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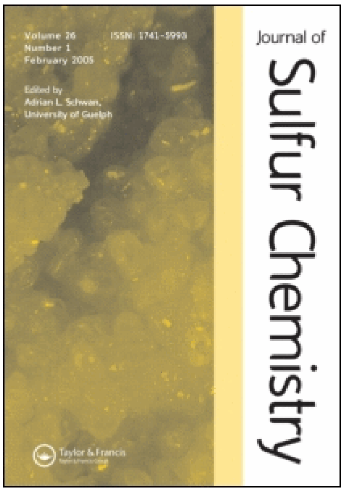

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Chiral tetrathienylene: synthesis and X-ray structure

Shuzhang Xiao[a], Maren Pink[b], Hua Wang[a], Suchada Rajca[a] and Andrzej Rajca[a]*

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Tetrakis(4-bromo-5-trimethylsilyl-2,3-thienylene) **1** with highly functionalized tetrathienylene ring may provide a building block for double helical oligothiophenes. Also, the tetrakis(2,3-thienylene) ring with relatively well-defined conformation provides an interesting probe for cross-conjugation and conjugation between thiophenes. Synthesis and X-ray structure of chiral tetrathienylene, tetrakis(4-bromo-5-trimethylsilyl-2,3-thienylene) **1**, are reported. Treatment of 5,5′-bis(trimethylsilyl)-4,4′-dibromo-3,3′-bithienyl with LDA, followed by oxidative coupling provided **1**. The compound crystallizes with one chloroform molecule per formula unit in the chiral space group $P2_12_12$ and is merohedrally twinned. The presence of four bromine atoms in the two bay areas of **1** leads to increased out-of-plane twisting (∼60°) of the chiral π-system along the β, β-linkages (CC bonds between the β-positions of thiophenes) within 3,3′-bithienylene units, compared to out-of-plane twisting (∼46°) in the parent tetrakis(2,3-thienylene). UV-vis spectra reveal a hypsochromic shift of about 50 nm for the onset of electronic absorption in **1**, compared to tetrakis(5-trimethylsilyl-2,3-thienylene). This hypsochromic shift is assigned to the decreased cross-conjugation in **1** due to the increased out-of-plane twisting along the β, β-linkages. A large bathochromic shift of about 100 nm for the onset of electronic absorption in **1**, compared to the corresponding acyclic 3,3′-bithienyl, *i.e.*, 5,5′-bis(trimethylsilane)-4,4′-dibromo-3,3′-bithienyl, is assigned to the increased conjugation due to the presence of the α, α-linkages (CC bonds between α-positions of thiophenes) in **1**.

Keywords: cross-conjugation; thiophene; oligothiophene; chirality; UV-vis spectra

1. Introduction

Organic materials based upon chiral π-conjugated molecules and polymers with strong chiral properties may find applications as components of optoelectronic devices (*1–6*). Recently, we developed a novel class of β-oligothiophenes in which thiophene rings are annelated into helices with the C_2S repeat unit (*2, 7–12*). The prototypical example of helical β-oligothiophene, such as [7]helicene, is prepared by an iterative synthesis starting from 5,5′-bis(trimethylsilane)-4,4′-dibromo-3,3′-bithienyl **2** (Scheme 1) (*7, 9*).

We also studied an alternative transformation of **2** to provide an entry to a chiral tetrathienylene, functionalized tetrakis(2,3-thienylene) **1**. Tetrakis(2,3-thienylene) **1** may be viewed as a potential

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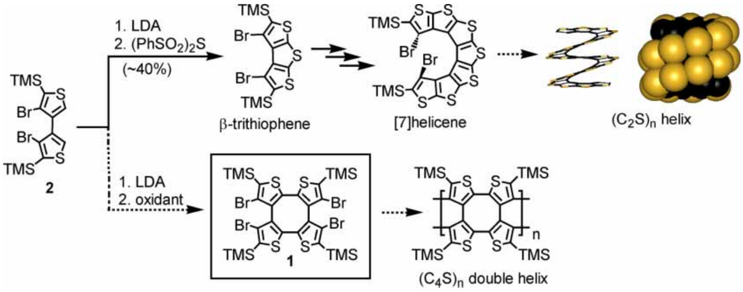


Scheme 1. Synthetic approaches to chiral annelated oligothiophenes: $(C_2S)_n$ helix and $(C_4S)_n$ double helix.

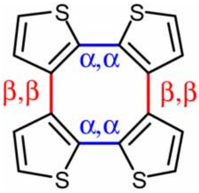


Figure 1. Tetrakis(2,3-thienylene).

building block for a double helical oligothiophene with the C_4S repeat unit (*13*). The only reported example of conjugated double helix that is devoid of alkyne moieties is an octaphenylene (*14*).

Tetrakis(2,3-thienylene) (*15–17*) is an interesting ring system in which adjacent thiophene rings are alternatively connected between the α-positions (α, α-linkages) and β-positions (β, β-linkages) (Figure 1). Because of the out-of-plane twisting between the adjacent thiophene rings, these linkages correspond to the chiral axes; both α, α-linkages adopt identical axial chirality but opposite to that of the β, β-linkages, analogously to the linkages in tetraphenylenes (*18–21*).

The CC frameworks of the adjacent thiophenes are formally conjugated for the α, α-linkages and they are cross-conjugated for the β, β-linkages. With its conformationally constrained tetraarylene ring system, (*18, 22*) tetrakis(2,3-thienylene) may provide a model system to probe conjugation and cross-conjugation between thiophenes. We postulate that in **1**, steric hindrance of bromines in the bay areas may allow us to probe the effect of out-of-plane twisting along the β, β-linkages on cross-conjugation between thiophenes. This probe would be complementary to the effect of helical out-of-plane distortion on cross-conjugated π-system in β-oligothiophenes such as derivatives of planar β-trithiophene and helical [7]helicene in Scheme 1 (*11, 12, 23*). The structure–property relationships in cross-conjugated π-systems with constrained conformations are relatively unexplored (*24*). Such studies are of general interest as cross-conjugated molecules and polymers attract increasing interest, especially due to the robust optical properties (*1, 2, 24, 25*).

