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Syntheses and Properties of Unsymmetrically Substituted Bi- and Quaterthiophenes

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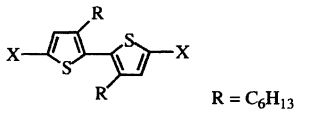
The unsymmetrically substituted bi- and quaterthiophene derivatives were synthesized. The unsymmetrically substituted bithiophenes carrying the electron-withdrawing substituent X on one of the outer thiophene rings exhibited the maxima of absorption bands at the longer wavelengths than the symmetrically disubstituted bithiophene derivatives, while the unsymmetrical quaterthiophenes had such maxima at the shorter wavelengths than the corresponding symmetrical ones. The trend of bathochromic shift of the longest wavelength absorption bands due to the electron-withdrawing substituent X was more pronounced in case of bi- or quaterthiophenes bearing push–pull substituents. The unsymmetrical quaterthiophenes exhibited the greater third-order nonlinear optical (TNLO) properties than the corresponding bithiophenes, similarly to the case between the symmetrical bi- and quaterthiophenes. However, the TNLO properties of the unsymmetrical bi- and quaterthiophenes showed no dependence on the electron-withdrawing strength of the substituent X, unlike those of the symmetrical ones.

In recent years, a wide variety of the thiophene-based derivatives have received considerable attention as good candidates for opto-electronic devices on the basis of their nonlinear optical (NLO) properties.[1] As one of the structure requirements for enhancement of the NLO properties such as second- and third-order hyperpolarizabilities, $\langle\beta\rangle$ and $\langle\gamma\rangle$ it is proposed that the polarized structural contribution at the ground state is effective for generation of the large photo-induced polarization.[2] Thus we previously reported the synthesis of dihexylbithiophenes (**1**—**5**) and tetrahexylquaterthiophenes (**7**—**11**) with head-to-head (HH) orientation (Chart 1), which carry the electron-withdrawing substituent X on both outer thiophene rings, and showed the features of their electronic absorption spectra.[3] From these results, it was proved that the inner bithiophene unit (IBU) with tail-to-tail (TT) orientation in the quaterthiophene system plays an important role as the electron-donor component to achieve the highly-polarized structure properties of the molecules.

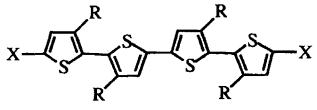
In continuation of our investigations on the molecular design for enhancement of the polarizable structural properties, two types of the unsymmetrical thiophene derivatives were prepared. One is the dihexylbi- (**13**—**17**) and tetrahexylquaterthiophenes (**18**—**22**) bearing the electron-withdrawing substituent X on one of the outer thiophene rings, another is the push–pull dihexylbi- (**23**—**32** and **38**—**47**) and quaterthiophenes (**33**—**36**) with the methoxy or methylthio group as the electron-donating substituent (Chart 2). In this paper, the syntheses and electronic absorption spectral behaviors of the title compounds will be described, in comparison with those of the symmetrical ones and also briefly with their third-order NLO (TNLO) properties.

Results and Discussion

Synthesis of the Monosubstituted 3,3′-Dihexyl-2,2′-bithiophenes (13—17) and 3,3′,3‴,4″-Tetrahexyl-2,2′ : 5′, 2″ : 5″,2‴-quaterthiophenes (18—22). Although various types of the unsymmetrical thiophene-based oligomers have been successfully synthesized by the cross-coupling reaction of the respective components,[4] the initial attempt for preparation of the bromobithiophene **13** from 2-bromo-3-hexylthiophene (**48**) and 2,5-dibromo-3-hexylthiophene (**49**) resulted in a very low yield and in a poor reproducibility. Therefore, series of the monosubstituted dihexylbi- and tetrahexylquaterthiophenes were prepared utilizing the substitution reactions of the corresponding bithiophene **1** and quaterthiophene **7**, according to the similar way for the sym-

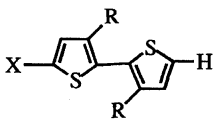


R = C_6H_{13}

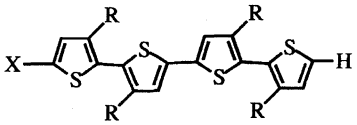


1	X = H	**7**	X = H
2	= Br	**8**	= Br
3	= CN	**9**	= CN
4	= CO_2H	**10**	= CO_2H
5	= CHO	**11**	= CHO
6	= NO_2	**12**	= NO_2

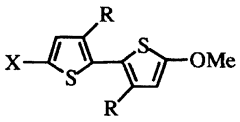
Chart 1.



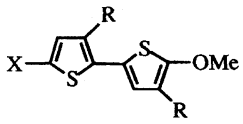
13 X = Br
14 = CN
15 = CO_2H
16 = CHO
17 = NO_2



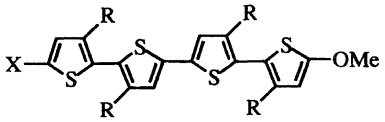
18 X = Br
19 = CN
20 = CO_2H
21 = CHO
22 = NO_2



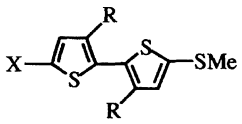
23 X = H
24 = Br
25 = CN
26 = CHO
27 = NO_2



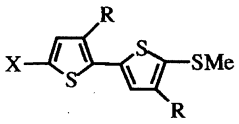
28 X = H
29 = Br
30 = CN
31 = CHO
32 = NO_2



33 X = H
34 = Br
35 = CN
36 = CHO
37 = NO_2



38 X = H
39 = Br
40 = CN
41 = CHO
42 = NO_2



43 X = H
44 = Br
45 = CN
46 = CHO
47 = NO_2

Chart 2.

metrically disubstituted oligothiophenes.[3]

Bromination of **1** with NBS[5] gave the bromide **13**, but in a fairly low yield (55%) because of a competitive formation of the dibromide **2**. However, substitution of **13** with Cu(I) cyanide[6] led to the carbonitrile **14** (90%), lithiation of **13** with butyllithium followed by introduction of gaseous CO_2[7] to the carboxylic acid **15** (77%), and lithiation of **13** with butyllithium followed by addition of DMF[8] to the carbaldehyde **16** (42%), respectively, in good yields comparably to those for the corresponding symmetrical ones.

The nitro function was for the first time incorporated into dihexylbithiophene and tetrahexylquaterthiophene. Reaction of **1** with 2 molar amounts of sodium nitrate ($NaNO_3$) in sulfuric acid[9] afforded the dinitro compound **6** in 28% yield along with tht trinitro compound **50** (10%) and some amount of the insoluble materials, but gave little amount of the mononitro bithiophene **17**. The nitration of **1** with 5 molar amounts of nitric acid (HNO_3) in acetic anhydride[10] afforded **6** as the major product (78%) and a small amount of **17**. Therefore, an attempt for the preparation of **17** from **1** was made using 2 molar amounts of HNO_3 in acetic anhydride. However, the result was almost the same as for that using 5 molar amounts of HNO_3, except for recovery of a considerable amount of **1**. On the other hand, it was found that tetrahydrofuran (THF) as a co-solvent with acetic anhydride employed for the nitration strongly affected the distribution of the mono- and dinitro compounds, although the mechanistic role of THF in this reaction is not clear. When the nitration of **1** was carried out with 1.5 molar amounts of HNO_3 in a mixture of acetic anhydride and THF (2 : 1), the mononitro bithiophene **17** was obtained in 58% yield together with a little amount of **6**.

Similarly, the respective reactions of the bithiophene **1** for the monosubstituted bithiophenes were applied to the quaterthiophene **7**[3] to afford the monosubstituted quaterthiophenes in moderate yields as follows: the bromide **18** (62%), the carbonitrile **19** (79%), the carboxylic acid **20** (47%), the carbaldehyde **21** (46%), and the nitro compound **22** (38%), respectively. Preparation of the dinitro quaterthiophene **12** was also attempted under similar conditions to those for **6** from **1**, but the yield of **12** was only 9% yield, resulting in a large amount of insoluble materials.

Synthesis of the Push–Pull Bi- and Quaterthiophenes (23—47). No convenient coupling reactions for 3,4′-dihexyl-2,2′-bithiophene (**51**: HT bithiophene) as one of the

starting materials for the title compounds are known.[11] Previously we reported that the Fe(III)-mediated homo coupling of the 2-lithiated species from the bromide **48** at −80 °C gave the HH bithiophene **1** as a viscous oil predominantly in an excellent yield (Chart 3).[3,12] In this reaction, however, it was suggested that both elevation of the reaction temperature and increase of the reaction scale were accompanied by the formation of the HT bithiophene **51** competitively with the normal product HH bithiophene **1**. This result indicates the cross coupling reaction of the 2-lithiated 3-hexylthiophene (**56**) with the 2-lithiated 4-hexylthiophene (**57**), which was formed via the thermal isomerization of **56**, as shown in Scheme 1.[13] Taking this finding into consideration, when iron(III) acetylacetonate ($Fe(acac)_3$) was added at 0 °C, the reaction afforded a mixture of the HH and HT bithiophenes in an almost 1 : 1 ratio in ca. 90% yield. The ratio of HT bithiophene **51** to HH isomer **1**, however, did not increase to more than 1 : 1 even in the reaction at ambient temperature, clearly indicating an equilibrium constant (K_{eq}) of 3 for **56**/**57**. It is noteworthy that in this coupling reaction little amount of 4,4′-dihexyl-2,2′-bithiophene **53** (TT bithiophene) was formed. Although the HT bithiophene **51** possessed almost the same properties as those for the HH isomer **1** at all points such as R_f value and boiling point, these isomeric bithiophenes **1** and **51** could be easily separated by means of column chromatography after employing the selective bromination of the HT bithiophene **51** to **52**, with the HH bithiophene **1** unreacted.[13] 5′-Bromo-3,4′-dihexyl-2,2′-bithiophene (**52**) is less polar than the HH bithiophene **1** and is readily reduced with $LiAlH_4$ to regenerate the HT bithiophene **51** quantitatively. Then, the bromides **13**, **52**, and **18** were first converted to the electron-donating derivatives carrying the methoxy or methylthio group.

The reaction of **13**, **52**, and **18** with sodium methoxide in refluxing methanol in the presence of catalytic amounts of CuO and NaI[14] afforded the methoxy-substituted bi- or quaterthiophenes **23**, **28**, or **33** in 62, 39, and 10% yields, respectively. 5,5′-Dimethoxybithiophene (**54**) and 5,5‴-dimethoxyquaterthiophene (**55**) could also be obtained in 56 and 23% yields, respectively, by the same way from the corresponding dibromides **2** and **8**. The procedures similar to those for incorporation of the electron-withdrawing substituent X described for preparation of the monosubstituted thiophenes were then applied to the methoxy-HH bithiophene **23** to give the bromide **24** (49% from **23**), the carbonitrile **25** (50% from **24**), the carbaldehyde **26** (61% from **24**), and the

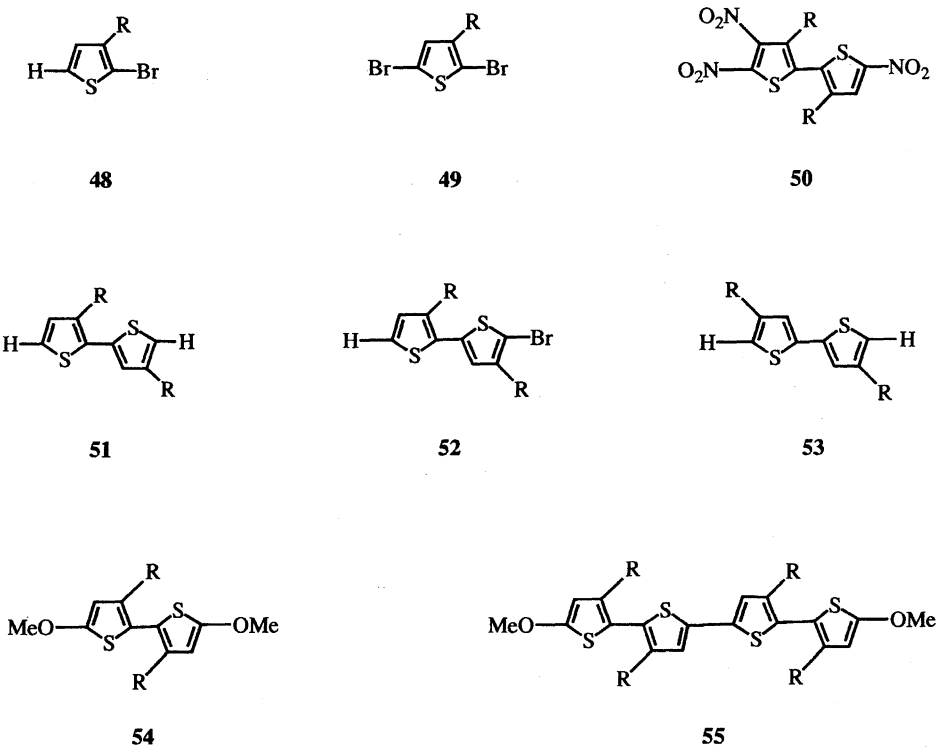
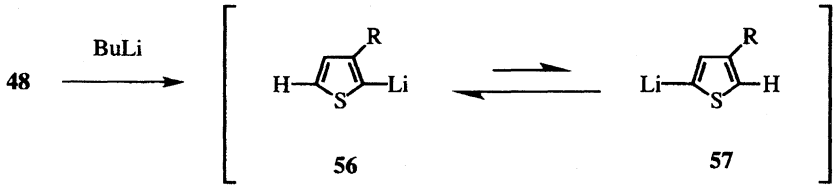


Chart 3.



