2$	1.051	1.276

Table 3. Crystallographic refinement information for HT<sub>3</sub>NO<sub>2</sub> and BrT<sub>3</sub>NO<sub>2</sub>.

**Fig. 1.** Crystal structure of  $BrT_3NO_2$ . Top left: molecule showing atom numbering and thermal ellipsoids. Top right: two coplanar molecules showing the lack of face-to-face  $\pi$ -stacking between layers. Bottom: the two-dimensional sheet forcing coplanarity on the molecules, showing the short O…Br contacts and hydrogen bonds.



analysis. However, we were unable to obtain even lowquality single crystals of purified BrT<sub>3</sub>NO<sub>2</sub>. Fortunately, the gross structure does give the necessary information on atomic connectivities, and it shows the molecules forming ribbons held together by the halo-nitro supramolecular synthon.<sup>37,38</sup> Contact between the bromo and one oxygen on the nitro (as opposed to both oxygens equally) is typical.<sup>39</sup> The ribbons stack cofacially, but they are offset so that the  $\pi$ -systems overlap very little. Interestingly, rings 1 (C1–C4) and 2 (C5–C8) are mutually syn, while rings 2 and 3 (C9– C12) are anti to each other. While the syn orientation is less common, it is not unheard of (in fact, compound **2** also has mutually syn rings in its crystal structure<sup>31</sup>). Figure 2 shows the crystal structure of  $HT_3NO_2$ . In this case, sublimation led to good-quality crystals. The molecules line up in head-to-tail ribbons joined by hydrogen bonds between each nitro oxygen and an aromatic hydrogen. There is also a cross-ribbon hydrogen bond, generating a two-dimensional sheet. These sheets stack in the third dimension, leading to  $\pi$ -stacks, the favored orientation for maximizing carrier mobility in molecular semiconductors. The  $\pi$ -stacking is not fully optimized, however, as consecutive ribbons run in opposite directions in the centrosymmetric space group.

Even though the  $\pi$ -stacking is not optimal in either structure, there are clearly intermolecular interactions that give

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**Fig. 2.** Crystal structure of  $HT_3NO_2$ . Top left: molecule showing atom numbering scheme and thermal ellipsoids. Top right: side view of the  $\pi$ -stack; the top and bottom molecules have one S pointing at the viewer while the middle molecule has two, demonstrating the alternation in the sense of the stacking. Bottom: two-dimensional sheets held together with hydrogen bonds.



rise to intermolecular interactions between molecules in the solid state. The normalized fluorescence spectra for  $H_2T_3$  and  $HT_3NO_2$  (in both  $CH_2Cl_2$  solution and powder solid) are shown in Fig. 3. The  $\lambda_{MAX}$  for all the solid-state data were presented in Table 1, along with the solution data. The  $\lambda_{MAX}$  increases significantly for the solids compared with the solutions, demonstrating that the solid-state optical band gap is smaller than the molecular HOMO–LUMO gap.

The electrostatic hydrogen bonds connecting the molecules in the solid state do not contribute to the formation of an extended three-dimensional electronic structure. This is verified by Extended Hückel band structure calculations on  $RT_3NO_2$  (R = H, Br), the results of which are shown in Fig. 4, along with the same calculation on  $H_2T_3$ , using the literature crystal structure;35 numerical data are given in Table 4. The bandwidths are narrow, with little dispersion along any of the reciprocal space axes. In triclinic space groups, in which all these structures crystallize, the directions X, Y, and Z do not correspond to the real-space axes a, b, and c; however, this does not affect the gross conclusion that the dispersion is small. The band gap is significantly lower in the nitro-substituted species than in the unsubstituted molecule, but this is a reflection of the change in the energies of the HOMO and LUMO not a reflection of an increase in the bandwidths. The bandwidths are much narrower than those published for  $H_2T_6^{41}$  but are comparable to  $H_2T_3$ , so longer nitro-substituted oligomers may have significantly larger bandwidths.