We report on the synthesis of functionalized tetrakis(2,3-thienylene) **1** and its characterization by X-ray crystallography and UV-vis absorption spectroscopy.

2. Results and discussion

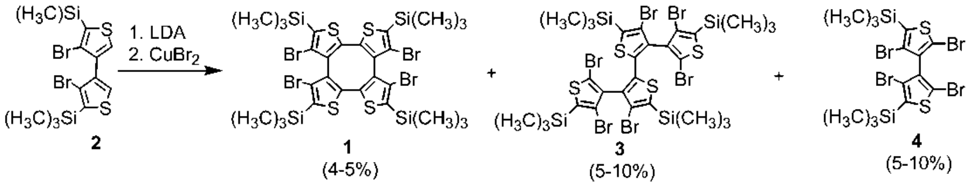
The LDA-mediated lithiation of the unprotected α-positions in 5,5′-bis(trimethylsilane)-4,4′-dibromo-3,3′-bithienyl (**2**) provided α, α'-dilithiated intermediate, which was oxidatively bis-homo-coupled using $CuBr_2$. ^1H NMR analyses of crude reactions mixtures suggested that the products derived from α, α'-dilithiated-3,3′-bithienyl, such as target tetrakis(2,3-thienylene) **1** and by-products **3** and **4**, were formed in 40–60% overall yield (Table S1, Supporting Information), though the isolated yields were much lower (Equation 1).

When starting from racemic **2**, α, α'-dilithiated-3,3′-bithienyls with the opposite as well as the identical axial chirality can form the first CC bond. Similarly to the formation of tetraphenylenes from 2,2′-dilithiobiphenyls (*14, 18, 19*), the formation of the second CC bond to form tetrathienylene unit requires that the axial chiralities for the 3,3′-bithienyl units are identical. Consequently, when the barrier for configuration inversion of the sterically hindered 3,3′-bithienyl units is high on the reaction time scale, the formation of by-products, including **3**, is more likely, thus leading to relatively low yields of tetrathienylene **1**. Based upon NMR spectra at room temperature, only one diastereomer of **3**, probably the *meso* compound with respect to the chiral axes of the 3,3′-bithienyl units, is isolated. After sublimation (or evaporation) under vacuum at temperatures up to 380 °C, both **1** and **3** are recovered with unchanged ^{1}H NMR spectra.

^{1}H and ^{13}C NMR spectra indicate the expected tetrafold symmetry for **1** with D_2 point group, while twofold symmetry consistent with C_2 point group is found for by-product **3**. In the low-resolution FAB mass spectra of **1** and **3**, isotopic clusters derived from M^+ have dominant intensities in the m/z 200 – 1500 range. For **1**, the M^+, $[M+2]^+$, $[M+4]^+$, $[M+6]^+$, and $[M+8]^+$ peaks have masses within less than 1.3 ppm of the calculated values for $C_{28}H_{36}Br_4S_4Si_4$.

The structure of **1** was confirmed by single-crystal X-ray analysis (Figure 2). Crystals of **1** were grown from chloroform. The compound crystallizes in the chiral space group $P2_12_12$. The structure is merohedrally twinned with a domain ratio of 65:35. The packing of the homochiral molecules of **1** leads to voids. In each void, one chloroform molecule is situated at a special position (two-fold), which is statistically disordered over two sites (Figure 3).

The conformation of **1** may be described by the torsion angles along the CC bonds connecting two thiophene rings at α-positions (α, α-linkage) and two thiophene rings at the β-positions (β, β-linkage) (Figure 1). The average values of the torsion angles for the α, α- and β, β-linkages are −53.3° and 60.4°, respectively. Analogous values for parent tetrakis(2,3-thienylene) are 52.5°



Equation 1. Synthesis of tetrathienylene **1**.

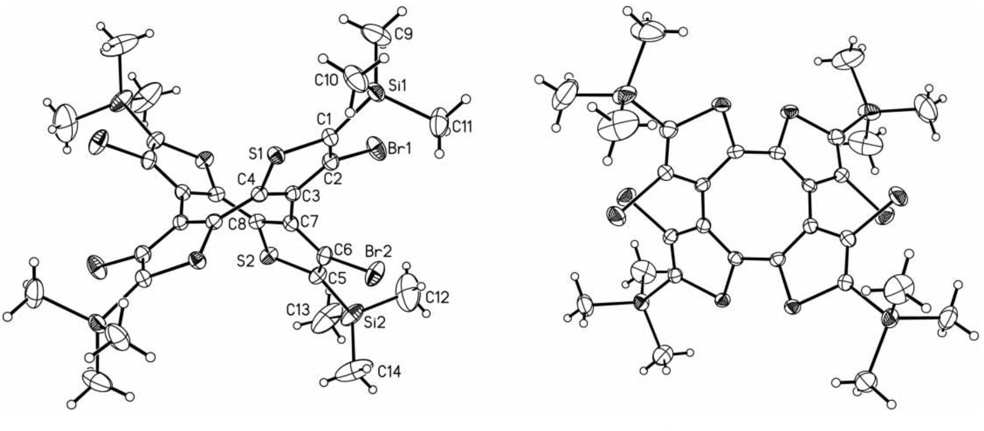


Figure 2. Molecular structure and conformation for tetrakis(2,3-thienylene) **1**. Carbon, bromine, silicon, and sulfur atoms are depicted with thermal ellipsoids set at the 50% probability level. Disordered solvent molecules are omitted for clarity.

