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Synthesis and Properties of α,ω-Disubstituted Oligo(3-hexylthiophene)s and Oligothienoquinonoids in Head-to-head Orientation

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The two types of highly-ordered oligo(3-hexylthiophene)s in head-to-head orientation, a series of α,ω-disubstituted oligothiophenes and a series of bis(dicyanomethylene)oligothienoquinonoids, were synthesized. The properties of these compounds are discussed on the basis of the electronic spectra and cyclic voltammetry.

We recently measured the third-order nonlinear optical responses of the α,ω-disubstituted oligo(3-hexylthiophene) derivatves **1**—**20** (Chart 1) and the bis(dicyanomethylene)oligothienoquinonoid compounds **21**—**23** (Chart 2) in regularly ordered head-to-head (H–H) orientation. We found that their third-order hyperpolarizabilities $\langle\gamma\rangle$ increase by introduction of the electron-withdrawing substituents at the terminal positions of the conjugated chain, with increasing the number of thiophene rings, and particularly with increasing the molecular planarity.$^{1)}$

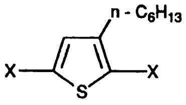
Nonlinear optical behavior observed in these oligo(3-hexylthiophene) derivatives in H–H orientation prompted us to investigate their electronic properties in detail. In this paper, we describe the electronic and electrochemical properties of the title compounds **1**—**23** (Charts 1 and 2) and the closely related derivatives **30**—**32** (Chart 3) as well as their syntheses.

Results and Discussion

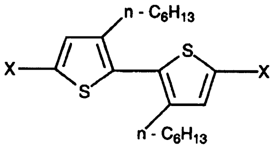
Synthesis of Oligo(3-hexylthiophene) Derivatives 2—20. Synthesis of the title compounds starts with the bromination of the oligo(3-hexylthiophene)s with *N*-bromosuccinimide (NBS); this is followed by the homo coupling, as shown in Scheme 1. Thus in every formed oligothiophene a regularly ordered orientation, i.e., in the H–H linkage of the 3-hexylthiophene unit, can be obtained. The α,ω-dibromides **2**, **7**, **12**, and **17** were converted to the corresponding disubstituted oligothiophenes by the direct or tandem substitution reactions, as illustrated in Scheme 2.

Monobromination of 3-alkylthiophenes with NBS in a mixture of chloroform and acetic acid is known to give the more crowded products: 3-alkyl-2-bromothiophenes selectively.$^{2)}$ In practice, treatment of 3-hexylthiophene (**1**) (thiophene number n=1) with 2 equivalents of NBS at room temperature first afforded 2-bromo-3-hexylthiophene (**24**) and then heating the mixture produced 2,5-dibromo-3-hexylthiophene (**2**) in 95% yield. 3,3′-Dihexyl-2,2′-bithiophene (**6**) (n=2) was prepared by an oxidative H–H homo coupling of the lithiated thiophene derived from the monobromide **24** in the presence of iron(III) acetylacetonate (Fe(acac)$_3$)$^{3)}$ in 63% yield, along with a small amount of its head-to-tail (H–T) isomer, 3,3′-dihexyl-2,5′-bithiophene, and a considerable amount of the reduction product **1**. Several coupling reactions using nickel or magnesium reagents which are known to be effective for symmetrical and unsymmetrical biaryl syntheses$^{4)}$ were attempted for the bithiophene synthesis, but all attempts were unsuccessful, yielding only the reduction product. The quaterthiophene **11** (n=4) could be prepared in 60% yield by a coupling reaction of the 5-bromobithiophene **25**, which was prepared from the compound **6**. Similarly, the octithiophene **16** (n=8) was prepared from the bromide **26** in 45% yield. The bithiophene **30** (n=2) with the bulky dodecyl side-chain could also be prepared in 70% yield by the homo coupling reaction of the bromide **29** (Chart 3). These oligo(3-alkylthiophene)s are liquid or low-melting substances. As expected, these are thermally stable and soluble in organic solvents such as hexane and benzene.

