Tetrahedron Letters 51 (2010) 2956–2958

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Tetrathiophenes with thiophene side chains: effect of substitution on packing and conjugation

Geeta Saini[a], Nigel T. Lucas[b], Josemon Jacob[a,*]

[a] Centre for Polymer Science and Engineering, Indian Institute of Technology, Hauz-Khas, New Delhi 110 016, India
[b] Department of Chemistry, University of Otago, Dunedin 9054, New Zealand

ARTICLE INFO

Article history:
Received 24 February 2010
Revised 19 March 2010
Accepted 20 March 2010
Available online 25 March 2010

ABSTRACT

The effect of substitution pattern on conjugation and packing has been investigated by synthesizing a series of tetrathiophenes with systematically varied alkyl thiophene substituents.

Thiophene based oligomers and polymers are of intense academic and industrial interest since they constitute the active materials in organic field-effect transistors and organic photovoltaics.[1] The type and nature of the substituents used to induce solubility and regioregularity in oligo and polythiophenes greatly influence the morphology and band gap in these materials. Several groups have reported the synthesis of well-defined oligomers of thiophenes, especially head-to-tail coupled ones, to understand the influence of substitution pattern on conjugation and packing.[2] Among the various thiophene based materials reported in the literature, regioregular poly(3-alkylthiophene)s have shown the best promise both in terms of conjugation and device performance.[3] In our efforts to identify new classes of thiophene based materials with improved π-conjugation and charge transport, we report here the synthesis and characterization of a series of structurally defined thiophene based tetramers as model compounds for polymers with thiophene based alkyl solubilizing groups. Three tetramers of thiophene bearing alkylthienyl side chains have been synthesized and two of them characterized by X-ray crystallography. The nature of the linkages is found to have a profound impact on solid state molecular conformation, packing and on the observed band gap.

The structures of the tetramers reported in this study are shown in Chart 1. These were synthesized either by Pd catalyzed cross-coupling reaction or by oxidative coupling using a hypervalent iodine(III) reagent.[4] The synthetic approach to the tetramers is shown in Scheme 1. Precursor **3** was synthesized through the Grignard coupling of 3-bromothiophene with 5-methyl-2-thienylmagnesium bromide in the presence of Ni(dppp)Cl_2.[5] Analogous to the regiospecific bromination of 3-alkylthiophenes, **3** was brominated selectively at the 2- position using NBS to give the bromo derivative **4** in 90% isolated yield. Suzuki coupling of **4** with 5-methyl-2-thiopheneboronic acid in a mixture of DME and aqueous sodium carbonate solution containing 2 mol % catalyst gave **5** in 64% yield. Compound **5** was converted to the corresponding bromo and boronate ester in 80% and 68% yields, respectively.

Standard Suzuki coupling of **6** and **7** gave tetramer **1a** in 60% yield. Compound **1a** has been synthesized earlier with a different alkyl group by a different method.[6] To synthesize **1b** and **1c**, **3** was converted to a boronate ester which was then Suzuki coupled with 2-bromo-5-methylthiophene to afford **8** in 50% yield. Oxidative dimerization of **8** using a combination of phenyliodide bis(trifluoroacetate) (PIFA) and $BF_3 \cdot OEt_2$ gave **1c** in 40% yield. The synthesis of **1c** was patented earlier[7] but no characterization data was given. Compound **8** was brominated by NBS to give the bromo derivative **9** in 78% yield, and subsequent Suzuki coupling of **9** with **7** gave the lower symmetry isomer **1b** in 58% yield. The three tetramers were further purified by recrystallization from THF and methanol. All the compounds described above show very good sol-