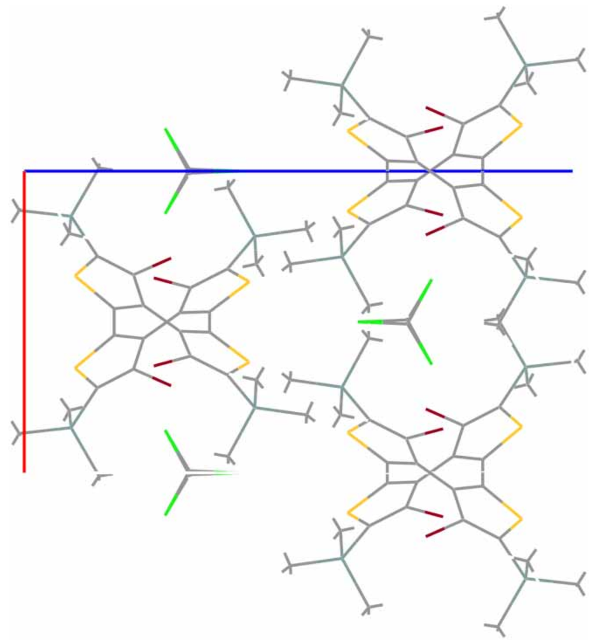


Figure 3. Crystal packing for tetrakis(2,3-thienylene) **1** showing projection along the *b*-axis. The red and blue lines correspond to the *a*-axis and *c*-axis, respectively.

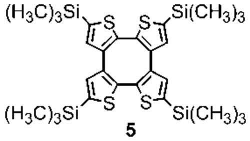


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Figure 4. Tetrakis(5-trimethylsilyl-2,3-thienylene) **5**.

and $-46.5°$, respectively (*26*). As the β, β-linkages in **1** are significantly more twisted and the α, α-linkages have similar torsion angles, UV-vis spectra of **1** and an appropriate reference compound may provide a probe for the effect out-of-plane twisting on cross-conjugation.

Tetrakis(5-trimethylsilyl-2,3-thienylene) **5** was selected as the reference compound (Figure 4) (*22*). The trimethylsilyl groups at all four α-positions of thiophenes in **1** and **5** are expected to provide similar bathochromic shift for both compounds (*9*); also, the trimethylsilyl groups should not significantly perturb the conformation of **5**, which would be similar to that of the parent tetrakis(2,3-thienylene).

Both **1** and **5** have a long-wavelength band with similar molar absorbances ($\varepsilon_{\mathrm{max}} \approx 3 \times 10^4\,\mathrm{L\,mol^{-1}\,cm^{-1}}$) at $\lambda_{\mathrm{max}} = 288$ nm and $\lambda_{\mathrm{max}} = 293$ nm, respectively (Figure 5). However, the absorption for **5** extends over much longer wavelengths ($\lambda_{\mathrm{onset}} \approx 430$ nm), corresponding to a hypsochromic shift of about 50 nm for an onset of absorption for **1** ($\lambda_{\mathrm{onset}} \approx 380$ nm). With reference to large out-of-plane twisting for the β, β-linkages in crystalline **1**, the hypsochromic shift suggests the out-of-plane twisting of the cross-conjugated π-system decreases electron delocalization in **1**. Notably, helical out-of-plane distortion of the cross-conjugated π-system in β-oligothiophenes leads to increased electron delocalization as the bathochromic shift of about 50 nm was found for derivatives of [*n*]helicenes ($n = 7$ and 11) versus the corresponding planar β-trithiophenes (Scheme 1) (*11, 12*).

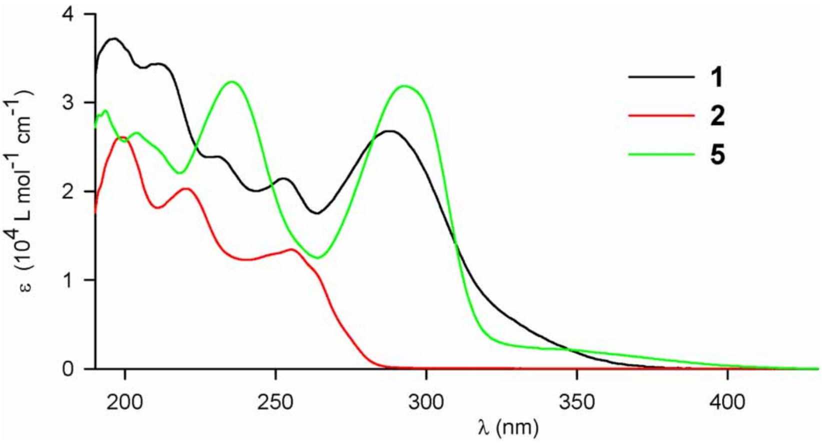

Figure 5. Electronic absorption UV-vis spectra for tetrakis(2,3-thienylene)s **1** and **5**, and 5,5′-bis(trimethylsilyl)-4,4′-dibromo-3,3′-bithienyl (**2**) in cyclohexane at room temperature.

The long-wavelength band for **1** shows a significant bathochromic of about 30 nm compared to $\lambda_{\max} = 255$ nm for **2**; much greater bathochromic shift of about 100 nm for λ_{onset} with $\lambda_{\text{onset}} \approx 285$ nm for **2** (Figure 5). Bathochromic shifts may be associated with the presence of two α, α-linkages in **1** leading to the increased conjugation between thiophenes; as in other tetraarylenes (*18, 19, 27*). This increase in conjugation is found in spite of considerable out-of-plane twistings of ~53° for the α, α-linkages in crystalline **1**.