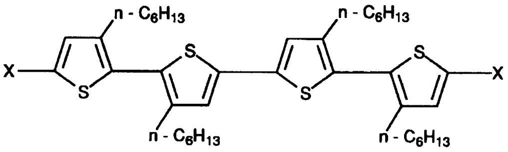
Using this elongation procedure, an oxidative coupling between bromides, **25** (n=2) and **26** (n=4), was also carried out under the same conditions as those for homo coupling to afford the hexamer **27** (n=6) (26%) of 3-hexylthiophene in H–H orientation together with **11** (18%) and **16** (15%), as shown in Scheme 3. However,



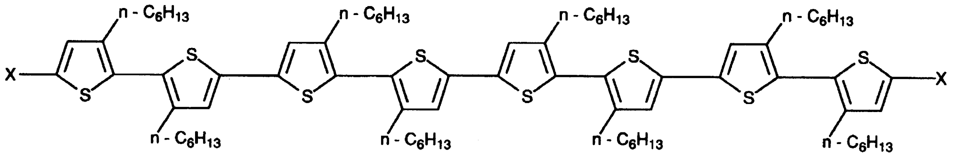
1 : X = H
2 : = Br
3 : = CN
4 : = CO_2H
5 : = CHO



6 : X = H
7 : = Br
8 : = CN
9 : = CO_2H
10 : = CHO

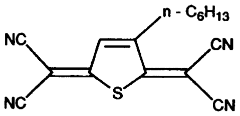


11 : X = H
12 : = Br
13 : = CN
14 : = CO_2H
15 : = CHO

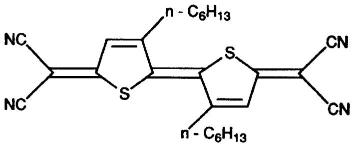


16 : X = H
17 : = Br
18 : = CN
19 : = CO_2H
20 : = CHO

Chart 1.



21



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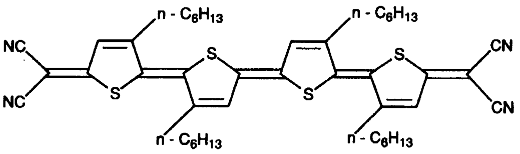
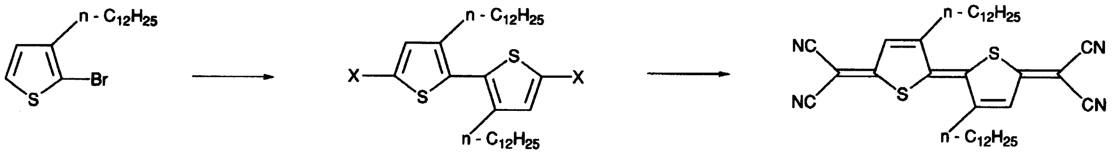


23

Chart 2.