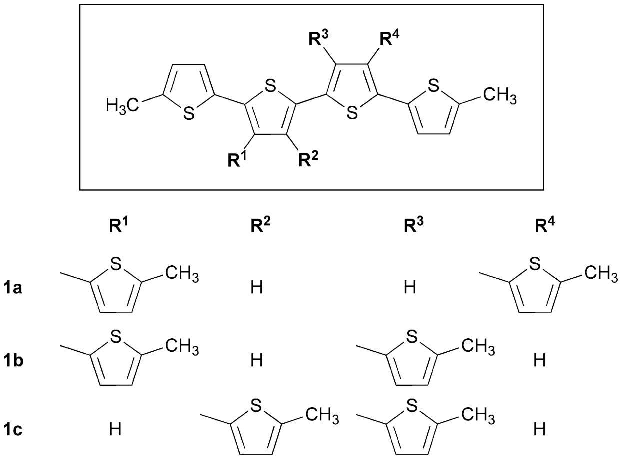
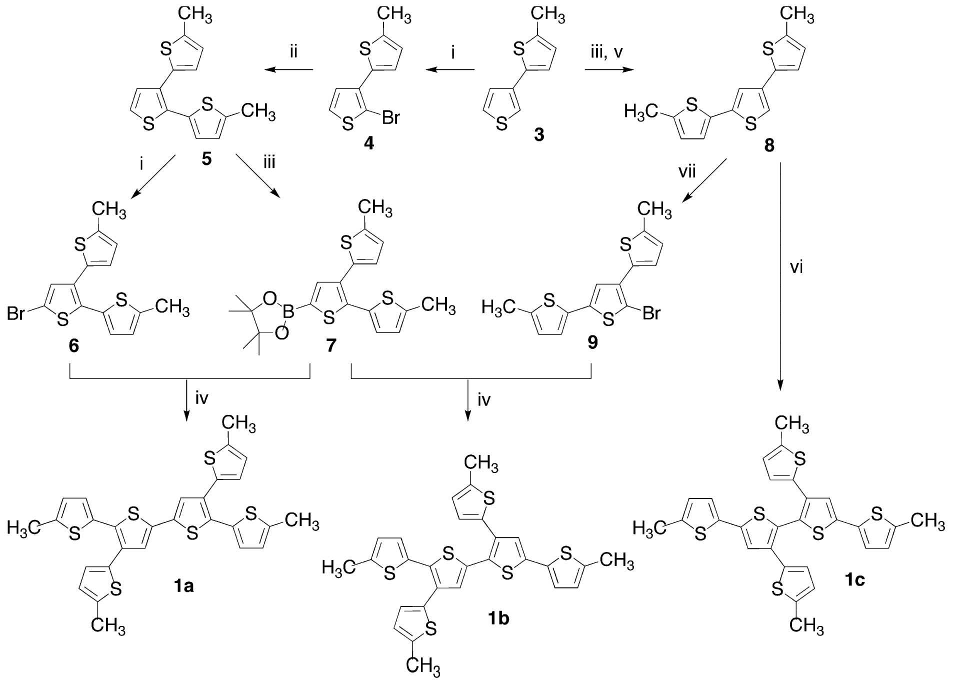


Chart 1. Structures of differently substituted tetramers.

---

* Corresponding author. Tel.: +91 9911061890; fax: +91 11 2659 1421.
E-mail address: jacob@polymers.iitd.ac.in (J. Jacob).

0040-4039/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2010.03.087



Scheme 1. Synthesis of tetramers. Reagents and conditions: (i) NBS, $CHCl_3$; (ii) 5-methyl-2-thiopheneboronic acid, $Pd(PPh_3)_4$, DME/2 M Na_2CO_3; (iii) *n*-BuLi, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; (iv) $Pd(PPh_3)_4$, DME/2 M Na_2CO_3; (v) 2-bromo-5-methylthiophene, $Pd(PPh_3)_4$, DME/2 M Na_2CO_3; (vi) PIFA, $BF_3{\cdot}OEt_2$, DCM; (vii) NBS, CCl_4.