3. Conclusion

In summary, functionalized tetrakis(2,3-thienylene) **1** was prepared and characterized by X-ray crystallography and UV-vis spectroscopy. The crystal of **1** grown from chloroform is a racemic twin (65:35) and crystallizes in the chiral $P2_12_12$ space group. The hypsochromic shift of about 50 nm for the onset of electronic absorption for **1** in solution, compared to tetrakis(5-trimethylsilyl-2,3-thienylene), is found. This shift may be correlated with the increased out-of-plane twisting of ~60° along the β, β-linkages for **1** in the solid state, compared to the twisting of ~46° for tetrakis(2,3-thienylene), thus suggesting that electron delocalization is significantly diminished by the out-of-plane twisting of the cross-conjugated π-system in **1**. This finding is in contrast to the helical out-of-plane distortion in cross-conjugated β-oligothiophenes that leads to the bathochromic shift, and thus increased electron delocalization.

4. Experimental section

4.1. *General procedures and materials*

Ether and tetrahydrofuran (THF) for use on the vacuum line were freshly distilled from sodium/benzophenone prior to use. n-BuLi (hexane) was obtained from either Aldrich or Acros; prior to use, its concentrations were determined by titration with N-pivaloyl-o-toluidine. Perdeuterated solvents for NMR spectroscopy were obtained from Cambridge Isotope Laboratories. All other commercially available chemicals were obtained from Aldrich, unless indicated otherwise. Column chromatography was carried out on TLC grade silica gel (Aldrich), using 0–20 psig pressure. Preparative TLC (PTLC) was carried out using Analtech silica plates (tapered with a preadsorbent zone). Standard techniques for synthesis under inert atmosphere, using Schlenk glassware and gloveboxes (Mbraun and Vacuum Atmospheres), were employed.

NMR spectra were obtained using Bruker and Omega spectrometers (^{1}H, 500 MHz and 300 MHz) using $CDCl_3$ as solvent. The chemical shift references were as follows: (^{1}H) $CHCl_3$, 7.260 ppm and (^{13}C) $CDCl_3$, 77.0 ppm. Typical 1D FID was subjected to exponential multiplication with an exponent of 0.1 Hz (for ^{1}H) and 1.0–2.0 Hz (for ^{13}C).

IR spectra were obtained using a Nicolet Avatar 360 FT-IR instrument, equipped with an ATR sampling accessory (Spectra Tech, Inc.). A few drops of the compound in CH_2Cl_2 were applied to the surface of a ZnSe ATR plate horizontal parallelogram (45°, Wilmad). After the solvent evaporated, the spectrum was acquired.

4.2. *X-ray crystallography*

A colourless crystal (approximate dimensions $0.42 \times 0.38 \times 28\,\mathrm{mm}^3$), obtained by slow evaporation of chloroform, was selected for data collection. Data collections were carried out using Mo Kα radiation ($\lambda = 0.71073$ Å, graphite monochromator). The intensity data were corrected for absorption.

The space group $P2_12_12$ was determined based on intensity statistics and systematic absences. Structures were solved with direct methods using SHELXS-86 and refined with full-matrix least squares/difference Fourier cycles using SHELXL-97 (*28*). All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with individual (or group as appropriate) isotropic displacement parameters.

Crystal data for tetrathienylene **1** • $CHCl_3$: colourless block, $C_{29}H_{37}Br_4Cl_3S_4Si_4$, $M = 1052.18$, monoclinic, $a = 10.0189(7)$ Å, $b = 12.0397(8)$ Å, $c = 18.190(1)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 2194(3)$ Å^3, $T = 173(2)$ K, space group $P2_12_12$, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.593\,\mathrm{Mg\,m^{-3}}$, $\mu = 4.171\,\mathrm{mm^{-1}}$, $2\theta_{\max} = 54.96$. A total of 19727 reflections were measured, of which 4998 were independent ($R_{\mathrm{int}} = 0.0320$). Final residuals were $R = 0.0290$ and $wR2 = 0.0704$ (for 4535 observed reflections with $I > 2\sigma(I)$, 211 parameters, 3 restraints) with GOF = 1.015 and largest residual peak $0.830\,\mathrm{e}\,$Å^{-3} and hole $-0.776\,\mathrm{e}\,$Å^{-3}. Absolute structure parameter (Flack parameter) was 0.356(7) and indicates the domain ratio (*29*). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC no. 673737.

4.3. *UV-vis spectroscopy*

UV-vis spectra were obtained on Shimadzu (UV–2401PC) spectrophotometer. The Lambert–Beer plots were obtained using 10-mm pathlength quartz cells; five concentrations, covering the 0.05–2.4 range in absorbance (A), were used. For all compounds studied linear plots were obtained ($R^2 > 0.9999$). The UV/vis data in cyclohexane, $\lambda_{\max}$/nm ($\varepsilon_{\max}$/L mol^{-1} cm^{-1}): for **2**, 255 (1.34×10^4), 220 (2.03×10^4); for **1**, 288 (2.63×10^4), 253 (2.09×10^4); for **5**, 293 (3.21×10^4), 235 (3.25×10^4).

4.4. *Synthesis*

Tetrathienylene 1 and tetrathiophene 3. *n*-BuLi (1.94 M in hexane, 0.98 mL, 1.90 mmol, 3.0 equiv) was added dropwise to diisopropylamine (0.28 mL, 2.00 mmol, 3.2 equiv) in ether (8 mL) at 0 °C. After 1 h at 0 °C, a solution of **2** (0.297 g, 0.63 mmol) in ether (4 mL) was added dropwise.

The reaction mixture was stirred for 2 h at 0 °C, and then cooled to −78 °C. $CuBr_2$ (1.477 g, 6.33 mmol, 10 equiv) was added, then kept at −78 °C for 3 h, and warmed slowly to ambient temperature over night. After extraction with ether (100 mL), the combined organic layers was washed with water (5 × 20 mL) and then dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by column chromatography (silica gel, hexane), and then recrystallized from $CHCl_3$-CH_3OH (v/v, 1:3) to yield tetrathienylene **1** (11.5 mg) and tetrathiophene **3** (36.8 mg, 11%). Another 3.4 mg of **1** was obtained by using PTLC for separation of the filtrate. Total 14.9 mg of **1** gave an isolated yield of 5%. From another reaction on the 1.00 g scale, 38.7 mg (3.9%) of **1** and 59.8 mg (5.1%) of **3** were obtained; this yield of **3** was obtained after recrystallizing six times from $CHCl_3$-CH_3OH (v/v, 1:3), CH_2Cl_2-hexane (v/v, 1:2) and CH_2Cl_2-CH_3OH (v/v, 5:3).