Scheme 1.

nitro derivative **27** (66% from **23**), respectively. Similarly, the methoxy-HT bithiophene **28** gave the bromide **29** (95% from **28**), the carbonitrile **30** (70% from **29**), the carbaldehyde **31** (55% from **29**), and the nitro compound **32** (63% from **28**), respectively. In the case of the methoxyquaterthiophene derivatives, the bromide **34** was obtained in 15% yield by replacing one of two bromo substituents in **8** with the methoxy group, since bromination of **33** with NBS gave a mixture of polybrominated products together with **34** and its isomers, all of which were difficult to separate by column chromatography. Then, from the bromide **34**, the carbonitrile **35** (34%) and the carbaldehyde **36** (21%) were also obtained. However, the nitration of **33** with HNO_3 in a mixture of acetic anhydride and THF for the methoxy-nitro-quaterthiophene **37** was not successful, only affording the insoluble materials.

Bromo-HH bithiophene **13** was treated with methyllithium in THF, followed by addition of S_8,[15] to afford the methylthio-HH bithiophene **38** in 57% yield. On the other hand, the bromo-HT bithiophene **52** gave the methylthio-HT bithiophene **43** only in 30% yield under the same conditions, probably due to the steric hindrance between the hexyl substituent and the S_8 reagent. Alternatively, the treatment of **52** with butyllithium, followed by addition of dimethyl disulfide (MeSSMe),[16] afforded **43** in ca. 60% yield. Incorporation of the electron-withdrawing substituent X to the methylthio-HH bithiophene **38** as stated above lead to the bromide **39** (68% from **38**), the carbonitrile **40** (80% from **39**), the carbaldehyde **41** (59% from 39), and the nitro derivative **42** (72% from **38**), respectively. Similarly, the methylthio-HT bithiophene **43** gave the bromide **44** (78% from **52**), the carbonitrile **45** (80% from **44**), the carbaldehyde **46** (48% from **44**), and the nitro compound **47** (44% from **43**), respectively.

Electronic Absorption Spectra: (a) the Unsymmetrically Substituted Dihexylbithiophenes (13—17) and Tetrahexylquaterthiophenes (18—22). Electronic absorption spectra of the unsymmetrical bi- and quaterthiophenes were measured in THF. The maxima (λ/nm) and molar extinction coefficients (ε) due to the longest wavelength absorption bands for each series of bi- **13—17** and quaterthiophenes **18—22** as well as those for the symmetrical ones **1—12** are summarized as shown in Table 1.

The molar extinction coefficients of the unsymmetrically substituted bithiophenes are much smaller than those of the symmetrical ones, while the molar extinction coefficients of the unsymmetrically substituted quaterthiophenes are almost comparable to those of the symmetrical ones. In the case of Br substituent, both symmetrical and unsymmetrical bithiophenes **2** and **13** exhibited the very similar maxima to the non-substituted bithiophene **1**. This is also the same case for the bromoquaterthiophenes **8** and **18**, which are similar to the non-substituted compound **7**. Furthermore, the maxima of the unsymmetrically substituted bi- and quaterthiophenes shifted to the longer wavelengths with increase of the electron-withdrawing property of the substituent X on the outer thiophene ring, similarly to those of the symmetrically disubstituted ones,[3] as has been observed for the benzene derivatives of the push-pull type such as para-substituted anisoles and anilines.[17] These results indicate that the unsymmetrical oligothiophenes **13—22** also possess the polarized structure properties at the ground state.

Although the maxima of the quaterthiophenes exhibit the bathochromic shifts by 40—100 nm from those of the corresponding bithiophenes, reflecting the higher molecular planarity of IBU assignable to the longest wavelength band,[3] the differences of the maxima values between bithiophenes and quaterthiophenes decrease with increase of the electron-withdrawing properties of the substituent X in the order of $Br > CN > CO_2H > CHO > NO_2$. Moreover, it is curious to realize that the maxima of the bithiophenes in the unsymmetrical system (**13—17**) always appear at the longer wavelengths than those in the symmetrical system (**1—6**), but this phenomenon for the maxima is entirely reverse between the symmetrical and unsymmetrical quaterthiophene systems. It is suggested that the magnitude of the polarized structure contribution induced by the substituent X for the bithiophenes is greater in the unsymmetrical system, while that for the quaterthiophenes is greater in the symmetrical system.

(b) the Push–Pull Bi- and Quaterthiophenes (23—47). Electronic absorption spectra of the push–pull bi- and quaterthiophenes were measured in THF. Figure 1 shows the absorption spectrum of the cyano-methoxy-bithiophene **25** with HH orientation together with the spectra of the symmetrical dicyano- **3** and dimethoxybithiophene **54**.

The unsymmetrical bithiophene **25** exhibited the peculiar spectra with two broad bands, similarly to the other push–pull bithiophene derivatives, indicating that the electronic structure of **25** is apparently different from those of the symmetrical bithiophene derivatives **3** and **54**. The band at the longer wavelength was assigned as an intramolecular charge transfer (CT) transition, from the fact that the more polar solvent induces the larger bathochromic shift of this band (see below).

The maxima (λ/nm) of CT bands for **23—47** except for the methoxy-nitro-quaterthiophene **37** are summarized as shown in Table 2. Reflecting the push–pull structural properties,

Table 1. Longest Wavelength Absorption Maxima (λ/nm) and Molar Extinction Coefficients of the Symmetrical and Unsymmetrical Bi- and Quaterthiophene Derivatives in THF

X = H		X = Br		X = CN		X = CO_2H		X = CHO		X = NO_2	
1 244	(12200)	**2** 244	(12500)	**3** 288	(14500)	**4** 297	(15500)	**5** 317	(16600)	**6** 347	(12600)
		13 243	(12200)	**14** 294	(9000)	**15** 297	(9650)	**16** 319	(9600)	**17** 357	(8380)
7 337	(17600)	**8** 343	(23300)	**9** 350	(27200)	**10** 351	(28400)	**11** 373	(26200)	**12** 403	(18900)
		18 341	(25000)	**19** 350	(24800)	**20** 348	(23400)	**21** 357	(23300)	**22** 392	(19500)

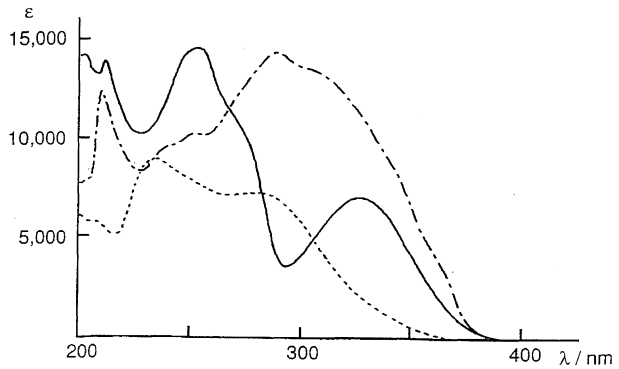


Fig. 1. Electronic absorption spectra of the HH dicyano- (**3**: –•–), cyano-methoxy- (**25**: ——), and dimethoxybithiophene (**54**: - - -) derivatives in THF.

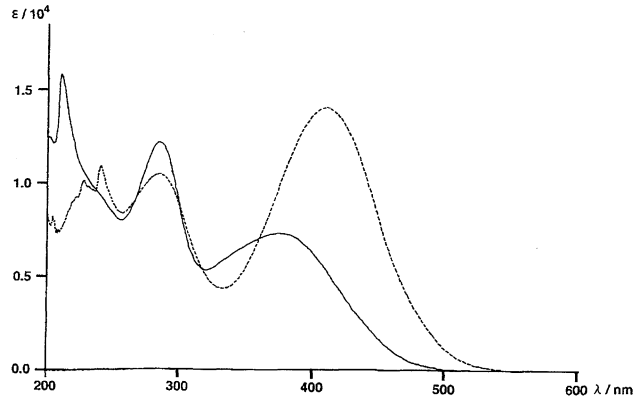


Fig. 2. Electronic absorption spectra of the HH (**42**: ——) and HT (**47**: - - -) methylthio-nitro-bithiophene drivatives in THF.

the much larger bathochromic shift was observed for **23**—**47** with increase of the electron-withdrawing property of the substituent X, as compared with that for the unsymmetrical bi- and quaterthiophene derivatives **13**—**22**. Although the methoxybithiophenes with X = H (**23** and **28**) or X = Br (**24** and **29**) exhibit the maxima at the shorter wavelengths by a little than the corresponding methylthiobithiophenes with X=H (**38** and **43**) or X=Br (**39** and **44**), it is noted that the CT bands of the methoxybithiophenes are largely more sensitive to the substituent X than those of the methylthiobithiophenes.

As a result of the steric influence of the hexyl substituent, the difference between HH and HT orientations of the 3-hexylthiophene components affects the electronic properties in both absorption maxima and molar extinction coefficients, as shown in Fig. 2. The HT methylthio-nitro-bithiophene **47** showed the maximum of CT band at the longer wavelength by 33 nm with the intensity twice as much as the HH isomer **42**, similarly to the other isomeric pairs of the push–pull HH and HT bithiophene derivatives (Table 2). These results clearly indicate that the HT bithiophene possesses the higher molecular planarity than the HH isomer with respect to the π-conjugation.[3,18]

Solvent Effect in the Electronic Absorption Spectra of the Unsymmetrical Bi- and Quaterthiophenes. To continue studies on the polarized structure properties, the solvent effect in the electronic absorption spectra of the bi- and quaterthiophene derivatives with the electron-withdrawing substituent X such as CN and NO_2 groups was examined. The longest wavelength absorption maxima of the symmetrical and unsymmetrical bi- and quaterthiophenes were plotted against four types of the solvent parameters: dielectric constant (DC),[19] donor number (DN),[20] $E_T(30)$,[21] and π^* scale,[22] as shown in Fig. 3.

The results of these relationships between absorption maxima and solvent parameters indicate that the shift changes of absorption maxima for the nitro compounds by changing solvents are more remarkable than those for the corresponding cyano ones in both symmetrical and unsymmetrical series. Although the DC shows no particular relationship with the shift changes in all series of bi- and quaterthiophenes, the DN seems to exhibit the V-shape relationship, and the $E_T(30)$ oppositely the Λ-shape. Among them, only the π^* scale which is defined as a measure of polarity and polarizability of solvent,[22] correlates almost proportionally with the shift changes, i.e., the maxima shifted to the longer wavelengths with increase of the π^* values (positive solvatochromism), indicating the polarizable structure property through the intramolecular CT interaction for the compounds of this type.[23] Moreover, it was proved that the π^* scale correlates with the transition energies of CT bands with a linear relationship ($r > 0.95$) rather than with the wavelength absorption maxima, as shown in Fig. 4(a) for the unsymmetrical bithiophenes **14** (X = CN) and **22** (X = NO_2).