ubility in common organic solvents. The oligomers and intermediates were characterized by ^1H and ^{13}C NMR, elemental analysis, mass spectrometry, UV–vis absorption and emission spectroscopies, and in two cases, by X-ray crystallography. The absorption and emission spectra of all oligomers were measured in THF solution and are shown in Figure 1. The long-wavelength absorption for **1c** has its maximum intensity at 356 nm while for **1a** and **1b**, the absorption spectra shift to longer wavelengths and show absorption maxima at 389 and 387 nm, respectively. This suggests a more severe disruption of conjugation in **1c** compared to **1a** and **1b** which is further evident from the X-ray data discussed below. The observed absorption maxima are comparable to analogous alkyl substituted tetrathiophenes reported previously.[8] Compounds **1a, 1b** and **1c** have emission maxima at 477, 501 and 525 nm, corresponding to a Stokes shift of 89, 112 and 169 nm, respectively. The observed large Stokes shift for **1c** in comparison to **1a** and **1b** can be attributed to its more twisted structure in solution with a corresponding large change in conformation between ground and excited state.[9]

The above data suggests that the substitution pattern in compounds **1a** and **1b** can potentially give materials with the best conjugation along the polymeric chain. The symmetric tetrathiophenes **1a** and **1c** were obtained as single plate crystals suitable for X-ray diffraction studies, and showed vastly different solid state conformations (see Supplementary data). In the case of the 3′,4″-di(5-methylthienyl)-substituted tetramer **1a** (Fig. 2), the α-tetrathiophene backbone shows only small deviations from planarity; the centre two thiophene rings (B, C) are perfectly co-planar (the molecule sits on an inversion centre at the midpoint of C1–C1*), and the terminal rings (A, D) twist out of this plane by 26.8°. The side group rings B′, C′ twist by 37.5° from the central plane and are involved in S···H–C interactions with neighboring molecules throughout the 3D crystal network (see Supplementary data).

Significant π–π interactions do not appear in this structure. The isomeric, head-to-head coupled 4′,3″-di(5-methylthienyl)tetrathiophene **1c** is revealed to assume a strongly twisted conformation

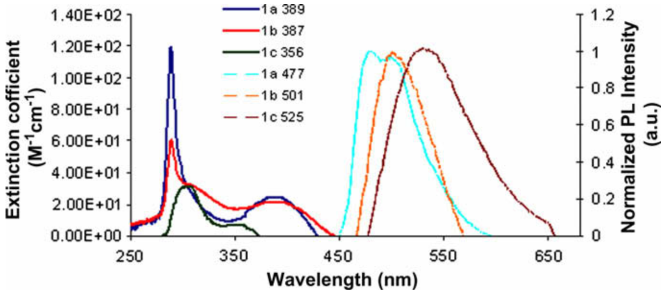


Figure 1. UV–vis absorption and emission spectra of **1a–c** in THF solution.

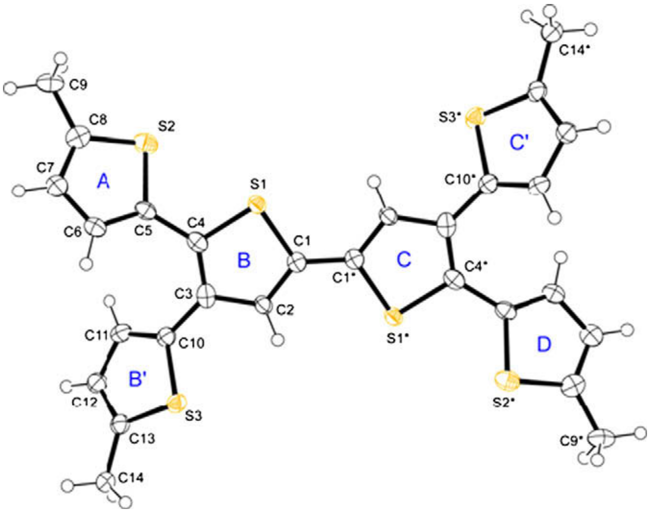


Figure 2. ORTEP representation of **1a** showing numbering scheme; displacement ellipsoids are depicted at 50% probability.