Tetrathienylene 1. M.p. 343–345 °C, ^{1}H-NMR ($CDCl_3$, 500 MHz): 0.42 (s, 36H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 138.20, 137.24, 137.08, 119.75, −0.87. IR (cm^{-1}): 2958, 2900 (C-H). LR/HR FABMS (3-NBA matrix): m/z (ion type, % RA for $m/z = 200$–1500, deviation for the formula) at 927.7499 ($[M]^+$, 12, 1.3 ppm for ${}^{12}C^{1}_{28}H^{28}_{36}Si^{32}_{4}S^{79}_{4}Br_4$), 929.7498 ($[M+2]^+$, 52, −0.8 ppm for ${}^{12}C^{1}_{28}H^{28}_{36}Si^{32}_{4}S^{79}_{4}Br^{81}_{3}Br_1$), 931.7469 ($[M+4]^+$, 100, 0.1 ppm for ${}^{12}C^{1}_{28}H^{28}_{36}Si^{32}_{4}S^{79}_{4}Br^{81}_{2}Br_2$), 933.7458 ($[M+6]^+$, 99, −1.0 ppm for ${}^{12}C^{1}_{28}H^{28}_{36}Si^{32}_{4}S^{79}_{4}Br^{81}_{1}Br_3$), 935.7433 ($[M+8]^+$, 50, −0.5 ppm for ${}^{12}C^{1}_{28}H^{28}_{36}Si^{32}_{4}S^{81}_{4}Br_4$).

Tetrathiophene 3. M.p. 259–261 °C, ^{1}H-NMR ($CDCl_3$, 500 MHz): 0.43 (s, 18H), 0.33 (s, 18H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 138.56, 138.42, 137.27, 134.35, 133.72, 119.64, 119.43, 119.15, −0.88, −0.92. IR (cm^{-1}): 2956, 2898 (C-H). LR/HR FABMS (3-NBA matrix): m/z (ion type, % RA for $m/z = 200$–1500, deviation for the formula) at 1085.5914 ($[M]^+$, 6, −3.4 ppm for ${}^{12}C^{1}_{28}H^{28}_{36}Si^{32}_{4}S^{79}_{4}Br_6$), 1087.5816 ($[M+2]^+$, 25, 3.7 ppm for ${}^{12}C^{1}_{28}H^{28}_{36}Si^{32}_{4}S^{79}_{4}Br^{81}_{5}Br_1$), 1089.5799 ($[M+4]^+$, 64, 3.4 ppm for ${}^{12}C^{1}_{28}H^{28}_{36}Si^{32}_{4}S^{79}_{4}Br^{81}_{4}Br_2$), 1091.5751 ($[M+6]^+$, 100, 5.9 ppm for ${}^{12}C^{1}_{28}H^{28}_{36}Si^{32}_{4}S^{79}_{4}Br^{81}_{3}Br_3$), 1093.5735 ($[M+8]^+$, 91, 5.5 ppm for ${}^{12}C^{1}_{28}H^{28}_{36}Si^{32}_{4}S^{79}_{4}Br^{81}_{2}Br_4$).

Attempted pyrolyses of tetrathienylene 1 and tetrathiophene 3. Starting material (0.5–1.0 mg) was placed in the sealed end of a Pasteur pipette and kept under vacuum for 2 h. While under vacuum, the sample was placed in a melting point apparatus and heated from room temperature to 265 °C. After 6 h at 265 °C, significant portion of the sample sublimed and no significant colour change was observed; ^{1}H NMR analyses of the remaining material indicated the presence of the starting material only. Similar results were obtained for both **1** and **3** when the sample was inserted to the melting apparatus at 380 °C, and then kept at 380 °C for 4 h.

Supporting information available

^{1}H NMR analyses of crude reaction mixtures, NMR and IR spectra for **1** and **3**. This material is available free of charge via the internet at www.informaworld.com

Acknowledgement

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References

(1) Rajca, A.; Miyasaka, M. Synthesis and Characterization of Novel Chiral Conjugated Materials. In *Functional Organic Materials – Syntheses, Strategies, and Applications*; Mueller, T.J.J.; Bunz, U.H.F., Eds.; Wiley-VCH: Weinheim, 2007; Chapter 15 (free download at http://digitalcommons.unl.edu/chemistryrajca/3).

(2) Rajca, A.; Rajca, S.; Pink, M.; Miyasaka, M. *Synlett* **2007,** 1799–1822.

(3) Hassey, R.; Swain, E.J.; Hammer, N.I.; Venkataraman, D.; Barnes, M.D. *Science* **2006,** *314*, 1437–1439.

(4) Jeukens, C.R.L.P.N.; Jonkheijm, P.; Wijnen, F.J.P.; Gielen, J.C.; Christianen, P.C.M.; Schenning, A.P.H. J.; Meijer, E.W.; Maan, J.C. *J. Am. Chem. Soc.* **2005,** *127*, 8280–8281.

(5) Wilson, J.N.; Steffen, W.; McKenzie, T.G.; Lieser, G.; Oda, M.; Neher, D.; Bunz, U.H.F. *J. Am. Chem. Soc.* **2002,** *124*, 6830–6831.

(6) Herman, W.N. *J. Opt. Soc. Am. A* **2001,** *18*, 2806–2818.