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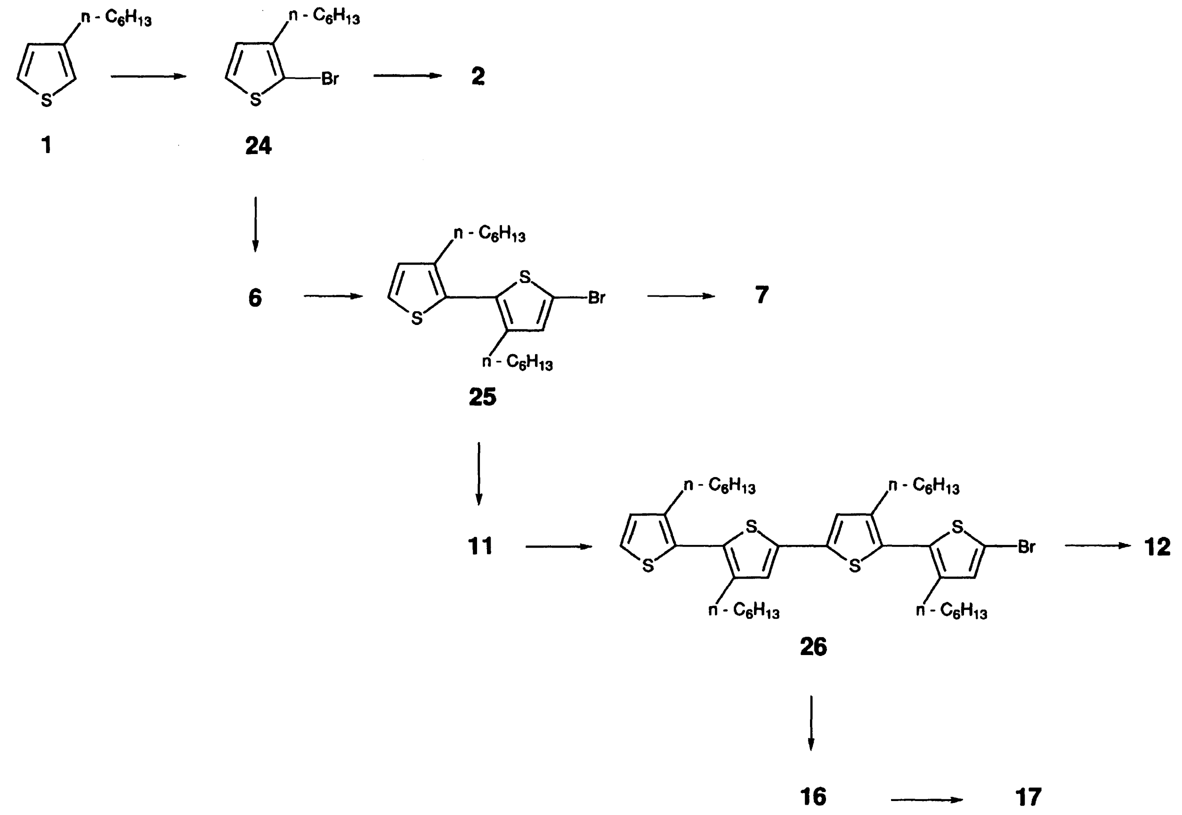
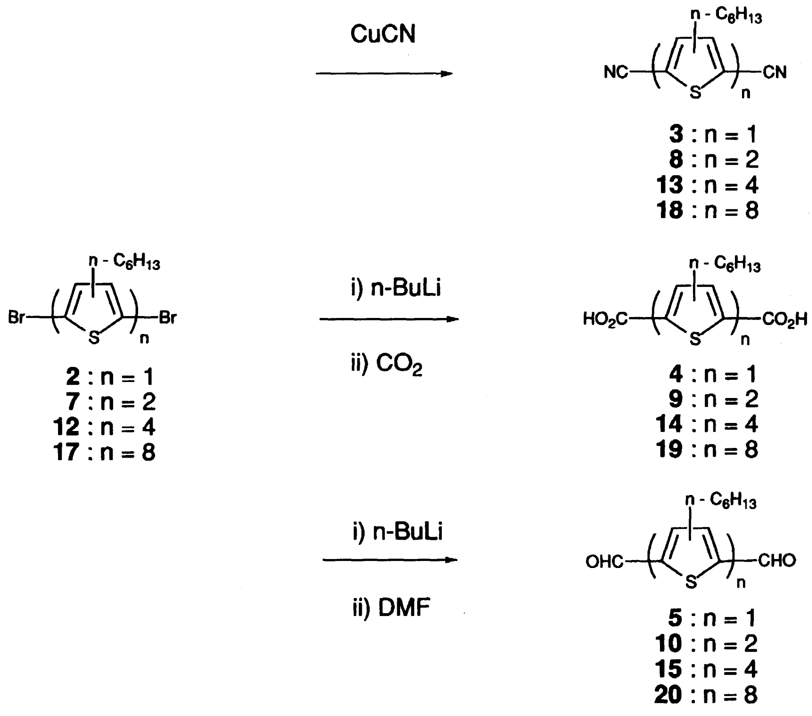
30 : X = H
31 : = Br

32

Chart 3.