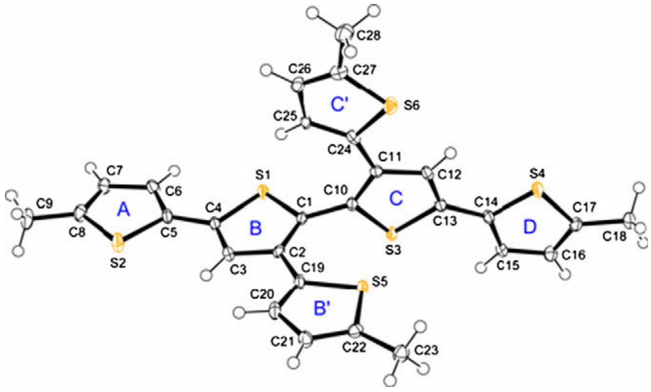


Figure 3. ORTEP representation of **1c** showing numbering scheme; displacement ellipsoids are depicted at 50% probability.

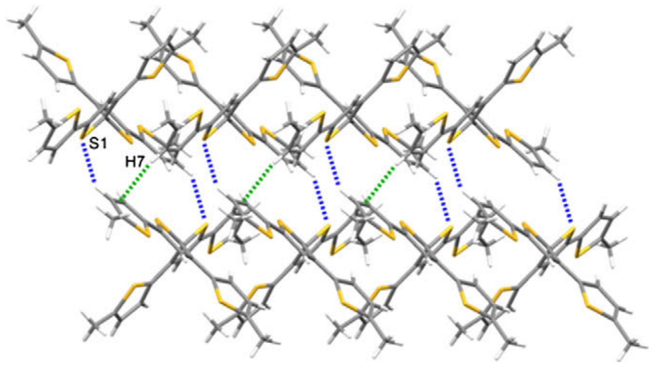


Figure 4. Packing diagram of **1c** showing two face-to-face stacked columns and some intercolumn interactions (S···H–C blue, π···H–C green).

in the solid state (Fig. 3). Steric hinderance involving the pendant thiophene rings B′ and C′ produces a dihedral angle of 85.2° between the centre rings B and C, while all other thiophene rings are close to co-planar with their neighbors (7.5–16.3°). As a result of the quasi-orthogonal disposition of the two halves of the molecule, the effective conjugation pathway is greatly reduced. The related compound 3,3′-di(2-thienyl)bithiophene (rings B, C, B′, C′ of **1c**) displays a similar twisted solid state conformation,[10] also seen in other 2,3-di(thienyl)thiophene structures.[11] Despite the non-planar backbone of **1c**, face-to-face π–π intermolecular interactions between the two planar regions are observed throughout the crystal structure. Pairs of inversion related molecules are stacked along the *a*-axis with translation by one unit cell (Fig. 4). Within the columns, π–π interactions (Ring A···B′(C19) 3.65 Å, Ring C′···D(S4) 3.55 Å), S···H (S1···H15 2.89 Å, S5···H15 2.91 Å) and S1···S3 interactions (3.57 Å) all appear to drive the packing. Between the double columns, pairs of S1···H15 (2.90 Å) and π (C15/16)···H7 contacts are observed (Fig. 4). Beyond the double columns, the only short intermolecular contacts that contribute to the 3D crystal structure involve methyl hydrogens of C18 and the C–H bonds of neighboring columns.

In conclusion, we have developed synthetic routes to tetrathiophenes bearing thienylalkyl side groups with different substitution patterns. It is found that a head–head coupled structure as in **1c** is not favorable for conjugation due to steric effects as evidenced from crystallography and UV–vis spectroscopy, whereas the other two substitution patterns do not appear to break the conjugation pathway. This must be taken into consideration while designing higher oligomers or polymers in the same series for potential electronic applications.