(7) Rajca, A.; Wang, H.; Pink, M.; Rajca, S. *Angew. Chem. Int. Ed.* **2000,** *39*, 4481–4483.

(8) Friedman, T.B.; Cao, X.; Rajca, X.; Wang, H.; Nafie, L.A. *J. Phys. Chem. A* **2003,** *107*, 7692–7696.

(9) Rajca, A.; Miyasaka, M.; Pink, M.; Wang, H.; Rajca, S. *J. Am. Chem. Soc.* **2004,** *126*, 15211–15222.

(10) Miyasaka, M.; Rajca, A. *Synlett* **2004,** 177–182.

(11) Miyasaka, M.; Rajca, A.; Pink, M.; Rajca, S. *J. Am. Chem. Soc.* **2005,** *127,* 13806–13807.

(12) Miyasaka, M.; Rajca, A. *J. Org. Chem.* **2006,** *71,* 3264–3266.

(13) Marsella, M.J.; Kim, I.T.; Tham, F. *J. Am. Chem. Soc.* **2000,** *122,* 974–975.

(14) Rajca, A.; Safronov, A.; Rajca, S.; Schoemaker, R. *Angew. Chem. Int. Ed.* **1997,** *36,* 488–491.

(15) Greving, B.; Woltermann, A.; Kauffmann, T. *Angew. Chem. Int. Ed. Engl.* **1974,** *13,* 467–468.

(16) Kauffmann, T.; Greving, B.; Kriegesmann, R.; Mitschker, A.; Woltermann, A. *Chem. Ber.* **1978,** *111,* 1330–1336.

(17) Marsella, M.J.; Reid, R.J.; Estassi, S.; Wang, L.-S. *J. Am. Chem. Soc.* **2002,** *124,* 12507–12510.

(18) Rajca, A.; Safronov, A.; Rajca, S.; Wongsriratanakul, J. *J. Am. Chem. Soc.* **2000,** *122,* 3351–3357.

(19) Rajca, A.; Wang, H.; Bolshov, P.; Rajca, S. *Tetrahedron* **2001,** *57,* 3725–3735.

(20) Wen, J.-F.; Hong, W.; Yuan, K.; Mak, T.C.W.; Wong, H.C.N. *J. Org. Chem.* **2003,** *68,* 8918–8931.

(21) Peng, H.-Y.; Lam, C.-K.; Mak, T.C.W.; Cai, Z.; Ma, W.-T.; Li, Y.-X.; Wong, H.N.C. *J. Am. Chem. Soc.* **2005,** *127,* 9603–9611.

(22) Das, K. Syntheses of Building Blocks for Organic Materials: Spin-Labeled Nucleosides and Thiophene-Based Oligomers. Ph.D. Dissertation, University of Nebraska, Lincoln, NE, 2007.

(23) Osuna, R.M.; Ortiz, R.P.; Hernández, V.; Navarrete, J.T.L.; Miyasaka, M.; Rajca, S.; Rajca, A.; Glaser, R. *J. Phys. Chem. C* **2007,** *111,* 4854–4860.

(24) Gholami, M.; Tykwinski, R.R. *Chem. Rev.* **2006,** *106,* 4997–5027.

(25) Zhao, Y.; Zhou, N.; Slepkov, A.D.; Ciulei, S.C.; McDonald, R.; Hegmann, F.A.; Tykwinski, R.R. *Helv. Chim. Acta* **2007**, *90,* 909–927.

(26) Marsella, M.J.; Reid, R.J. *Macromolecules* **1999,** *32,* 5982–5984; Cambridge Crystallographic Data Base (CCDC no. 606349).

(27) Rashidi-Ranjbar, P.; Man, Y.-M.; Sandstrom, J.; Wong, H.N.C. *J. Org. Chem.* **1989,** *54,* 4888–4892.

(28) SHELXL-97: Bruker Analytical X-Ray Systems, Madison, WI.

(29) Flack, H.D. *Acta Cryst. A* **1983,** *39,* 876–881.

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Chiral tetrathienylene: synthesis and X-ray structure

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Supporting Information

(1) ^{1}H NMR analyses of crude reaction mixtures (Table S1)
(2) NMR and IR spectra for **1** and **3**.

Table S1. ^{1}H NMR integrations for the TMS-group region for three representative crude reaction mixtures.

					Integration (entire 0.25–0.55 ppm region was set to 100)		
Run No.	Label	**2** (g)	LDA (eq)	$CuBr_2$ (eq)	**1** (δ 0.42)	**3** (δ 0.43)[a]	**4** (δ 0.39)
1	hw-1-50	0.030	3	10	17.5	22.4	3.5
2	hw-1-62	0.297	3	10	12.4	13.4	5.0
3	hw-2-46	1.000	3	10	10.3	11.1	11.4
4	hw-2-80	0.500	3	10	16.9	14.8	6.2

[a] Two singlets at δ 0.33 and 0.43 ppm with ~1 : 1 integration were observed for tetrathiophene **3**.