The solvatochromism of CT bands for the push–pull bi- and quaterthiophenes was also examined and found to be positive and almost linear with the π^* scale, as shown in Figs. 4(b), 4(c), and 4(d) for methoxybithiophenes ($r > 0.96$), methoxyquaterthiophenes ($r > 0.92$), and methylthiobithiophenes ($r > 0.96$), respectively. The slope of the linear relationship of the solvatochromism for the push–pull bithiophenes increases with increase of the electron-withdrawing ability of the substituent X, which corresponds to the

Table 2. Longest Wavelength Absorption Maxima (λ/nm) and Molar Extinction Coefficients of the Push-Pull Bi- and Quaterthiophenes in THF

X = H			X = Br			X = CN			X = CHO			X = NO_2		
23	277	(5670)	**24**	284	(7500)	**25**	328	(7060)	**26**	350	(7100)	**27**	400	(6020)
28	312	(9270)	**29**	321	(11400)	**30**	355	(13300)	**31**	384	(14200)	**32**	441	(14100)
33	346	(23400)	**34**	350	(25700)	**35**	357	(24100)	**36**	364	(23300)	**37**	—	
38	291	(10100)	**39**	295	(12200)	**40**	294	(9560)	**41**	335	(10900)	**42**	376	(7400)
43	315	(10650)	**44**	323	(14870)	**45**	340	(14780)	**46**	365	(14230)	**47**	409	(14260)

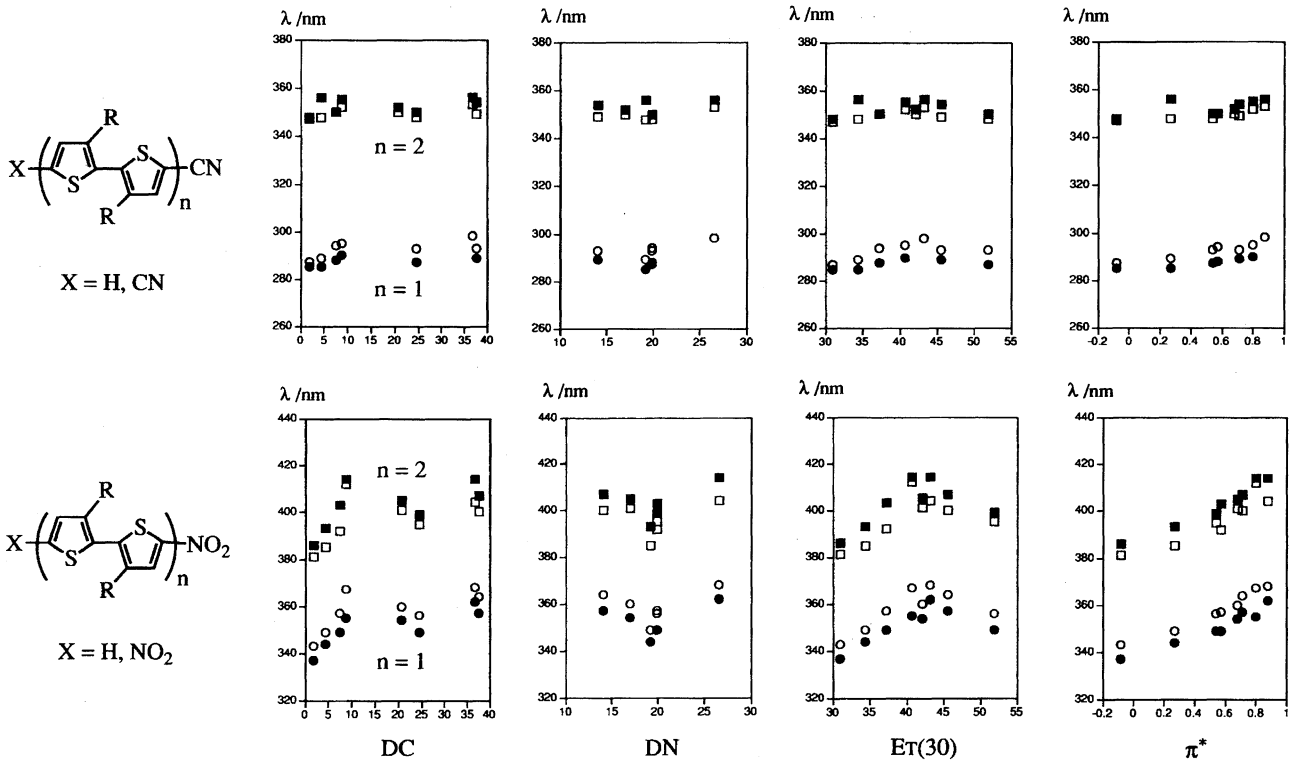


Fig. 3. Correlation of the shift changes of the longest wavelength absorption bands for the cyano and nitro derivatives of bi- ($n = 1$) and quaterthiophenes ($n = 2$) against the solvent parameters; DC, DN, $E_T(30)$, and π^* values (black marks for the disubstituted compounds and white marks for the monosubstituted ones). Solvents used in this study are hexane, diethyl ether, ethanol, THF, acetone, acetonitrile, dichloromethane, and DMF.

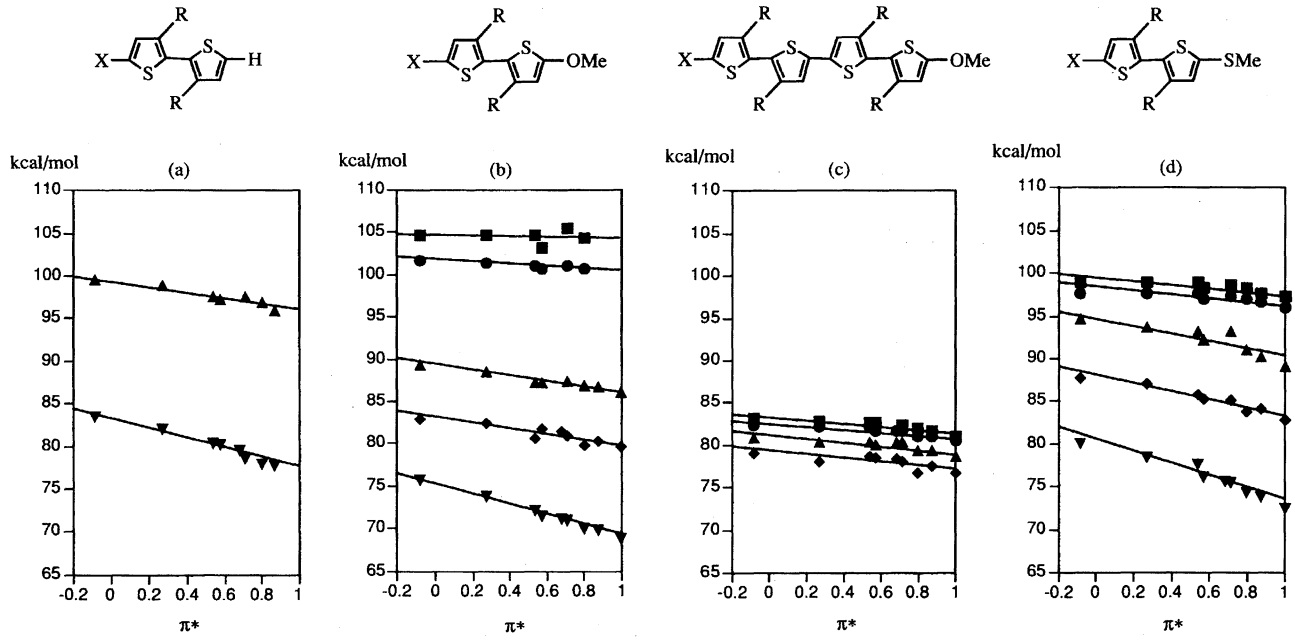


Fig. 4. Linear relationships of the transition energies due to the CT bands for the unsymmetrical derivatives of bi- ($n = 1$) and quaterthiophenes ($n = 2$) with π^* values (■: X = H, ●: X = Br, ▲: X = CN, ◆: X = CHO, and ▼: X = NO_2). (a) for **14** and **22**, (b) for **23**—**27**, (c) for **33**—**37**, and (d) for **38**—**42**. Solvents used in this study are hexane, diethyl ether, ethanol, THF, acetone, acetonitrile, dichloromethane, DMF, and DMSO.

solvatochromic sensitivity S defined in Eq. 1 where E_0 is the transition energy of the CT band observed in cyclohexane ($\pi^* = 0$), as shown in Table 3. Thus, the S values go down to the negative values in the order of substituent: X = H > Br > CN > CHO > NO_2, indicating the largest contribution of the polarizable structural property for the nitro-

Table 3. Solvatochromic Sensitivities of the Push-Pull Bithiophene Derivatives

$$E = E_0 + S \cdot \pi^* \quad (1)$$

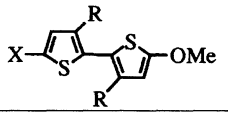
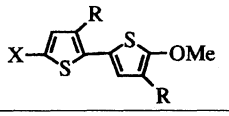
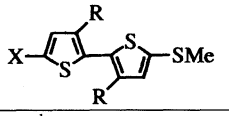
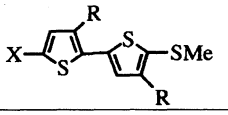
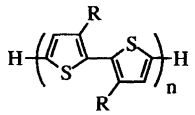
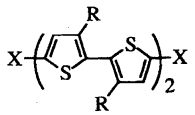
X				
	S/kcal mol^{-1}			
H	−0.2	−0.3	−1.5	−1.1
Br	−1.2	−2.0	−1.3	−1.3
CN	−2.9	−2.5	−4.8	−2.3
CHO	−3.0	−3.1	−4.5	−2.1
NO_2	−6.4	−6.2	−7.1	−5.0

Table 4. Third-Order Hyperpolarizability for the Symmetrical Oligothiophene Derivatives[26]

		$\langle\gamma\rangle/10^{-36}$esu
	n=2	68
	n=4	320
	X=Br (**8**)	190
	X=CN (**9**)	170
	X=CHO (**11**)	300

Sample preparation; thin films of poly(methyl methacrylate) (PMMA) doped with various concentration of thiophene oligomers (0.1—1 mm thick) on a fused silica substrate by spin-coating of $CHCl_3$ polymer solution.
THG measurement; at fundamental wavelength of 1907 nm in a vacuum of several Torr to eliminate the effect of air, with the standard Maker fringe technique by Kajzar et al.[25] by rotating the film sample and analysis using a $\chi^{(3)}$ value for fused silica, 1.4×10^{-14} esu as a reference.

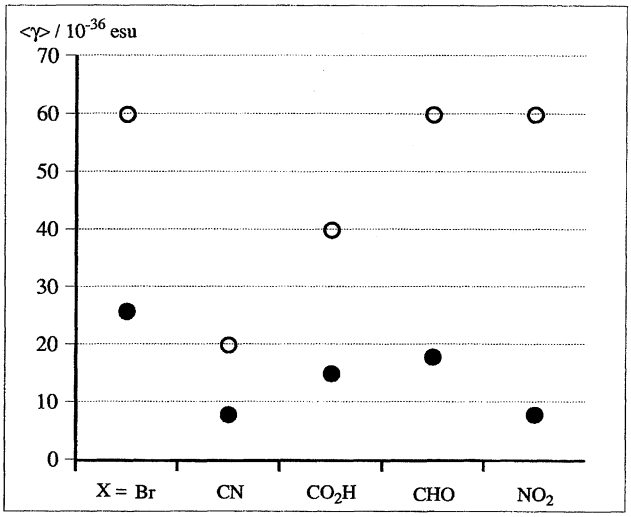


Fig. 5. Third-order hyperpolarizabilities $\langle\gamma\rangle$ for the monosubstituted derivatives of bi- (**13**—**17**; ●) and quaterthiophenes (**18**—**22**; ○).