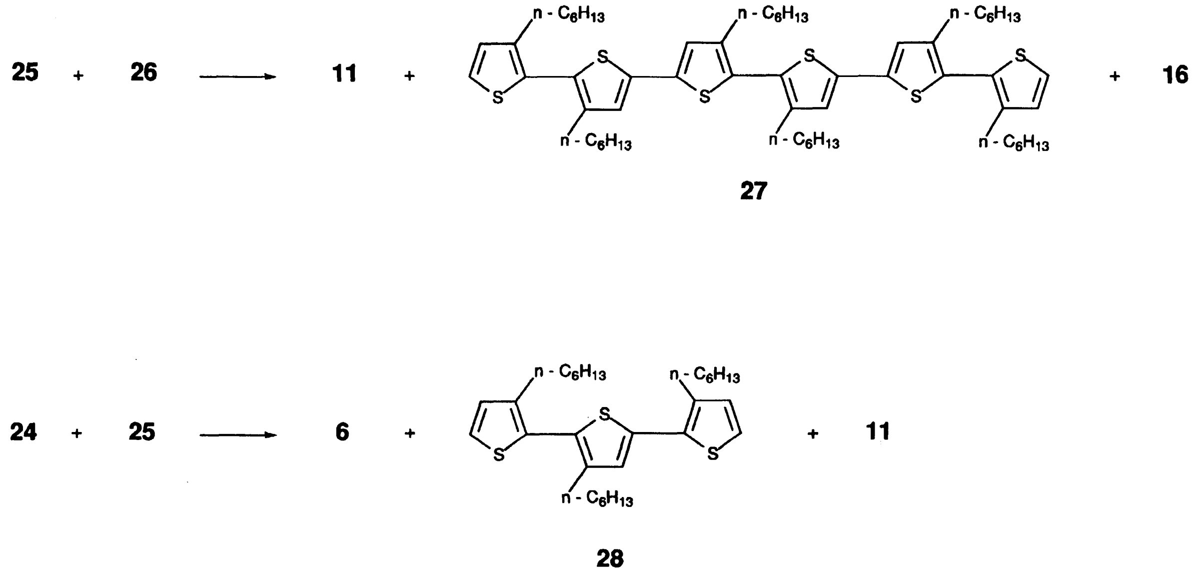
Scheme 1.



Scheme 2.

in the case of cross coupling reaction of the bromides, **24** (n=1) and **25** (n=2), the compound **28** (n=3) in H–H : T–H orientation was obtained in 43% yield along with **6** (50%) and **11** (20%).

The dibromides **2** (n=1), **7** (n=2), **12** (n=4), and **17** (n=8) were converted to other α,ω-disubstituted oligothiophene derivatives as follows. Treatment with copper(I) cyanide (CuCN) in N-methyl-2-pyrrolidone (NMP) gave the corresponding dicyanides **3**, **8**, **13**, and **18** in 59—76% yields.



Scheme 3.

Recently Nakayama and Fujimori reported that reaction of the lithiated α-terthiophene with *N*,*N*-dimethylformamide (DMF) gave α-terthiophene-5,5″-dicarbaldehyde.[5] Using this method, the lithiated oligothiophenes prepared from the dibromides (**2**, **7**, and **12**) were also converted to the corresponding dialdehydes, **5** (n=1), **10** (n=2), and **15** (n=4), in moderate yields. In spite of the presence of eight thiophene rings, dilithiated octithiophene from the dibromide **17** was readily formed and was converted to the octithiophenedicarbaldehyde **20** (n=8), but the yield was low (32%).

Reactions of the lithiated oligothiophenes with gaseous carbon dioxide afforded the dicarboxylic acids **4** (n=1), **9** (n=2), **14** (n=4), and **19** (n=8).