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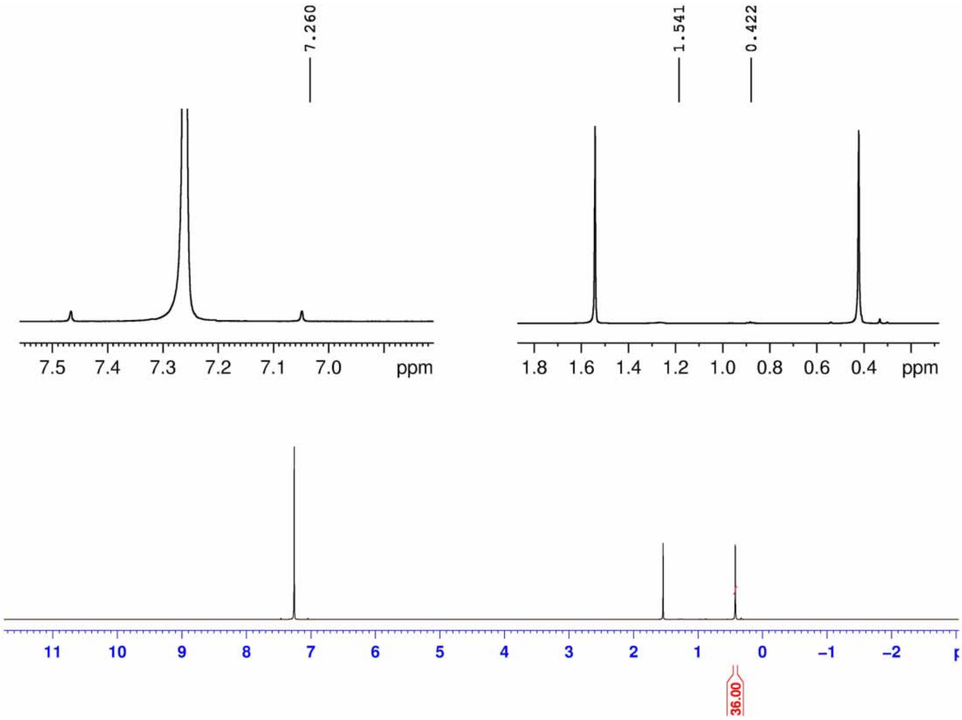
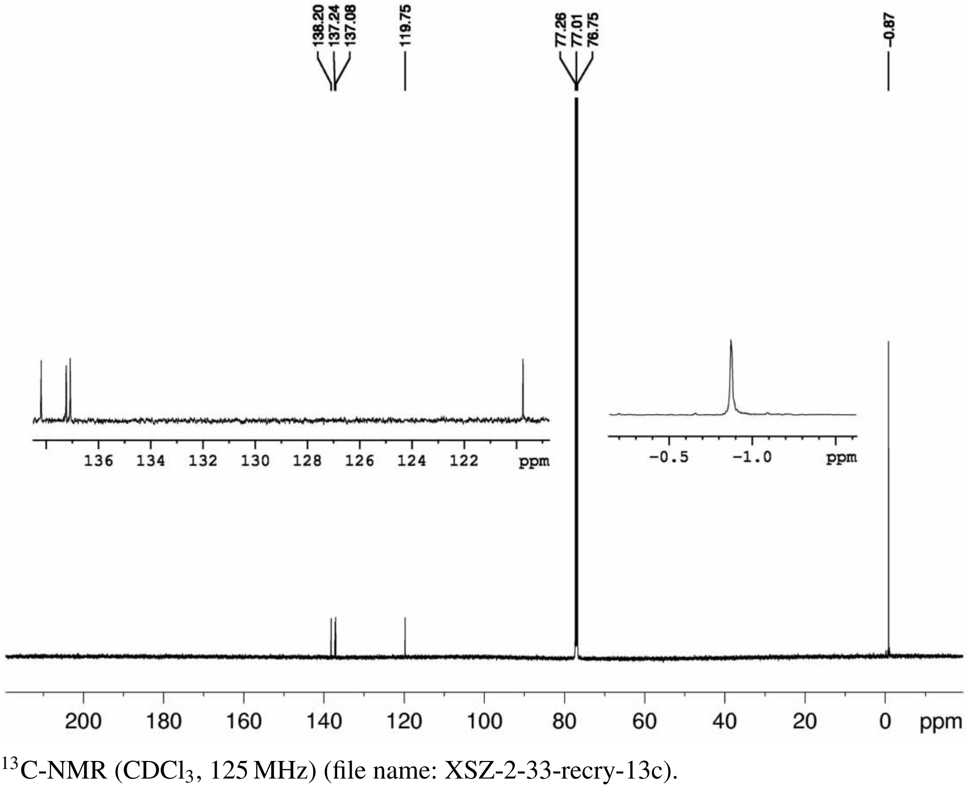
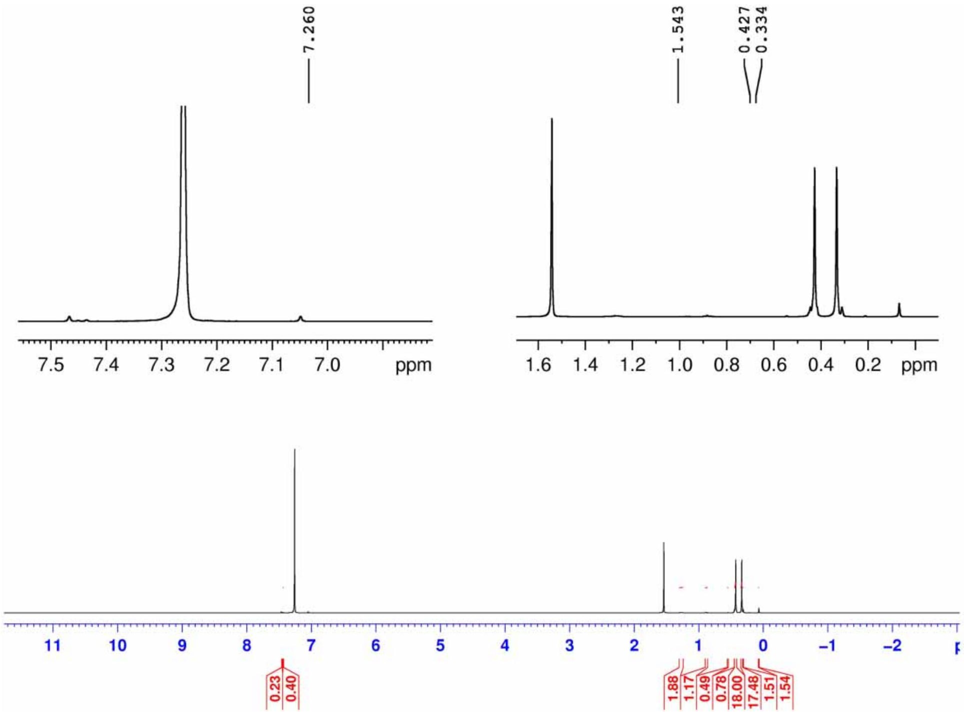