Table 5. Third-Order Susceptibilities of the Methoxy-nitrobithiophenes

	wt/%	$\chi^{(3)}/10^{-14}$esu
27 (HH)	2.6	1.33
	8.1	1.65
32 (HT)	2.4	1.42
	8.0	2.90

bithiophenes in each series. It is noted that the S values for methoxybithiophenes are very similar between HH and HT isomers,[24] while those for methylthiobithiophenes different between them, resulting in the much smaller S values for the HH isomers.

The CT bands of the push–pull bithiophenes arise from the HH bithiophene chromophore directly perturbed with the substituents X and OMe or SMe, while the CT bands of the push–pull quaterthiophenes from the IBU chromophore[3] perturbed with the two outer thiophene rings bearing the substituent X and OMe or SMe. As a result of these electronic structural properties, the bathochromic shift of CT bands by changing the substituent X for the quaterthiophenes is not so large as that for the bithiophenes. The solvatochromism for the quaterthiophenes, however, is comparably positive to that for the bithiophenes, implying that the larger distance between donor and acceptor sites in the quaterthiophene system compensates the smaller polarized structural property, as compared with the bithiophene system.

TNLO Properties of the Unsymmetrical Bi- and Quaterthiophenes. The TNLO properties of the bi- and quaterthiophene derivatives were examined by means of the standard Maker fringe technique by Kajzar.[25] The third-order hyperpolarizabilities $\langle\gamma\rangle$ of the symmetrical oligothiophene derivatives are shown in Table 4. The TNLO property increases with increase of the HH bithiophene unit and the electron-accepting ability of the substituent X on the outer thiophene ring,[26] in accordance with a tendency of the bathochromic shift in their electronic absorption spectra.[3] On the other hand, the correlation of TNLO properties for the unsymmetrical bi- (**13**—**17**) and quaterthiophenes (**18**—**22**) was far from proportional with the electron-accepting ability of the substituent X, in spite of the high similarity between the electronic spectral properties of the unsymmetrical and symmetrical thiophene derivatives, as shown in Fig. 5. Although the quaterthiophenes possessed the greater TNLO properties than the corresponding bithiophenes, the bromo

derivative exhibited the largest value and the nitro derivative the smallest value among each series of bi- and quaterthiophenes.[27] Table 5 shows the third-order susceptibilities $\chi^{(3)}$ of the methoxy-nitro-bithiophenes **27** and **32**. In both cases, no particular aggregation of the molecule in PMMA film was observed in a range of concentration of the sample below 8% in weight, regardless of their highly polarized structure properties. Although the $\chi^{(3)}$ values of **27** and **32** are much smaller as compared with their second-order NLO (SNLO) $\chi^{(2)}$ values,[28] it is clearly shown that the HT methoxy-nitro-bithiophene **32** with the higher molecular planarity for π-conjugation always exhibits the greater $\chi^{(3)}$ values than the HH isomer **27** with the lower molecular planarity.

Conclusion

The electronic absorption spectra of the unsymmetrical bi- and quaterthiophene derivatives as well as those of the push–pull bi- and quaterthiophenes were examined and the effects of both solvent and orientation of the 3-hexylthiophene moiety on their spectral and TNLO behaviors were studied. With increase of the electron-withdrawing ability of the substituent X on one of the outer thiophene rings, the maxima of the longest wavelength absorption bands exhibited the bathochromic shifts in all series, similarly to those of the corresponding symmetrical ones, and their transition energies were also found to be in an almost linear relationship with the π^* value of solvent. The TNLO properties of the unsymmetrically monosubstituted bi- and quaterthiophene derivatives, however, were different from the symmetrically disubstituted ones, resulting in no particular relationship with the substituent X. Nevertheless, it was suggested that the TNLO property is greater for the more extended π-conjugated thiophenes with the higher molecular planarity.

Experimental

The melting points were determined on a hot-stage apparatus and are uncorrected. IR spectra were measured on a JASCO FT/IR 7300 spectrophotometer as KBr disks, unless otherwise stated; only significant absorptions are reported. Electronic spectra were determined in THF solution on a Shimadzu UV-2200A spectrophotometer (sh=shoulder), unless otherwise stated. ^{1}H NMR spectra were taken in $CDCl_3$ solution on JEOL MAC-FX (90 MHz) or JEOL A400 (400 MHz) spectrometers, and were recorded in δ-values with TMS as an internal standard. Mass spectra were recorded with a JEOL JMS-D300 spectrometer operating at 75 eV in a direct inlet system. Silica gel (Daiso gel 1001W or Merck 60) and alumina (Merck, Act. II—III) were used for column chromatography. CH_2Cl_2 and $CHCl_3$ were distilled over calcium hydride and THF was distilled from sodium diphenylketyl under argon before use. The reactions were followed by TLC aluminum sheets precoated with Merck silica gel F_{254} or with Merck aluminum oxide GF_{254}. Organic extracts were dried over anhydrous sodium sulfate or magnesium sulfate prior to removal of the solvents.

Preparation of 3,3′-Dihexyl-2,2′-bithiophene (1) and 3,4′-Dihexyl-2,2′-bithiophene (51) from 2-Bromo-3-hexylthiophene (48): To a solution of **48**[3] (6.0 g, 24.0 mmol) in THF (100 cm^3) were added drops of butyllithium (1.6 M (1 M=1 mol dm^{-3}); 16.8 cm^3, 27.0 mmol) in hexane at −80 °C over 15 min under Ar atmosphere. The mixture was stirred for 20 min at −80 °C and then gradually warmed to room temperature. $Fe(acac)_3$ (8.5 g, 24.0 mmol) was added in portions over 10 min at an ambient temperature. After being stirred for 2 h, the mixture was diluted with water (300 cm^3), neutralized with 3 M HCl, and extracted with dichloromethane. The extracts were washed with brine and dried. The residue obtained after removal of the solvents was chromatographed on silica gel (3.2×50 cm) with hexane to afford a mixture (4.7 g) containing HH bithiophene **1**, HT bithiophene **51**, and 3-hexylthiophene. Distillation of the liquid (bp 50 °C/532 Pa (1 mmHg=133 Pa)) gave 3-hexylthiophene (370 mg, 9%), leaving a mixture of HH and HT bithiophenes (3.5 g, 88%) in a flask.

Measurement of the ^{1}H NMR spectrum of the mixture showed a ratio of almost 1 : 1 of HH and HT bithiophenes.[13]

To a solution of the bithiophene mixture (3.5 g, 10.5 mmol) in a mixture of $CHCl_3$ and AcOH (80 cm^3, 1 : 1 v/v), NBS (9.0 g, 5.0 mmol corresponding to the HT bithiophene **51**) was added in portions at 0 °C over 15 min. The reaction mixture was stirred for 2 h at 0 °C and then gradually warmed to room temperature. Poured into water, the mixture was extracted with dichloromethane. The extracts were washed successively with brine, dil aq $NaHCO_3$, and brine, and then dried. The residue obtained after removal of the solvents was chromatographed on silica gel (4×45 cm) with hexane to afford 5′-bromo-3,4′-dihexyl-2,2′-bithiophene **52** (1.92 g) from the first fractions and the HH bithiophene **1** (1.78 g, 44.5% based on **48**) from the second fractions. **1**:[3] Colorless oil; ^{1}H NMR (400 MHz) δ=7.23 (2H, d, J=4.8 Hz, ThH), 6.96 (2H, d, J=4.8 Hz, ThH), 2.50 (4H, t, J=7.4 Hz, $\underline{CH_2}$–C_5H_{11}), 1.69—0.78 (22H, m, CH_2–$\underline{C_5H_{11}}$). **52**:[3] Colorless oil; ^{1}H NMR (90 MHz) δ=7.13 (2H, d, J=5 Hz, ThH), 6.88 (2H, d, J=5 Hz, ThH), 6.78 (2H, s, ThH), 2.72 (4H, t, J=7 Hz, Th$\underline{CH_2}$), 2.56 (4H, t, J=8 Hz, Th$\underline{CH_2}C_5H_{11}$), and 1.66—0.89 (22H, m, $CH_2\underline{C_5H_{11}}$).

To a solution of **52** (1.92 g, 4.7 mmol) in THF (80 cm^3), $LiAlH_4$ (190 mg, 5.0 mmol) was added in portions at 0 °C under Ar atmosphere. The reaction mixture was stirred at an ambient temperature for 1 h and then heated under gentle reflux for 30 min. After addition of ethyl acetate (5 cm^3) at room temperature, the mixture was stirred for 30 min, poured into water, and extracted with dichloromethane. The extracts were washed with brine and dried. The residue obtained after removal of the solvents was chromatographed on a short column of silica gel (4×4 cm) with hexane to afford the HT bithiophene **51**[3] (1.46 g, 36.5% based on **48**): Colorless oil; ^{1}H NMR (400 MHz) δ=7.12 (1H, d, J=4.6 Hz, ThH), 6.94 (1H, s, ThH), 6.90 (1H, d, J=4.6 Hz, ThH), 6.86 (1H, s, ThH), 2.75 (2H, t, J=7.6 Hz, $\underline{CH_2}$–C_5H_{11}), 2.60 (2H, t, J=7.8 Hz, $\underline{CH_2}$–C_5H_{11}), and 1.70—0.82 (22H, m, CH_2–$\underline{C_5H_{11}}$).

5-Bromo-3,3′-dihexyl-2,2′-bithiophene (13): To a solution of **1** (1.80 g, 5.39 mmol) in a mixture of chloroform and acetic acid (50 : 50 v/v, 100 cm^3) portions of *N*-bromosuccinimide (NBS; 1.16 g, 6.52 mmol) were added at 0 °C over 30 min. After stirring for 30 min, the mixture was diluted with water and extracted with chloroform. The extracts were washed first with aq 2 M KOH and then with water. The residue obtained after removal of the solvent was chromatographed on silica gel (3.2×5 cm) with hexane to give **13**[3] (1.22 g, 55%): Pale yellow oil; ^{1}H NMR (90 MHz) δ=7.28 (1H, d, J=5 Hz, ThH), 6.94 (1H, d, J=5 Hz, ThH), 6.91 (1H, s, ThH), 2.50 (2H, t, J=7 Hz, $\underline{CH_2}$–C_5H_{11}), 2.41 (2H, t, J=7 Hz, $\underline{CH_2}$–C_5H_{11}), and 1.54—0.78 (22H, m, CH_2–$\underline{C_5H_{11}}$).

5-Bromo-3,3′,3‴,4″-tetrahexyl-2,2′ : 5′,2″ : 5″,2‴-quaterthiophene (18): Reaction of **7**[3] (2.0 g, 3.0 mmol) with NBS (5.9 g, 3.3 mmol) in a mixture of chloroform and acetic acid (50 : 50 v/v, 80 cm^3) gave **18**[3] (1.38 g, 62%): Pale yellow oil; ^{1}H NMR (400 MHz) δ=7.29 (1H, d, J=5.5 Hz, ThH), 7.02 (1H, s, ThH), 7.00 (1H,

s, ThH), 6.97 (1H, d, J=5.5 Hz, ThH), 6.92 (1H, s, ThH), 2.62—2.39 (8H, m, $\underline{CH_2}$–C_5H_{11}), and 1.68—0.79 (44H, m, CH_2–$\underline{C_5H_{11}}$).

5-Cyano-3,3′-dihexyl-2,2′-bithiophene (14): A mixture of **13** (500 mg, 1.21 mmol) and copper(I) cyanide (CuCN; 176 mg, 1.96 mmol) in *N*-methyl-2-pyrrolidone (NMP; 15 cm^3) was refluxed for 1 h. The mixture was poured into a 25% aq ammonia (100 cm^3). The mixture was extracted with benzene and the extracts were washed with brine and then dried. The residue obtained after removal of the solvent was chromatographed on silica gel (3.2×10 cm) with hexane to afford **14** (391 mg, 90%): Colorless oil; Mass *m/z* 359 and 360 (M^+ and M^++1); IR (neat) 2215 (CN), 1460 and 1130 cm^{-1}; ^{1}H NMR (90 MHz) δ=7.38 (1H, s, ThH), 7.25 (1H, d, J=5 Hz, ThH), 6.89 (1H, d, J=5 Hz, ThH), 2.42 (4H, br t, J=7 Hz, $\underline{CH_2}$–C_5H_{11}), and 1.54—0.78 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 246 (ε 11400) and 294 nm (ε 9000). Found: C, 70.35; H, 8.11; N, 3.81%. Calcd for $C_{12}H_{29}NS_2$: C, 70.14; H, 8.13; N, 3.90%.