## Conclusions

The attachment of one nitro group to a terthiophene oligomer is possible by using the relatively mild conditions of nitric acid in acetic anhydride. The resultant product,  $HT_3NO_2$  has an unusually small HOMO–LUMO energy gap, which we attribute to the effect of the quinoidal reso-

Fig. 3. Normalized solution and powder fluorescence spectra for  $H_2T_3$  and  $HT_3NO_2$ .



nance structure. The solid-state crystal structure consists of two-dimensional planes of molecules held together by hydrogen bonds. Although the sheets do not superimpose, there is some  $\pi$ -stacking between the sheets. Bromination and iodination of this molecule is possible, and the BrT<sub>3</sub>NO<sub>2</sub> molecule also has a  $\pi$ -sheet crystal structure, with hydrogen bonds and NO<sub>2</sub>...Br contacts. In this case, there is little  $\pi$ interaction between the sheets. Neither solid has large dispersion in the band structure, but the bandwidths are similar to unsubstituted H<sub>2</sub>T<sub>3</sub>, so longer nitrated oligomers may have more electronically useful band structures. The band gap is significantly smaller in nitro-substituted species, but this is simply a reflection of the smaller HOMO–LUMO gap. These results suggest that the nitro group is a good candidate for inducing  $\pi$ -stacking in oligothiophenes.

# **Experimental**

## Materials

Starting reagents were purchased from Aldrich and used

## Fig. 4. Extended-Hückel band structures of H<sub>2</sub>T<sub>3</sub>, HT<sub>3</sub>NO<sub>2</sub>, and BrT<sub>3</sub>NO<sub>2</sub>. The dashed line is the Fermi level.



Table 4. Band structures of selected oligothiophenes.

Compound	Band gap	Valence bandwidth	Conduction bandwidth	Reference
H <sub>2</sub> T <sub>3</sub>	2.08	0.013	0.11	This work <sup>a</sup>
HT <sub>3</sub> NO <sub>2</sub>	0.92	0.083	0.048	This work
$BrT_3NO_2^b$	0.60	0.016	0.023	This work
$H_2T_4$	2.24	0.52	0.44	40
$H_2T_6$	1.94	0.79	0.52	41

<sup>a</sup>The band structure calculation is new to this work, using the literature crystal structure (ref. 35).

<sup>b</sup>The crystal structure contains sites with partial Br occupancy; the band structure calculation has assumed 100% H for those sites.

without purification, except N-bromosuccinimide (NBS), which was recrystallized from water. Solvents were purchased from Anachemia or Caledon and purified prior to use: dichloromethane, diethyl ether, and tetrahydrofuran (THF) by passage through an alumina column under  $N_2$ ; alcohols by distillation from magnesium under N<sub>2</sub>. Oligothiophenes 2,2'-bithiophene ( $H_2T_2$ ); 2,2':5',2"-terthiophene  $(H_2T_3)$ ; 2,2':5',2":5",2"'-quaterthiophene  $(H_2T_4)$ ; and  $2,2':5',2'':\overline{5}'',2''':5''',2''''$ -quinquethiophene (H<sub>2</sub>T<sub>5</sub>) were synthesized by Grignard couplings of thienylmagnesium bromide (HTMgBr) to 2-bromothiophene (BrTH); 2,5-dibromothiophene  $(Br_2T)$ ; 5,5'-dibromo-2,2'-bithiophene  $(Br_2T_2)$ ; and 5,5'-dibromo-2,2':5',2"-terthiophene ( $Br_2T_3$ ), respectively, using the Kumada coupling catalyst (Ni(dppp)Cl<sub>2</sub>) [1,3-bis(diphenylphosphino)propane]dichloronickel(II).42 The method of Bäuerle<sup>43</sup> was used for monobromination to create 5-bromo-2,2'-bithiophene (BrT<sub>2</sub>H), and for all dibrominations. 5-Bromo-2,2':5',2"-terthiophene-5'-carbonitrile (BrT<sub>3</sub>CN) was prepared by the literature route.<sup>10</sup> All reactions were performed under an atmosphere of N<sub>2</sub> (using Schlenk conditions).