Acknowledgments

The present work was supported by Department of Science and Technology, New Delhi, India. G.S. acknowledges a research fellowship from Council for Scientific and Industrial Research (CSIR), New Delhi, India.

Supplementary data

Synthesis and characterization data for **1a**–**c**, **4**–**9**, NMR spectra, additional crystallographic diagrams and data in CIF format are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.03.087.

References and notes

1. (a) Chisaka, J.; Lu, M.; Nagamatsu, S.; Chikamatsu, M.; Yoshida, Y.; Goto, M.; Azumi, R.; Yamashita, M.; Yase, K. *Chem. Mater.* **2007**, *19*, 2694–2701; (b) Marcus, H.; Hagen, K.; Ute, Z.; Gunter, S.; Wolfgang, R.; Sergei, P.; Stephan, K.; Werner, W. *J. Appl. Phys.* **2003**, *93*, 2977–2981; (c) Sakai, J.; Taima, T.; Saito, K. *Org. Electron.* **2008**, *9*, 582–590; (d) Katz, H. E.; Torsi, L.; Dodabalapur, A. *Chem. Mater.* **1995**, *7*, 2235–2237; (e) Deman, A. L.; Tardy, J.; Nicolas, Y.; Blanchard, P.; Roncali, J. *Synth. Met.* **2004**, *146*, 365–371.
2. (a) Kirschbaum, T.; Azumi, R.; Mena-Osteritz, E.; Bauerle, P. *New J. Chem.* **1999**, *23*, 241–250; (b) Bidan, G.; De Nicola, A.; Enee, V.; Guillerez, S. *Chem. Mater.* **1998**, *10*, 1052–1058; (c) Barbarella, G.; Bongini, A.; Zambianchi, M. *Macromolecules* **1994**, *27*, 3039–3045; (d) Bäuerle, P.; Fischer, T.; Bidlingmeier, B.; Stabel, A.; Rabe, J. P. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 303–307.
3. (a) McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93–112; (b) Osaka, I.; McCullough, R. D. *Acc. Chem. Res.* **2008**, *41*, 1202–1214.
4. (a) Tohma, H.; Iwata, M.; Maegawa, T.; Kiyono, Y.; Maruyama, A.; Kita, Y. *Org. Biomol. Chem.* **2003**, *1*, 1647–1649; (b) Mohanakrishnan, A. K.; Amaladass, P.; Arul Clement, J. *Tetrahedron Lett.* **2007**, *48*, 779–784.
5. Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M.; Minato, A.; Suzuki, K. *Tetrahedron* **1982**, *38*, 3347–3354.
6. Xia, C. J.; Fan, X. W.; Locklin, J.; Advincula, R. C. *Org. Lett.* **2002**, *4*, 2067–2070.
7. Hwang, I. H.; Jeong, L. M. (LG Chem, Ltd, S. Korea), PCT Int. Appl. 2007, 40.
8. (a) Tour, J. M.; Wu, R. L. *Macromolecules* **1992**, *25*, 1901–1907; (b) Takahashi, M.; Masui, K.; Sekiguchi, H.; Kobayashi, N.; Mori, A.; Funahashi, M.; Tamaoki, N. *J. Am. Chem. Soc.* **2006**, *128*, 10930–10933.
9. Miguel, L. S.; Matzger, A. J. *Macromolecules* **2007**, *40*, 9233–9237.
10. Karpe, S.; Cravino, A.; Frere, P.; Allain, M.; Mabon, G.; Roncali, J. *Adv. Funct. Mater.* **2007**, *17*, 1163–1171.
11. (a) Ma, C. Q.; Mena-Osteritz, E.; Debaerdemaeker, T.; Wienk, M. M.; Janssen, R. A. J.; Bäuerle, P. *Angew. Chem., Int. Ed.* **2007**, *46*, 1679–1683; (b) Li, X. C.; Tian, H. *Tetrahedron Lett.* **2005**, *46*, 5409–5412.