5-Cyano-3,3′,3‴,4″-tetrahexyl-2,2′ : 5′,2″ : 5″,2‴-quaterthiophene (19): Reaction of **18** (500 mg, 0.67 mmol) with CuCN (108 mg, 1.09 mmol) in NMP (15 cm^3) afforded **19** (363 mg, 79%): Pale yellow fine needles from hexane–benzene; mp 26—27 °C; Mass *m/z* 691 and 692 (M^+ and M^++1); IR (neat) 2215 (CN), 1460 and 830 cm^{-1}; ^{1}H NMR (90 MHz) δ=7.48 (1H, s, ThH), 7.31 (1H, d, J=5 Hz, ThH), 7.04 (2H, br s, ThH), 6.97 (1H, d, J=5 Hz, ThH), 2.63—2.39 (8H, m, $\underline{CH_2}$–C_5H_{11}), and 1.68—0.72 (44H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 245 (ε 19500) and 350 nm (ε 24800). Found: C, 70.95; H, 8.32; N, 1.99%. Calcd for $C_{41}H_{57}NS_4$: C, 71.15; H, 8.30; N, 2.02%.

3,3′-Dihexyl-2,2′-bithiophene-5-carboxylic Acid (15): To a solution of **13** (800 mg, 1.93 mmol) in THF (20 cm^3) drops of butyllithium (1.6 mol dm^{-3}; 1.27 cm^3, 2.03 mmol) in hexane were added during 10 min at −80 °C under Ar atmosphere. After the mixture was stirred for 20 min at −80 °C, gaseous carbon dioxide was bubbled into it for 30 min. After being stirred for 1 h at room temperature, the mixture was poured into 4 M HCl (50 cm^3) and then extracted with ether (50 cm^3×2). The extracts were washed with brine and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (3.2×10 cm) with a mixture of ether and dichloromethane (1 : 9) to afford **15** (565 mg, 77%): Colorless oil; Mass *m/z* 378 (M^+); IR (neat) 3200 (br, OH), 1675 (C=O), 1430, and 1280 cm^{-1}; ^{1}H NMR (90 MHz) δ=11.68 (1H, s, CO_2H), 7.77 (1H, s, ThH), 7.32 (1H, d, J=5 Hz, ThH), 6.97 (1H, d, J=5 Hz, ThH), 2.54 (4H, br t, J=7 Hz, $\underline{CH_2}$–C_5H_{11}), and 1.68—0.74 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 248 (ε 10900) and 297 nm (ε 9650). Found: C, 66.44; H, 7.93%. Calcd for $C_{21}H_{30}O_2S_2$: C, 66.62; H, 7.99%.

3,3′,3‴,4″-Tetrahexyl-2,2′ : 5′,2″ : 5″,2‴-quaterthiophene-5-carboxylic Acid (20): Reaction of **18** (500 mg, 0.67 mmol) in THF (20 cm^3) with butyllithium (1.6 mol dm^{-3}; 0.44 cm^3, 0.70 mmol) and gaseous carbon dioxide afforded **20** (223 mg, 47%): Yellow fine needles from hexane–dichloromethane; mp 38.5—40.0 °C; Mass *m/z* 710 and 711 (M^+ and M^++1); IR (neat) 3200 (br, OH), 1675 (C=O), 1460, 1440, 1300, and 1270 cm^{-1}; ^{1}H NMR (90 MHz) δ=9.40 (1H, br s, OH), 7.77 (1H, s, ThH), 7.29 (1H, d, J=5 Hz, ThH), 7.04 (2H, br s, ThH), 6.96 (1H, d, J=5 Hz, ThH), 2.68—2.30 (8H, m, $\underline{CH_2}$–C_5H_{11}), and 1.78—0.74 (44H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 348 nm (ε 23400). Found: C, 69.28; H, 8.15%. Calcd for $C_{41}H_{58}O_2S_4$: C, 69.25; H, 8.22%.

3,3′-Dihexyl-2,2′-bithiophene-5-carbaldehyde (16): To a solution of **13** (500 mg, 1.21 mmol) and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA; 151 mg, 1.27 mmol) in THF (10 cm^3) drops of butyllithium (1.6 mol dm^{-3}; 0.79 cm^3, 1.27 mmol) in hexane were added below −80 °C, over 10 min under Ar atmosphere. After this mixture was stirred for 20 min at −80 °C, DMF (442 mg, 6.05 mmol) was added over 10 min at −80 °C. The mixture stirred for 5 h at room temperature was poured into 1 M HCl at −10 °C with stirring and then neutralized by addition of saturated aq $NaHCO_3$. The organic layer and the extracts from the aqueous solution with dichloromethane were combined and washed with brine. The residue obtained after removal of the solvent was chromatographed on silica gel (3.2×10 cm) with a mixture of hexane and benzene (3 : 2) to afford **16** (183 mg, 42%): Colorless oil; Mass *m/z* 362 and 363 (M^+ and M^++1); IR (neat) 1675 (C=O), 1460, and 1155 cm^{-1}; ^{1}H NMR (90 MHz) δ=9.30 (1H, s, CHO), 7.65 (1H, s, ThH), 7.35 (1H, d, J=5 Hz, ThH), 6.98 (1H, d, J=5 Hz, ThH), 2.53 (4H, br t, J=8 Hz, $\underline{CH_2}$–C_5H_{11}), and 1.67—0.70 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 254 (ε 9500) and 319 nm (ε 9600). Found: C, 69.60; H, 8.27%. Calcd for $C_{21}H_{30}OS_2$: C, 69.56; H, 8.34%.

3,3′,3‴,4″-Tetrahexyl-2,2′ : 5′,2″ : 5″,2‴-quaterthiophene-5-carbaldehyde (21): Reaction of **18** (500 mg, 0.67 mmol) with TMEDA (83 mg, 0.72 mmol), butyllithium (1.6 mol dm^{-3}; 0.44 cm^3, 0.70 mmol), and DMF (248 mg, 3.4 mmol) in THF (8 cm^3) afforded **21** (213 mg, 46%): Pale yellow oil; Mass *m/z* 694 and 695 (M^+ and M^++1); IR (neat) 1675 (C=O), 1460, 1240, and 1155 cm^{-1}; ^{1}H NMR (90 MHz) δ=9.86 (1H, s, CHO), 7.65 (1H, s, ThH), 7.30 (1H, d, J=5 Hz, ThH), 7.05 (2H, br s, ThH), 6.97 (1H, d, J=5 Hz, ThH), 2.73—2.35 (8H, m, $\underline{CH_2}$–C_5H_{11}), and 1.72—0.70 (44H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 357 nm (ε 23300). Found: C, 71.04; H, 8.25%. Calcd for $C_{41}H_{58}OS_4$: C, 70.84; H, 8.41%.

3,3′-Dihexyl-5,5′-dinitro-2,2′-bithiophene (6): (Method A with $NaNO_3$);[9] To a solution of **1** (1.0 g, 3.0 mmol) in H_2SO_4 (20 cm^3) was added dropwise a solution of $NaNO_3$ (560 mg, 6.58 mmol) in H_2SO_4 (20 cm^3) at 5 °C over 30 min. The reaction mixture was stirred for 15 min, poured into ice water, and extracted with CH_2Cl_2. The extracts were washed with brine. The residue after removal of the solvent was chromatographed on silica gel (3.2×8 cm) with a mixture of hexane and benzene (9 : 1) to afford **6** (360 mg, 28%) from the first fractions, 4,5,5′-trinitro-3,3′-dihexyl-2,2′-bithiophene (**50**; 137 mg, 9.7%) from the second fractions, and the insoluble yellow materials (680 mg) from the last fractions.

(Method B with HNO_3);[10] To a solution of **1** (300 mg, 1.0 mmol) in acetic anhydride (3 cm^3) was added dropwise a solution of HNO_3 (0.38 cm^3, 5.1 mmol) in acetic anhydride (1.5 cm^3) by a syringe at −10 °C over 15 min. The reaction mixture was stirred for 1.5 h and kept in a refrigerator overnight. Poured into aq KOH (2 M, 40 ml), the mixture was extracted with CH_2Cl_2. The extracts were washed with brine. The residue after removal of the solvent was chromatographed on silica gel (3.2×8 cm) with a mixture of hexane and benzene (9 : 1) to give **6** (297 mg, 78%) from the second fractions together with the mononitro compound **17** (12 mg, 3.5%) from the first fractions (see below). **6**: Pale yellow oil; Mass *m/z* 424 (M^+); IR (neat) 1510 and 1330 (N=O) and 815 cm^{-1} (C–N); ^{1}H NMR (90 MHz) δ=7.84 (2H, s, ThH), 2.56 (4H, t, J=7 Hz, $\underline{CH_2}$–C_5H_{11}), and 1.75—0.87 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 349 nm (ε 15800). Found: C, 56.58; H, 6.65; N, 6.60%. Calcd for $C_{20}H_{28}N_2O_4S_2$: C, 56.51; H, 6.52; N, 6.60%. **50**: Pale yellow needles from ethanol–hexane; mp 63—64 °C; Mass *m/z* 469 (M^+); IR (neat) 1510 and 1330 (N=O) and 815 cm^{-1} (C–N); ^{1}H NMR (90 MHz) δ=7.84 (1H, s, ThH), 2.56 (4H, t, J=7 Hz, $\underline{CH_2}$–C_5H_{11}), and 1.75—0.87 (22H, m,CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 293 (ε 9150) and 347 nm (ε 12600). Found: C, 51.45; H, 5.87; N, 8.95%. Calcd for $C_{20}H_{27}N_3O_6S_2$: C, 51.16; H, 5.80; N, 8.95%.

3, 3′, 3‴, 4″- Tetrahexyl- 5, 5‴- dinitro- 2, 2′ : 5′, 2″ : 5″, 2‴- quaterthiophene (12): According to Method B, nitration of **7** (300 mg, 0.45 mmol) in acetic anhydride (3 cm^3) with HNO_3

(0.11 cm^3, 1.48 mmol) in acetic anhydride (0.33 cm^3) gave **12** (30 mg, 9%): Pale yellow fine needles from hexane–ethanol; mp 69—70 °C; MS *m/z* 756 (M^+); IR (neat) 1505 and 1340 (N=O) and 815 cm^{-1} (C–N); ^{1}H NMR (90 MHz) δ=7.81 (2H, br s, ThH), 7.08 (2H, br s, ThH), 2.54 (8H, br t, J=7 Hz, $\underline{CH_2}$–C_5H_{11}), and 1.55—0.87 (44H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 333 (ε 18800) and 403 nm (ε 18900). Found: C, 63.27; H, 7.30; N, 3.58%. Calcd for $C_{40}H_{56}N_2O_4S_4$: C, 63.45; H, 7.45; N, 3.70%.

3,3′-Dihexyl-5-nitro-2,2′-bithiophene (17): Similarly for **12**, reaction of **1** (500 mg, 1.5 mmol) in a mixture of THF and acetic anhydride (1 : 2, 3 cm^3) with HNO_3 (0.17 cm^3, 2.3 mmol) in acetic anhydride (0.5 cm^3) gave **17** (330 mg, 58%) from the first fractions and **6** (36 mg, 5.7%) from the second fractions. **17**: Pale yellow oil; Mass *m/z* 379 and 380 (M^+ and M^++1); IR (neat) 1505, 1450, 1330, and 815 cm^{-1}; ^{1}H NMR (90 MHz) δ=7.80 (1H, s, ThH), 7.38 (1H, d, J=5 Hz, ThH), 7.00 (1H, d, J=5 Hz, ThH), 2.52 (4H, m, $\underline{CH_2}$–C_5H_{11}), and 1.55—0.86 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 242 (ε 12900) and 357 nm (ε 8380). Found: C, 63.18; H, 7.69; N, 3.60%. Calcd for $C_{20}H_{29}NO_2S_2$: C, 63.28; H, 7.70; N, 3.69%.