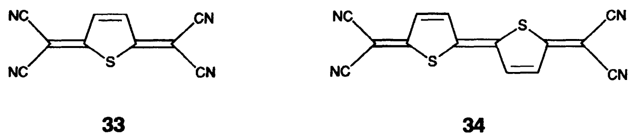
Synthesis of Oligothienoquinonoid Compounds 21, 22, 23, and 32. In connection with studies on properties of the acceptor molecules, many synthetic methods for 7,7,8,8-tetracyanoquinodimethane (TCNQ) and its polynuclear benzenoid derivatives, as well as the isoelectronic ones such as furan and thiophene ring, have been developed.[6] Gronowitz and Uppstrom reported that 2,5-dibromothiophene reacts with tetracyanoethylene oxide (TCNEO)[7] in 1,2-dibromoethane to afford 2,5-bis(dicyanomethylene)-2,5-dihydrothiophene (**33**) (Chart 4).[8] Also Yui et al. reported that the reaction of sodium dicyanomethanide with 5,5′-dibromo-2,2′-bithiophene and then oxidation with bromine–water gave the binucleic quinonoid compound **34** (Chart 4).[9]

We applied these methods to the preparation of compounds **21**, **22**, and **23**, as illustrated in Scheme 4. The reaction of **2** with TCNEO in 1,2-dibromoethane gave no desired bis(dicyanomethylene) product. When the reaction was carried out in 1,3-dibromopropane in the presence of copper(I) chloride (CuCl),[9] the compound **21** was obtained in 32% yield. Treatment of **7** with TCNEO in the presence of CuCl gave the binucleic quinonoid **22** in only 10% yield, while the reaction with sodium dicyanomethanide afforded the compound **22** in 46% yield. The latter reaction also took place for 5,5′-dibromo-3,3′-didodecyl-2,2′-bithiophene (**31**), yielding the corresponding quinonoid **32** in 34% yield (Chart 3). The quaterthienoquinonoid **23** was similarly obtained from the dibromide **12** in 27% yield. The bis(dicyanomethylene) compounds **21**, **22**, **23**, and **32** thus obtained were thermally stable and soluble in ordinary organic solvents.

Attempts to synthesize the higher homolog, octithienoquinonoid compound from the dibromooctithiophene **17**, using TCNEO or sodium dicyanomethanide, were unsuccessful.

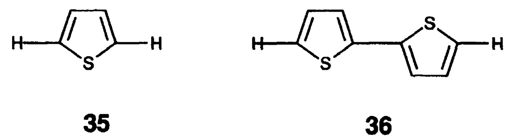
Electronic Absorption Spectra of Oligothiophenes and Bis(dicyanomethylene)oligothienoquinonoids. The longest wavelength absorption maxima (λ/nm) and the molar extinction coefficients (ε) of the oligo(3-hexylthiophene) compounds **1**—**20** together with those of the unsubstituted compounds, thiophene (**35**) and 2,2′-bithiophene (**36**) (Chart 5), taken in tetrahydrofuran (THF), are listed in Table 1.

Table 1 shows that there is little difference in absorption maxima ($\Delta\lambda$=3 nm) and molar extinction coeffi-



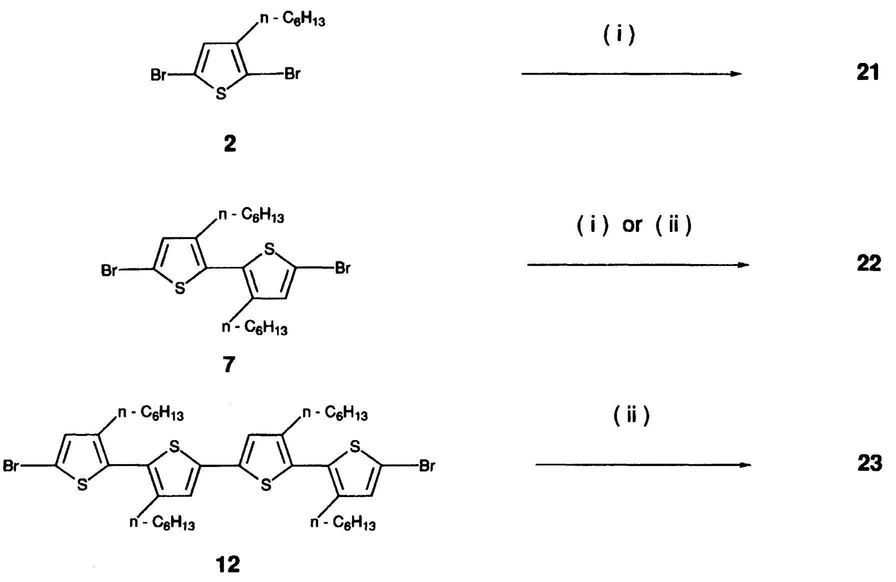
33 **34**

Chart 4.