#### Instruments

FTIR spectra were recorded as nujol mulls on a Nicolet 380 FTIR spectrometer; vibrational frequencies are reported as wavenumbers (cm<sup>-1</sup>), with an experimental resolution of 4 cm<sup>-1</sup>. NMR spectra were recorded on a Varian Unity Inova 500 at room temperature in CDCl<sub>3</sub> or DMSO- $d_6$  solutions, referenced to TMS added to the sample or to the residual protonated solvent peak. Fluorescence measurements were taken on a PerkinElmer LS50B luminescence

spectrometer, while UV–vis absorption spectra were recorded on a PerkinElmer Lambda 11 UV–vis spectrometer; both were recorded as CH<sub>2</sub>Cl<sub>2</sub> solutions. Combustion analyses were performed on a CEC (SCP) 240-XA Analyzer. Gradient vacuum sublimations and crystal growth for X-ray crystallography were performed on an Applied Test Systems model 3210 split tube furnace attached to a series 2404 three-zone temperature control system. Melting points were recorded on an Electrothermal 9100 apparatus and are uncorrected. Mass spectra were recorded on a Micromass VG Autospec electron impact mass spectrometer at Lakehead University or on a Bruker Reflex III laser desorption/ionization time-of-flight mass spectrometer at the Mass Spectrometry Facility in the Advanced Analysis Centre at the University of Guelph.

#### X-ray crystallography

Single-crystal data were collected using the Smart Apex CCD (Bruker) equipped with an area detector utilizing graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The data were corrected for Lorentz and polarization effects. Absorption corrections were based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements of numerous reflections using the scale function of the APEX II software. The space groups for all compounds were determined on the basis of the systematic absences using symmetry and space group of the APEX II package. Structure solution and refinement using the SHELXTL package of APEX II were successful in the chosen centrosymmetric space groups. The structure solution

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via direct method led to the identification of the heavy atoms and the refinement on  $F^2$  using least-square method resulted in good *R* values. Full details of the structures have been deposited with the Cambridge Crystallographic Data Centre (see Supplementary data for details).

#### **Computational details**

Calculations used the PBE0 hybrid functional<sup>44–46</sup> and the large basis set  $6-311++G(2df, pd)^{47,48}$  as implemented in the Gaussian 03 package.<sup>49</sup>

#### Synthesis of 5-bromo-5'-nitro-2,2'-bithiophene (BrT<sub>2</sub>NO<sub>2</sub>)

Although this compound was often made in the method outlined in the Scheme 1, we found that the following method gave a higher-purity product. In 25 mL of acetic anhydride, 4.79 g (20 mmol) of BrT<sub>2</sub> was dissolved, and the mixture was cooled to 0 °C. To this solution (maintaining 0 °C) was added dropwise with stirring a mixture of 1.50 g (24 mmol) of nitric acid in 20 mL of acetic anhydride. The resultant mustard-yellow solution was quenched with saturated sodium bicarbonate and extracted into dichloromethane. Rotary evaporation followed by recrystallization (from ethanol) and sublimation (two times) yielded 1.45 g (25.6%) of analytically pure material. Mp 190–193 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ (ppm): 8.12 (d, *J*<sub>AB</sub> 4.0 Hz, 1 H), 7.56 (d,  $J_{AB}$  4.0 Hz, 1 H), 7.45 (d,  $J_{AB}$  4.0 Hz, 1H), 7.36 (d,  $J_{AB}$ 4.0 Hz, 1 H). Mass spectrum m/z: 291 (M+, 98%), 261 ([M -NO]+, 26%), 245 ([M - NO<sub>2</sub>]+, 23%), 201 ([M - SCNO<sub>2</sub>]+, 100%). Anal. calcd. for C<sub>8</sub>H<sub>4</sub>BrNO<sub>2</sub>S<sub>2</sub>: C 33.12, H 1.38, N 4.83; found: C 32.75, H 1.62, N 4.51%.

## Synthesis of 5-nitro-2,2':5',2"-terthiophene (HT<sub>3</sub>NO<sub>2</sub>)

In 100 mL of acetic anhydride, 8.75 g (35 mmol) of H<sub>2</sub>T<sub>3</sub> was dissolved, and the mixture was warmed until the oligothiophene dissolved. To this solution was added dropwise with stirring 2.75 g (44 mmol) of nitric acid. The dark-coloured solution was quenched with saturated sodium bicarbonate, at which time a dark-red precipitate formed. The solid was suction-filtered and washed with toluene and hexanes to give 3.19 g (31%) of an orange powder. Gradient sublimation in a tube furnace (95-70 °C) afforded analytically pure red crystals suitable for X-ray crystallography. Rotary evaporation followed by recrystallization (from ethanol) and sublimation (two times) yielded 1.45 g (25.6%) of analytically pure material. Mp 157-160 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ (ppm): 8.12 (d, *J*<sub>AB</sub> 4.5 Hz, 1 H), 7.69 (d, *J*<sub>AB</sub> 4.0 Hz, 1 H), 7.63 (d,  $J_{AB}$  6.0 Hz, 1H), 7.46 (d,  $J_{AB}$  4.5 Hz, 2 H), 7.41 (d,  $J_{AB}$  4.0 Hz, 1 H), 7.15 (dd,  $J_{AB} = J_{AC}$  4.5 Hz, 1 H). Mass spectrum m/z: 293 (M<sup>+</sup>, 100%), 247 ([M –  $NO_2$ ]<sup>+</sup>, 25%), 203 (87%). Anal. calcd. for  $C_{12}H_7NO_2S_3$ : C 49.13, H 2.40, N 4.77; found: C 49.14, H 2.46, N 4.77%.