3,3′,3‴,4″-Tetrahexyl-5-nitro-2,2′ : 5′,2″ : 5″,2‴-quaterthiophene (22): Similarly for **12**, reaction of **7** (580 mg, 0.87 mmol) in a mixture of THF and acetic anhydride (1 : 2, 4 cm^3) with HNO_3 (0.10 cm^3, 1.35 mmol) in acetic anhydride (0.5 cm^3) gave **22** (235 mg, 38%): Pale yellow fine needles from hexane–ethanol; mp 32.0—32.5 °C; Mass *m/z* 711 and 712 (M^+ and M^++1); IR (neat) 1510, 1455, 1330, 880, and 730 cm^{-1}; ^{1}H NMR (90 MHz) δ=7.81 (1H, s, ThH), 7.31 (1H, d, J=5 Hz, ThH), 7.05 (2H, br s, ThH), 6.97 (1H, d, J=5 Hz, ThH), 2.70—2.36 (8H, m, $\underline{CH_2}$–C_5H_{11}), and 1.75—0.76 (44H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 337 (ε 24600) and 392 nm (ε 19500). Found: C, 67.46; H, 7.97; N, 1.96%. Calcd for $C_{40}H_{57}NO_2S_4$: C, 67.46; H, 8.07; N, 1.97%.

3,3′-Dihexyl-5-methoxy-2,2′-bithiophene (23): To a solution of sodium methoxide (NaOMe from 1.5 g of Na, 65 mmol) in methanol (30 cm^3) were added a solution of **13** (2.63 g, 6.37 mmol) in THF (10 cm^3), CuO (178 mg, 2.2 mmol), and a catalytic amount of NaI (3 mg), successively. The reaction mixture was gently refluxed with stirring for 30 h. After filtration of the insoluble materials, the mixture was poured into water and extracted with dichloromethane. The extracts were washed with brine. The residue obtained after removal of the solvents was chromatographed on alumina (3.2×18 cm) with hexane to give **23** (1.44 g, 62%): Pale yellow oil; Mass *m/z* 364 and 365 (M^+ and M^++1); IR (neat) 1540, 1495, 1460, 1240, 1195, 1160, and 1005 cm^{-1}; ^{1}H NMR (90 MHz) δ=7.23 (1H, d, J=5 Hz, ThH), 6.92 (1H, d, J=5 Hz, ThH), 6.07 (1H, s, ThH), 3.88 (3H, s, OCH_3), 2.6—2.3 (4H, m, $\underline{CH_2}$–C_5H_{11}), and 1.75—0.79 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 243 (ε 8910) and 277 nm (ε 5670, sh). Found: C, 69.42; H, 8.83%. Calcd for $C_{21}H_{32}OS_2$: C, 69.18; H, 8.85%.

3,4′-Dihexyl-5′-methoxy-2,2′-bithiophene (28): Reaction of **52** (2.0 g, 4.8 mmol) in THF (10 cm^3) with NaOMe (1.1 g of Na, 48 mmol) in methanol (20 cm^3) in the presence of CuO (200 mg, 2.5 mmol) and NaI (6 mg) gave **28** (0.69 g, 39%): Pale yellow oil; Mass *m/z* 364 and 365 (M^+ and M^++1); IR (neat) 1580, 1540, 1490, 1420, 1240, 1015, and 830 cm^{-1}; ^{1}H NMR (90 MHz) δ=7.09 (1H, d, J=5 Hz, ThH), 6.88 (1H, d, J=5 Hz, ThH), 6.65 (1H, s, ThH), 3.90 (3H, s, OCH_3), 2.71 (2H, d, J=8 Hz, $\underline{CH_2}$–C_5H_{11}), 2.47 (2H, d, J=8 Hz, $\underline{CH_2}$–C_5H_{11}), and 1.75—0.79 (22H, m, CH_2–$\underline{C_5H_{11}}$): UV λ_{max} 243 (ε 6460) and 312 nm (ε 9270). Found: C, 69.09; H, 8.85%. Calcd for $C_{21}H_{32}OS_2$: C, 69.18; H, 8.85%.

3,3′,3‴,4″-Tetrahexyl-5-methoxyl-2,2′ : 5′,2″ : 5″,2‴-quaterthiophene (33): Reaction of **18** (5.58 g, 7.48 mmol) in THF (10 cm^3) with NaOMe (1.72 g of Na, 74.7 mmol) in methanol (30 cm^3) in the presence of CuO (298 mg, 3.73 mmol) and NaI (6 mg) gave **33** (0.53 g, 10%): Pale yellow oil; Mass *m/z* 696 and 697 (M^+ and M^++1); IR (neat) 1525, 1500, 1455, 1375, 1235, 1195, 1155, 1005, and 830 cm^{-1}; ^{1}H NMR (90 MHz) δ=7.29 (1H, d, J=5 Hz, ThH), 7.00 (1H, s, ThH), 6.99 (1H, s, ThH), 6.96 (1H, d, J=5 Hz, ThH), 6.08 (1H, s, ThH), 3.89 (3H, s, OCH_3), 2.62—2.35 (8H, m, $\underline{CH_2}$–C_5H_{11}), and 1.77—0.79 (44H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 346 nm (ε 23450). Found: C, 70.62; H, 8.81%. Calcd for $C_{41}H_{60}OS_4$: C, 70.63; H, 8.67%.

3,3′-Dihexyl-5,5′-dimethoxy-2,2′-bithiophene (54): Reaction of **2** (2.0 g, 4.06 mmol) in THF (10 cm^3) with NaOMe (2.8 g of Na, 122 mmol) in methanol (30 cm^3) in the presence of CuO (336 mg, 4.3 mmol) and NaI (8 mg) gave **54** (0.89 g, 56%): Pale yellow oil; Mass *m/z* 394 and 395 (M^+ and M^++1); IR (neat) 1550, 1510, 1480, 1425, 1225, 1195, 1160, 1005, and 785 cm^{-1}; ^{1}H NMR (90 MHz) δ=6.03 (2H, s ThH), 3.86 (6H, s, OCH_3), 2.40 (4H, t, J=7 Hz, $\underline{CH_2}$–C_5H_{11}), and 1.65—0.76 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 236 (ε 9140) and 283 nm (ε 7320). Found: C, 66.99; H, 8.74%. Calcd for $C_{22}H_{34}O_2S_2$: C, 66.96; H, 8.68%.

3,3′,3‴,4″-Tetrahexyl-5,5‴-dimethoxy-2,2′ : 5′,2″ : 5″,2‴-quaterthiophene (55): Reaction of **8** (1.0 g, 1.2 mmol) in THF (5 cm^3) with NaOMe (828 mg of Na, 36 mmol) in methanol (10 cm^3) in the presence of CuO (200 mg, 2.5 mmol) and NaI (3 mg) gave **34** (316 mg, 34%, see below) from the first fractions. The second fractions afforded **55** (200 mg, 23%): Pale yellow oil; Mass *m/z* 726, 727, and 728 (M^+, M^++1, and M^++2); IR (neat) 1535, 1495, 1460, 1425, 1240, 1195, 1160, 1005, and 830 cm^{-1}; ^{1}H NMR (90 MHz) δ=6.97 (2H, s, ThH), 6.07 (2H, s, ThH), 3.89 (6H, s, OCH_3), 2.6—2.3 (8H, m, $\underline{CH_2}$–C_5H_{11}), and 1.68—0.76 (44H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 249 (ε 17200) and 352 nm (ε 23400). Found: C, 69.09; H, 8.47%. Calcd for $C_{42}H_{62}O_2S_4$: C, 69.37; H, 8.59%.

5-Bromo-3,3′-dihexyl-5′-methoxy-2,2′-bithiophene (24): To a solution of **23** (466 mg, 1.28 mmol) in a mixture of chloroform and acetic acid (10 : 1 v/v, 165 cm^3) was added NBS (171 mg, 0.96 mmol) in small portions at room temperature. The mixture was stirred for 30 min. Poured into water, the mixture was extracted with chloroform. The extracts were washed with aq KOH and then with brine. The residue obtained after removal of the solvents was chromatographed on alumina (3.2×18 cm) with hexane to give **24** (520 mg, 49%): Pale yellow oil; Mass *m/z* 442 and 444 (M^+ and M^++2 based on ^{79}Br); IR (neat) 1540, 1500, 1460, 1425, 1240, 1195, 1160, 1005, and 830 cm^{-1}; ^{1}H NMR (90 MHz) δ=6.88 (1H, s, ThH), 6.06 (1H, s, ThH), 3.87 (3H, s, OCH_3), 2.53—2.30 (4H, m, $\underline{CH_2}$–C_5H_{11}), and 1.54—0.79 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 243 (ε 12200) and 284 nm (ε 7460). Found: C, 57.11; H, 6.94%. Calcd for $C_{21}H_{31}OS_2Br$: C, 56.87; H, 7.05%.

5-Bromo-3,4′-dihexyl-2′-methoxy-2,2′-bithiophene (29): Reaction of **28** (300 mg, 0.82 mmol) in a mixture of chloroform and acetic acid (1 : 1 v/v, 20 cm^3) with NBS (146 mg, 0.82 mmol) gave **29** (361 mg, 99%): Pale yellow oil; Mass *m/z* 442 and 444 (M^+ and M^++2 based on ^{79}Br); IR (neat) 1580, 1545, 1485, 1455, 1420, 1240, 1015, and 830 cm^{-1}; ^{1}H NMR (90 MHz) δ=6.83 (1H, s, ThH), 6.60 (1H, s, ThH), 3.90 (3H, s, OCH_3), 2.64 (2H, t, J=7 Hz, $\underline{CH_2}$–C_5H_{11}), 2.45 (2H, t, J=7 Hz, $\underline{CH_2}$–C_5H_{11}), and 1.60—0.75 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 239 (ε 9210) and 321 nm (ε 11400). Found: C, 56.91; H, 6.98%. Calcd for $C_{42}H_{62}O_2S_4$: C, 56.87; H, 7.05%.

5-Bromo-3,3′,3‴,4″-tetrahexyl-5‴-methoxy-2,2′ : 5′,2″ : 5″,2‴-quaterthiophene (34): To a solution of NaOMe (1.98 g of Na, 86 mmol) in methanol (30 cm^3) were added a solution of **8** (7.1 g, 8.6 mmol) in THF (10 cm^3), CuO (250 mg, 3.1 mmol), and a catalytic amount of NaI (5 mg), successively. The reaction mixture

was gently refluxed with stirring for 30 h. After removal of the insoluble materials by filtration, the mixture was poured into water and extracted with dichloromethane. The extracts were washed with brine. The residue obtained after removal of the solvents was chromatographed on silica gel (3.2×15 cm) with a mixture of hexane and benzene (100:0 to 100:25) to give **34** (984 mg, 15%): Pale yellow fine needles from ethanol; mp 32—33 °C; Mass *m/z* 774 and 776 (M^+ and M^++2 based on ^{79}Br); IR (neat) 1530, 1500, 1460, 1430, 1235, 1195, 1160, 1005, and 830 cm^{-1}; ^1H NMR (90 MHz) δ=6.99 (2H, br s, ThH), 6.91(1H, s, ThH), 6.08 (1H, s, ThH), 3.87 (3H, s, OCH_3), 2.52—2.37 (8H, m, $\underline{CH_2}$–C_5H_{11}), and 1.55—0.81 (44H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 244 (ε 20100) and 350 nm (ε 25700). Found: C, 63.63; H, 7.63%. Calcd for $C_{41}H_{59}OS_4Br$: C, 63.45; H, 7.66%.