35 **36**

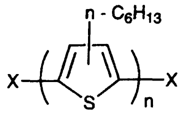
Chart 5.



(i) TCNEO / CuCl in $BrCH_2CH_2CH_2Br$, (ii) NaH / $CH_2(CN)_2$ - Br_2 (H_2O)

Scheme 4.

Table 1. Longest Wavelength Absorption Maxima (λ/nm)[a] and Molar Extinction Coefficients (ε) of Compounds **1**—**20**, **35**, and **36** in THF



Thiophene number n	X=H	X=Br	X=CN	X=CO_2H	X=CHO
1	**1** 234 (6850) **35** 231 (7100)	**2** 241 (8600)	**3** 269 (15000)	**4** 273 (14500)	**5** 294 (14300)
2	**6** 244 (14000) **36** 303 (10600)	**7** 244 (12500)	**8** 288 (14500)	**9** 297 (15500)	**10** 317 (16600)
4	**11** 337 (17600)	**12** 343 (23300)	**13** 348 (27200)	**14** 351 (28400)	**15** 365 (26200)
8	**16** 367 (55700)	**17** 367 (58100)	**18** 371 (57400)	**19** 373 (55000)	**20** 379 (59200)

a) For other absorption maxima see Experimental.

cients ($\Delta\varepsilon$=250) between 3-hexylthiophene (**1**) and the non-alkylated thiophene **35**, indicating that the hexyl substituent at 3-position of the thiophene ring does not produce any change of the electronic structure of thiophene. In a series of oligothiophenes **1** (n=1, λ=234), **6** (n=2, λ=244), **11** (n=4, λ=337), and **16** (n=8, λ=367), the bathochromic shift of the absorption maxima is observed with increasing numbers of thiophene rings. However, the extent of the shift is not regular among these compounds. The shift on going from the bithiophene **6** to the quaterthiophene **11** is larger than that from **1** to **6** or from **11** to **16**. As for the intensities, a large reduction of the molar extinction coefficient for the quaterthiophene **11** (ε=17600) from the calculated value ($\varepsilon = 2\times14000$) for the compound, which is regarded as a dimer of the bithiophene **6** (ε=14000), is observed, but the molar extinction coefficient for the octithiophene **16** (ε=55700) is three times greater than that for the quaterthiophene **11**.

These results suggest that the steric crowding between the hexyl group and the sulfur atom in the neighboring thiophene ring renders the main chain of the molecule less planar. In the case of bithiophene **6**, an additional steric hindrance between two hexyl substituents in H–H orientation exists, as shown in Chart 6, and prevents the conjugation through two thiophene rings, resulting in a small bathochromic shift (10 nm from **1**) and a large hyperchromism (almost twice from the molar extinction coefficient of **1**). On the contrary, 2,2′-bithiophene (**36**) corresponding to 3,3′-dihexyl-2,2′-bithiophene (**6**) exhibits the extended π-electronic conjugation through two thiophene rings because of absence of the steric hindrance. It shows a large bathochromic shift ($\Delta\lambda$=72 nm from **35**) and a large