# Synthesis of 5-bromo-5'-nitro-2,2':5',2"-terthiophene (BrT<sub>3</sub>NO<sub>2</sub>)

In 100 mL of DMF was dissolved 0.78 g (2.7 mmol)  $HT_3NO_2$ . While stirring in the dark, 1.84 g (10 mmol) was added portionwise over the course of 2 h, after which the solution was stirred overnight. Crude material precipitated upon addition of water. The red solid was recrystallized from toluene and repeatedly sublimed (120–90 °C) to obtain analytically pure material. Mp 172–175 °C. Mass spec-

trum m/z: 373 (M<sup>+</sup>, 100%), 327 ([M – NO<sub>2</sub>]<sup>+</sup>, 27%), 283 ([M – SCNO<sub>2</sub>]<sup>+</sup>, 73%), 145 (33%). Anal. calcd. for C<sub>12</sub>H<sub>6</sub>BrNO<sub>2</sub>S<sub>3</sub>: C 38.72, H 1.62, N 3.76; found: C 38.57, H 1.94, N 3.84%. Crystals suitable for X-ray crystallography were prepared by repeatedly recrystallizing the crude, i. e., isolating and redissolving material in toluene; this had the effect of concentrating the multibrominated byproducts, giving the structure as discussed in the text.

### Synthesis of 5-iodo-5'-nitro-2,2':5',2"-terthiophene ( $IT_3NO_2$ )

To a solution of 3.19 g (11 mmol) HT<sub>3</sub>NO<sub>2</sub> in 250 mL of DMF was added portionwise (in the dark) 2.48 g (11 mmol) of NIS. The mixture was then stirred overnight, followed by precipitation upon addition of water, giving 2.7 g (64%) of red-orange material. This material was purified by sublimation in vacuo. Mp 232–233 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 7.86 (d,  $J_{AB}$  4.5 Hz, 1 H), 7.26 (d,  $J_{AB}$  3.0 Hz, 1 H), 7.20 (d,  $J_{AB}$  4.0 Hz, 1 H), 7.09 (d,  $J_{AB}$  4.0 Hz, 1 H), 7.07 (d,  $J_{AB}$  4.0 Hz, 1 H), 6.91 (d,  $J_{AB}$  4.0 Hz, 1 H). Mass spectrum *m*/*z*: 419 (M<sup>+</sup>, 100%), 373 ([M – NO<sub>2</sub>]<sup>+</sup>, 23%), 329 (40%), 293 ([M – I]<sup>+</sup>, 11%). Anal. calcd. for C<sub>12</sub>H<sub>6</sub>INO<sub>2</sub>S<sub>3</sub>: C 34.38, H 1.44, N 3.34; found: C 34.50, H 1.65, N 3.11%.

## Supplementary data

Supplementary data for this article (computational data, including optimized geometries, orbital energies, and vertical excitation energies on the series  $R^{1}T_{n}R^{2}$  (n = 1-3;  $R^{1} =$ H or Br,  $R^2 = H$  or NO<sub>2</sub>) and experimental information on the synthesis of  $XT_4NO_2$  (X = H, Br)) are available on the journal Web site (http://canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 5327. For more information on obtaining material, refer to http://cisti-icist.nrc-cnrc. gc.ca/eng/ibp/cisti/collection/unpublished-data.html. CCDCs 739773 (HT<sub>3</sub>NO<sub>2</sub>) and 739774 (BrT<sub>3</sub>NO<sub>2</sub>) contain the X-ray data in CIF format for this manuscript. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/ conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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