5-Cyano-3,3′-dihexyl-5′-methoxy-2,2′-bithiophene (25): A mixture of **24** (601 mg, 1.36 mmol) with CuCN (218 mg, 2.44 mmol) in NMP (18 cm^3) was refluxed for 2 h. The mixture was poured into 25% aq ammonia (20 cm^3). The mixture was extracted with benzene and the extracts were washed with brine and then dried. The residue obtained after removal of the solvent was chromatographed on alumina (3.2×16 cm) with a mixture of hexane and benzene (7:3) to afford **25** (262 mg, 50%): Pale yellow oil; Mass *m/z* 389 and 390 (M^+ and M^++1); IR (neat) 2215 (CN), 1535, 1495, 1435, 1240, 1195, and 1160 cm^{-1}; ^1H NMR (90 MHz) δ=7.44 (1H, s, ThH), 6.10 (1H, s, ThH), 3.90 (3H, s, OCH_3), 2.52 (2H, t, J=7 Hz, $\underline{CH_2}$–C_5H_{11}), 2.39 (2H, t, J=7 Hz, $\underline{CH_2}$–C_5H_{11}), and 1.55—0.86 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 252 (ε 14700), 267 (ε 11600, sh), and 328 nm (ε 7060). Found: C, 67.67; H, 7.96; N, 3.41%. Calcd for $C_{22}H_{31}ONS_2$: C, 67.82; H, 8.02; N, 3.59%.

5-Cyano-3,4′-dihexyl-5′-methoxy-2,2′-bithiophene (30): Reaction of **29** (150 mg, 0.34 mmol) with CuCN (110 mg, 1.1 mmol) in NMP (3 cm^3) afforded **30** (104 mg, 70%): Pale yellow oil; Mass *m/z* 389, 390, and 391 (M^+, M^++1, and M^++2); IR (neat) 2210 (CN), 1480, 1440, 1245, and 1015 cm^{-1}; ^1H NMR (90 MHz) δ=7.38 (1H, s, ThH), 6.79 (1H, s, ThH), 3.93 (3H, s, OCH_3), 2.71 (2H, t, J=7 Hz, $\underline{CH_2}$–C_5H_{11}), 2.48 (2H, t, J=7 Hz, $\underline{CH_2}$–C_5H_{11}), and 1.65—0.86 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 355 nm (ε 13300). Found: C, 67.52; H, 7.74; N, 3.62%. Calcd for $C_{22}H_{31}ONS_2$: C, 67.82; H, 8.02; N, 3.59%.

5-Cyano-3,3′,3‴,4″-tetrahexyl-5‴-methoxy-2,2′ : 5′,2″ : 5″, 2‴-quaterthiophene (35): Reaction of **34** (202 mg, 0.26 mmol) with CuCN (84 mg, 0.94 mmol) in NMP (4 cm^3) afforded **35** (63 mg, 34%): Pale yellow fine needles from ethanol; mp 34—35 °C; Mass *m/z* 721, 722, and 723 (M^+, M^++1, and M^++2); IR (neat) 2215 (CN), 1500, 1465, 1430, 1240, 1150, and 820 cm^{-1}; ^1H NMR (90 MHz) δ=7.48 (1H, s, ThH), 7.01 (2H, br s, ThH), 6.09 (1H, s, ThH), 3.89 (3H, s, OCH_3), 2.63—2.35 (8H, m, $\underline{CH_2}$–C_5H_{11}), and 1.57—0.86 (44H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 249 (ε 17900) and 357 nm (ε 24100). Found: C, 69.76; H, 8.03; N, 1.88%. Calcd for $C_{42}H_{59}ONS_4$: C, 69.85; H, 8.23; N, 1.94%.

3,3′-Dihexyl-5′-methoxy-2,2′-bithiophene-5-carbaldehyde (26): To a solution of **24** (100 mg, 0.23 mmol) and TMEDA (28 mg, 0.24 mmol) in THF (10 cm^3) drops of butyllithium (1.6 mol dm^{-3}; 0.14 cm^3, 0.24 mmol) in hexane were added below −80 °C over 10 min under Ar atmosphere. After this mixture was stirred for 20 min at −80 °C, DMF (87 mg, 1.13 mmol) was added over 10 min at −80 °C. The mixture was stirred for 1 h at room temperature and was poured into 1 M HCl at −10 °C with stirring and then neutralized by addition of saturated aq $NaHCO_3$. The organic layer and the extracts from the aqueous solution with dichloromethane were combined and washed with brine. The residue obtained after removal of the solvent was chromatographed on alumina (3.2×12 cm) with a mixture of hexane and benzene (1:1) to afford **26** (54 mg, 61%): Pale green oil; Mass *m/z* 392 and 393 (M^+ and M^++1); IR (neat) 1675 (CO), 1495, 1435, 1245, 1155, and 1000 cm^{-1}; ^1H NMR (90 MHz) δ=9.83 (1H, s, CHO), 7.61 (1H, s, ThH), 6.11 (1H, s, ThH), 3.90 (3H, s, OCH_3), 2.64—2.34 (4H, m, $\underline{CH_2}$–C_5H_{11}), and 1.68—0.76 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 262 (ε 12600) and 350 nm (ε 7100). Found: C, 67.40; H, 8.22%. Calcd for $C_{22}H_{32}O_2S_2$: C, 67.30; H, 8.22%.

3,4′-Dihexyl-5′-methoxy-2,2′-bithiophene-5-carbaldehyde (31): Reaction of **29** (450 mg, 1.01 mmol) with TMEDA (120 mg, 1.02 mmol), butyllithium (1.6 mol dm^{-3}; 0.65 cm^3, 1.05 mmol), and DMF (350 mg, 5.05 mmol) in THF (10 cm^3) afforded **31** (220 mg, 55%): Pale yellow oil; Mass *m/z* 392 and 393 (M^+ and M^++1); IR (neat) 1665 (CO), 1475, 1445, 1245, 1010, and 675 cm^{-1}; ^1H NMR (90 MHz) δ=9.76 (1H, s, CHO), 7.53 (1H, s, ThH), 6.89 (1H, s, ThH), 3.93 (3H, s, OCH_3), 2.76 (2H, t, J=8 Hz, $\underline{CH_2}$–C_5H_{11}), 2.48 (2H, t, J=8 Hz, $\underline{CH_2}$–C_5H_{11}), and 1.72—0.76 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 384 nm (ε 14200). Found: C, 67.31; H, 8.06%. Calcd for $C_{22}H_{32}O_2S_2$: C, 67.30; H, 8.22%.

3, 3′, 3‴, 4″- Tetrahexyl- 5‴- methoxy- 2, 2′ : 5′, 2″ : 5″, 2‴-quaterthiophene-5-carbaldehyde (36): Reaction of **34** (204 mg, 0.26 mmol) with TMEDA (33 mg, 0.28 mmol), butyllithium (1.6 mol dm^{-3}; 0.17 cm^3, 0.28 mmol), and DMF (0.1 cm^3, 1.31 mmol) in THF (10 cm^3) afforded **36** (40 mg, 21%): Yellow oil; Mass *m/z* 724 and 725 (M^+ and M^++1); IR (neat) 1675 (CO), 1500, 1445, 1430, 1240, 1195, and 1155 cm^{-1}; ^1H NMR (90 MHz) δ=9.86 (1H, s, CHO), 7.65 (1H, s, ThH), 7.03 (1H, s ThH), 7.01 (1H, s, ThH), 6.09 (1H, s, ThH), 3.89 (3H, s, OCH_3), 2.68—2.35 (4H, m, $\underline{CH_2}$–C_5H_{11}), and 1.72—0.76 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 261 (ε 18600) and 364 nm (ε 23300). Found: C, 69.73; H, 8.33%. Calcd for $C_{42}H_{60}O_2S_4$: C, 69.56; H, 8.34%.

3,3′-Dihexyl-5-methoxy-5′-nitro-2,2′-bithiophene (27): To a solution of **23** (232 mg, 0.64 mmol) in a mixture of THF and acetic anhydride (3:5, 10 cm^3) was added dropwise a solution of HNO_3 (72 mg, 0.68 mmol) in acetic anhydride (0.15 cm^3) by a syringe at −10 °C over 15 min. The reaction mixture was stirred for 4 h and kept in a refrigerator for 15 h. Poured into aq KOH (2 M, 25 cm^3), the mixture was extracted with CH_2Cl_2. The extracts were washed with brine. The residue after removal of the solvent was chromatographed on alumina (3.2×5 cm) with a mixture of hexane and benzene (7:3) to give **27** (173 mg, 66%): Brown oil; Mass *m/z* 409 and 410 (M^+ and M^++1); IR (neat) 1540, 1495, 1430, 1330, 1240, 1160, 1000, and 815 cm^{-1}; ^1H NMR (90 MHz) δ=7.77 (1H, s, ThH), 6.32 (1H, s, ThH), 3.94 (1H, s, OCH_3), 2.66—2.47 (4H, m, $\underline{CH_2}$–C_5H_{11}), and 1.78—0.86 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 255 (ε 12700) and 400 nm (ε 6020). Found: C, 61.34; H, 7.73; N, 3.37%. Calcd for $C_{21}H_{31}NO_3S_2$: C, 61.58; H, 7.63; N, 3.42%.

3′,4-Dihexyl-5-methoxy-5′-nitro-2,2′-bithiophene (32): Reaction of **28** (200 mg, 0.55 mmol) in a mixture of THF and acetic anhydride (3:5, 8 cm^3) with HNO_3 (60 mg, 0.57 mmol) in acetic anhydride (0.13 cm^3) gave **32** (141 mg, 63%): Brown oil; Mass *m/z* 409 and 410 (M^+ and M^++1); IR (neat) 1470, 1430, 1315, 1260, 1160, and 1010 cm^{-1}; ^1H NMR (90 MHz) δ=7.72 (1H, s, ThH), 6.91 (1H, s, ThH), 3.95 (3H, s, OCH_3), 2.72 (2H, t, J=8 Hz, $\underline{CH_2}$–C_5H_{11}), 2.48 (2H, t, J=8 Hz, $\underline{CH_2}$–C_5H_{11}), and 1.75—0.85 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 280 (ε 8050) and 441 nm (ε 14100). Found: C, 61.37; H, 7.40; N, 3.44%. Calcd for $C_{21}H_{31}NO_3S_2$: C, 61.58; H, 7.63; N, 3.42%.

3,3′-Dihexyl-5-methylthio-2,2′-bithiophene (38): To a solution of **13** (3.49 g, 8.43 mmol) in THF (60 cm^3) were added drops of methyllithium (1.5 mol dm^{-3}; 5.79 cm^3, 8.68 mmol) in diethyl ether at −80 °C under Ar atmosphere. The resulting mixture was

stirred at −80 °C for 20 min. Sulfur (S_8; 270 mg, 8.43 mmol) was added in portions to the solution at −80 °C. The mixture was stirred at −80 °C for 10 min and was allowed to warm up to room temperature. Poured into 2 M HCl (70 cm^3), the mixture was extracted with dichloromethane. The extracts were washed with brine. The residue obtained after removal of the solvents was chromatographed on silica gel (3.2×30 cm) with hexane to **38** (2.21 g, 57%): Pale yellow oil; Mass *m/z* 380, 381, and 382 (M^+, M^++1, and M^++2); IR (neat) 1455, 1375, 965, and 725 cm^{-1}; ^{1}H NMR (90 MHz) δ=7.25 (1H, d, J=5 Hz, ThH), 6.93 (1H, d, J=5 Hz, ThH), 6.91 (1H, s, ThH), 2.59—2.35 (4H, m, $\underline{CH_2}$–C_5H_{11}), 2.50 (3H, s, SCH_3), and 1.75—0.85 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 249 (ε 9610) and 291 nm (ε 10100). Found: C, 66.55; H, 8.54%. Calcd for $C_{21}H_{32}S_3$: C, 66.26; H, 8.47%.