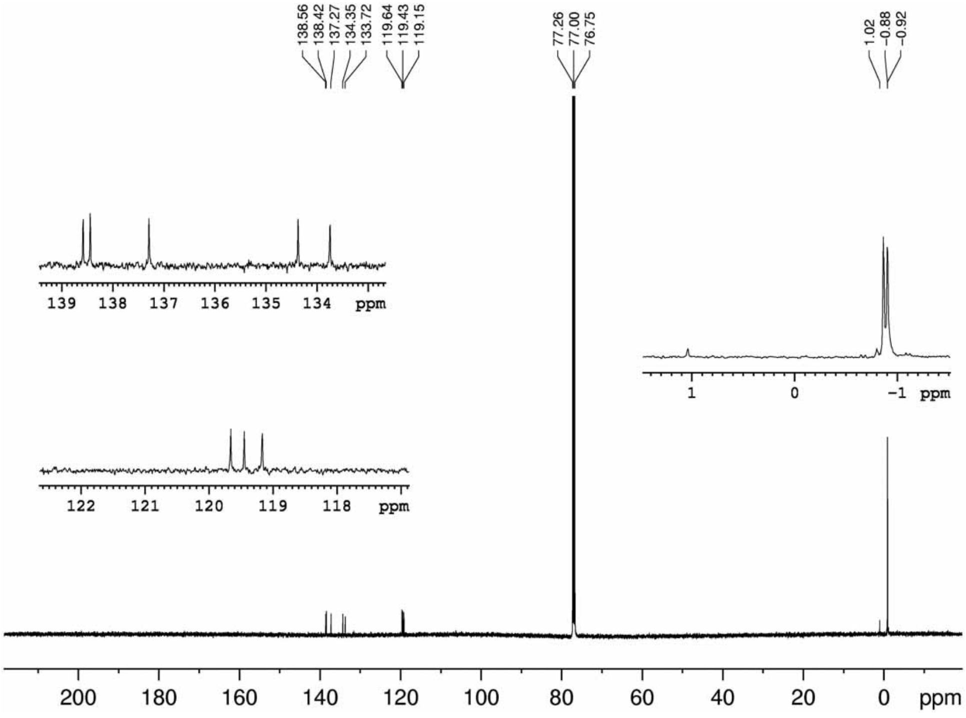
1,^{1}H-NMR($CDCl_3$, 500 MHz) (file name; hw2-46.sep 1-2-cryst).



1, ^{13}C-NMR ($CDCl_3$, 125 MHz) (file name: XSZ-2-33-recry-13c).



3, ^{1}H-NMR (CDCl$_3$, 500 MHz) (file name: hw-1-71.sep3-recryst).



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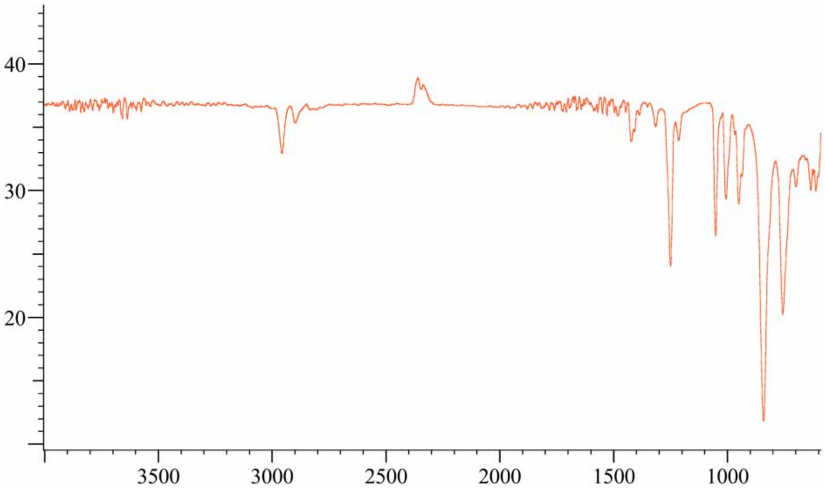
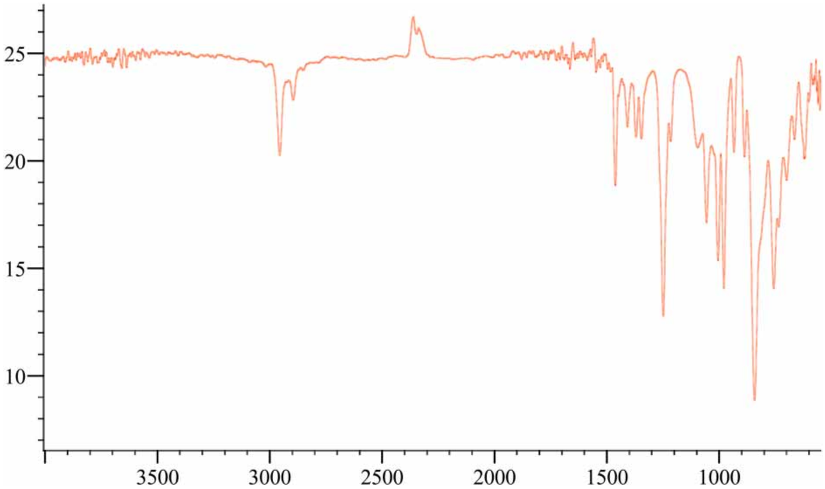


1, IR (file name: hw-1-62.sep1-2-smooth.spa).



3, IR (file name: hw-1-62.sep2-c-smooth.spa).