3,4′-Dihexyl-5′-methylthio-2,2′-bithiophene (43): (Method A with S_8);[14] To a solution of **52** (432 mg, 1.05 mmol) in THF (60 cm^3) were added drops of methyllithium (1.5 mol dm^{-3}; 0.73 cm^3, 1.10 mmol) in diethyl ether at −80 °C under Ar atmosphere. The resulting mixture was stirred at −80 °C for 20 min. Sulfur (S_8; 35 mg, 1.10 mmol) was added in portions to the solution at −80 °C. The mixture was stirred at −80 °C for 10 min and was allowed to warm up to room temperature. Poured into 2 M HCl (40 cm^3), the mixture was extracted with dichloromethane. The extracts were washed with brine. The residue obtained after removal of the solvents was chromatographed on silica gel (3.2×30 cm) with hexane to **43** (121 mg, 30%): Pale yellow oil; Mass *m/z* 380, 381, and 382 (M^+, M^++1, and M^++2); IR (neat) 1465, 1380, 965, and 830 cm^{-1}; ^{1}H NMR (400 MHz) δ=7.14 (1H, d, J=5 Hz, ThH), 6.91 (1H, d, J=5 Hz, ThH), 6.89 (1H, s, ThH), 2.74 (2H, t, J=8 Hz, $\underline{CH_2}$–C_5H_{11}), 2.67 (2H, t, J=8 Hz, $\underline{CH_2}$–C_5H_{11}), 2.41 (3H, s, SCH_3), and 1.75—0.85 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 252 (ε 8500) and 316 nm (ε 9650). Found: C, 66.42; H, 8.41%. Calcd for $C_{21}H_{32}S_3$: C, 66.26: H, 8.47%.

(Method B with MeSSMe);[15] To a solution of **52** (2.13 g, 5.2 mmol) in THF (180 cm^3) at −80 °C were added drops of butyllithium (1.6 mol dm^{-3}; 6.8 cm^3, 10.9 mmol) in hexane during 15 min under Ar atmosphere. The resulting mixture was stirred at −80 °C for 1 h. Dimethyl disulfide (MeSSMe; 1.1 cm^3, 12.0 mmol) was added to the solution at −80 °C at a time. The mixture was stirred at −80 °C for 3 h and then allowed to warm up to room temperature. Poured into 2 M HCl (40 cm^3), the mixture extracted with dichloromethane. The extracts were washed with brine. The residue obtained after removal of the solvents was chromatographed on silica gel (3.2×60 cm) with hexane to give **43** (1.18 g, 59%).

5-Bromo-3,3′-dihexyl-5′-methylthio-2,2′-bithiophene (39): To a solution of **38** (1.01 g, 2.64 mmol) in a mixture of chloroform and acetic acid (1 : 1 v/v, 20 cm^3) was added in small portions NBS (416 mg, 2.34 mmol) at room temperature. The mixture was stirred for 1 h. Poured into water, the mixture was extracted with chloroform. The extracts were washed with aq KOH and then with brine. The residue obtained after removal of the solvents was chromatographed on alumina (3.2×30 cm) with hexane to give **39** (820 mg, 68%): Pale yellow oil; Mass *m/z* 458 and 460 (M^+ and M^++2 based on ^{79}Br); IR (neat) 1455, 1415, 1190, 965, and 830 cm^{-1}; ^{1}H NMR (90 MHz) δ=6.90 (1H, s, ThH), 6.88 (1H, s, ThH), 2.50 (3H, s, SCH_3), 2.44 (4H, t, J=7 Hz, $\underline{CH_2}$–C_5H_{11}), and 1.64—0.79 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 240 (ε 13200) and 295 nm (ε 12200). Found: C, 54.93; H, 6.69%. Calcd for $C_{21}H_{31}BrS_3$: C, 54.89; H, 6.80%.

5-Bromo-3,4′-dihexyl-5′-methylthio-2,2′-bithiophene (44): Reaction of **43** (746 mg, 1.96 mmol) in a mixture of chloroform and acetic acid (1 : 1 v/v, 20 cm^3) with NBS (322 mg, 1.87 mmol) gave **44** (668 mg, 78%): Pale yellow oil; Mass *m/z* 458 and 460 (M^+ and M^++2 based on ^{79}Br); IR (neat) 1520, 1455, 1415, 1310, 1190, 965, and 830 cm^{-1}; ^{1}H NMR (90 MHz) δ=6.86 (1H, s, ThH), 6.82 (1H, s, ThH), 2.7—2.5 (4H, m, $\underline{CH_2}$–C_5H_{11}), 2.40 (3H, s, SCH_3), and 1.68—0.75 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 241 (ε 10100), 257 (ε 9300, sh), and 326 nm (ε 14900). Found: C, 54.73; H, 6.72%. Calcd for $C_{21}H_{31}BrS_3$: C, 54.89; H, 6.80%.

5-Cyano-3,3′-dihexyl-5′-methylthio-2,2′-bithiophene (40): A mixture of **39** (400 mg, 0.87 mmol) and CuCN (312 mg, 3.46 mmol) in NMP (3 cm^3) was refluxed for 4 h. The mixture was poured into a 25% aqueous ammonia (10 cm^3). The mixture was extracted with benzene and the extracts were washed with brine and then dried. The residue obtained after removal of the solvent was chromatographed on silica gel (3.2×10 cm) with a mixture of hexane and benzene (9 : 1) to afford **40** (270 mg, 80%): Pale yellow oil; Mass *m/z* 405, 406, and 407 (M^+, M^++1, and M^++2); IR (neat) 2215 (CN), 1455, 1130, and 855 cm^{-1}; ^{1}H NMR (90 MHz) δ=7.46 (1H, s, ThH), 6.91 (1H, s, ThH), 2.7—2.2 (4H, m, $\underline{CH_2}$–C_5H_{11}), 2.52 (3H, s, SCH_3), and 1.65—0.86 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 255 (ε 14500), 271 (ε 13100, sh), and 310 nm (ε 9560). Found: C, 65.36; H, 7.73; N, 3.40%. Calcd for $C_{22}H_{31}NS_3$: C, 65.14; H, 7.70; N, 3.45%.

5-Cyano-3,4′-dihexyl-5′-methylthio-2,2′-bithiophene (45): Reaction of **44** (196 mg, 0.43 mmol) with CuCN (73 mg, 0.82 mmol) in NMP (3 cm^3) afforded **45** (139 mg, 80%): Pale yellow oil; Mass *m/z* 405, 406, and 407 (M^+, M^++1, and M^++2); IR (neat) 2215 (CN), 1455, 1380, 1130, 855, and 725 cm^{-1}; ^{1}H NMR (90 MHz) δ=7.40 (1H, s, ThH), 6.97 (1H, s, ThH), 2.8–2.5 (4H, m, $\underline{CH_2}$–C_5H_{11}), 2.44 (3H, s, SCH_3), and 1.65—0.86 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 266 (ε 8010) and 341 nm (ε 14800). Found: C, 65.35; H, 7.77; N, 3.38%. Calcd for $C_{22}H_{31}NS_3$: C, 65.14; H, 7.70; N, 3.45%.

3,3′-Dihexyl-5′-methylthio-2,2′-bithiophene-5-carbaldehyde (41): To a solution of **39** (404 mg, 0.88 mmol) and TMEDA (109 mg, 0.93 mmol) in THF (10 cm^3) drops of butyllithium (1.6 mol dm^{-3}; 0.58 cm^3, 0.93 mmol) in hexane were added below −80 °C over 10 min under Ar atmosphere. After this mixture was stirred for 20 min at −80 °C, DMF (0.34 cm^3, 4.4 mmol) was added at −80 °C over 10 min. The mixture was stirred for 1 h at room temperature and was poured into 1 M HCl at −10 °C with stirring and then neutralized by addition of saturated aq $NaHCO_3$. The organic layer and the extracts from the aqueous solution with dichloromethane were combined and washed with brine. The residue obtained after removal of the solvent was chromatographed on silica gel (2.8×8 cm) with a mixture of hexane and benzene (3 : 2) to afford **41** (212 mg, 59%): Pale green oil; ; Mass *m/z* 408, 409, and 410 (M^+, M^++1, and M^++2); IR (neat) 1675 (CO), 1455, 1240, 1155, and 670 cm^{-1}; ^{1}H NMR (90 MHz) δ=9.85 (1H, s, CHO), 7.63 (1H, s, ThH), 6.91 (1H, s, ThH), 2.7—2.3 (4H, m, $\underline{CH_2}$–C_5H_{11}), 2.53 (3H, s, SCH_3), and 1.68—0.76 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 267 (ε 16600) and 335 nm (ε 10900). Found: C, 64.75; H, 7.90%. Calcd for $C_{22}H_{32}OS_3$: C, 64.66; H, 7.89%.

3,4′-Dihexyl-5′-methylthio-2,2′-bithiophene-5-carbaldehyde (46): Reaction of **44** (228 mg, 0.50 mmol) with TMEDA (62 mg, 0.53 mmol), butyllithium (1.6 mol dm^{-3}; 0.33 cm^3, 0.53 mmol), and DMF (0.30 cm^3, 3.9 mmol) in THF (10 cm^3) afforded **46** (97 mg, 48%): Pale green oil; ; Mass *m/z* 408, 409, and 410 (M^+, M^++1, and M^++2); IR (neat) 1670 (CO), 1455, 1245, 1155, and 670 cm^{-1}; ^{1}H NMR (90 MHz) δ=9.74 (1H, s, CHO), 7.49 (1H, s, ThH), 6.99 (1H, s, ThH), 2.8—2.4 (4H, m, $\underline{CH_2}$–C_5H_{11}), 2.37 (3H, s, SCH_3), and 1.68—0.75 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 272 (ε 7800) and 365 nm (ε 14200). Found: C, 64.50; H, 7.85%. Calcd

for $C_{22}H_{32}OS_3$: C, 64.66; H, 7.89%.

3,3′-Dihexyl-5-methylthio-5′-nitro-2,2′-bithiophene (42): To a solution of **38** (400 mg, 1.05 mmol) in a mixture of THF and acetic anhydride (3 : 5, 8 cm^3) was added dropwise a solution of HNO_3 (111 mg, 1.16 mmol) in acetic anhydride (0.20 cm^3) by a syringe at 5 °C over 15 min. The reaction mixture was stirred for 3 h and kept in a refrigerator for 24 h. Poured into aq KOH (2 M, 25 cm^3), the mixture was extracted with CH_2Cl_2. The extracts were washed with brine. The residue after removal of the solvent was chromatographed on alumina (3.2×15 cm) with a mixture of hexane and benzene (9 : 1) to give **42** (322 mg, 72%): Orange oil; Mass *m/z* 425, 426, and 427 (M^+, M^++1, and M^++2); IR (neat) 1505, 1445, 1330, 1240, 1080, 865, and 815 cm^{-1}; ^{1}H NMR (90 MHz) δ=7.79 (1H, s, ThH), 6.92 (1H, s, ThH), 2.6—2.3 (4H, m, $\underline{CH_2}$–C_5H_{11}), 2.53 (1H, s, SCH_3) and 1.78—0.86 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 285 (ε 12250) and 376 nm (ε 7400). Found: C, 59.47; H, 7.30; N, 3.24%. Calcd for $C_{21}H_{31}NO_2S_3$: C, 59.26; H, 7.34; N, 3.29%.

3,4′-Dihexyl-5′-methylthio-5-nitro-2,2′-bithiophene (47): Reaction of **43** (183 mg, 0.48 mmol) in a mixture of THF and acetic anhydride (1 : 3, 6 cm^3) with HNO_3 (56 mg, 5.3 mmol) in acetic anhydride (0.50 cm^3) gave **47** (91 mg, 44%): Orange oil; Mass *m/z* 425, 426, and 427 (M^+, M^++1, and M^++2); IR (neat) 1500, 1435, 1400, 1325, 1200, 1080, 815, and 735 cm^{-1}; ^{1}H NMR (90 MHz) δ=7.74 (1H, s, ThH), 7.05 (1H, s, ThH), 2.8—2.5 (4H, m, $\underline{CH_2}$–C_5H_{11}), 2.47 (1H, s, SCH_3), and 1.80—0.76 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 284 (ε 11400) and 409 nm (ε 14300). Found: C, 59.51; H, 7.38; N, 3.11%. Calcd for $C_{21}H_{31}NO_2S_3$: C, 59.26; H, 7.34; N, 3.29%.

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