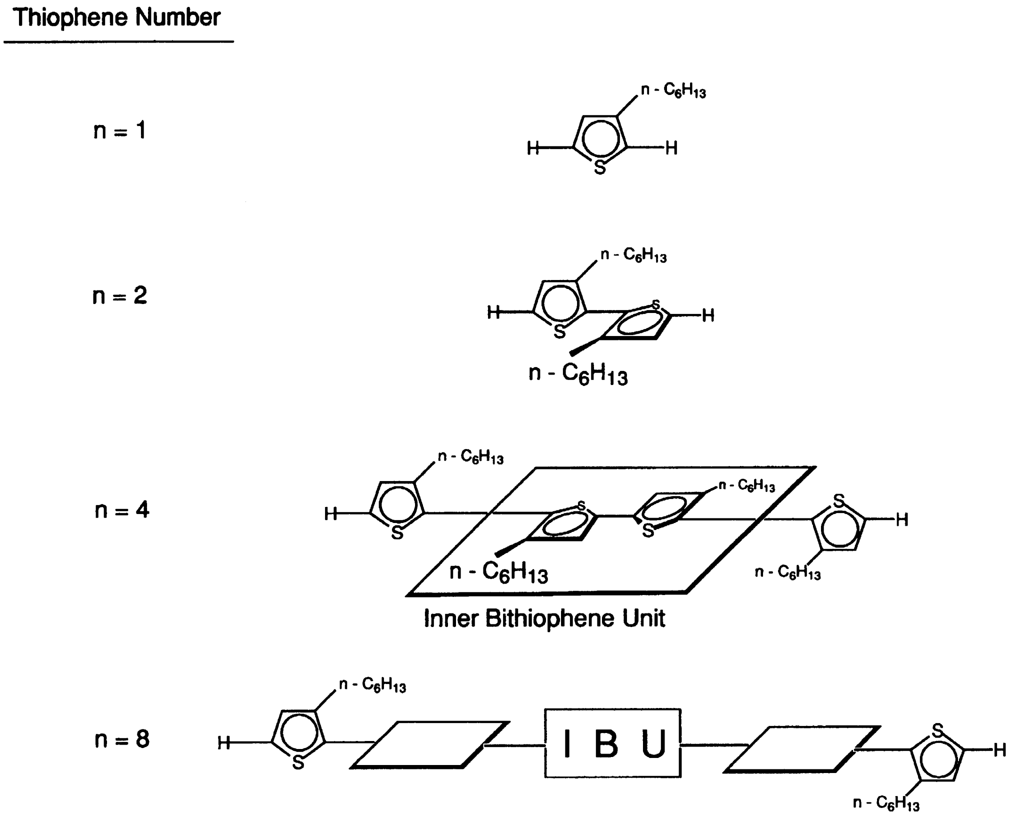


Chart 6.

reduction of the intensity from the calculated value ($\varepsilon = 2 \times 7100$) for the twisted thiophene dimer with no π-electronic conjugation.

As has been observed in the polymer composed of 3-alkylthiophene,[10] the hexyl side-chain in these oligo(3-hexylthiophene)s seem sterically large enough to cause the π-conjugation between thiophene rings to be small. However, as is seen from Table 1, the large bathochromic shift (93 nm) of the longest wavelength band for the quaterthiophene **11** with hexyl substituent from the longest wavelength band for the bithiophene **6** appears similar to the bathochromic shift of that for the bithiophene **36** without hexyl substituent from that for the thiophene **35**, as described above. This indicates that the internal bithiophene unit (IBU) in tail-to-tail (T–T) orientation is a good conjugation chromophore because of the absence of steric hindrance between two internal thiophene rings. In the same manner, the octithiophene **16** should be regarded as a trimer of the IBU with two additional thiophene rings at the terminal positions. However, again the alternately twisting linkage between these three IBUs results in the relatively small bathochromic shift (30 nm from the quaterthiophene **11**) along with the large hyperchromic effect (3.2 times based on the ε value of **11**), suggesting the zigzag structure for the octithiophene **16**, as shown in Chart 6.

The bathochromic shift and change of molar extinction coefficient with an increase of thiophene rings in a series of the unsubstituted oligo(3-hexylthiophene)s are also observed in a series of the bromides. The other three derivatives bearing the substituents of CN, CO_2H, and CHO also showed the similar tendency, but the extent of the bathochromic shifts varies depending on the substituents at the terminals. For example, the dicarbaldehyde **15** with four thiophene rings shows the absorption maximum at 365 nm, which is almost the same wavelength as those of the unsubstituted and bromo derivatives (**16** and **17**) with eight thiophene rings.

Table 1 shows that in each series of oligothiophenes with the same number of thiophene rings the absorption maxima shift to the longer wavelength in the order of substituent $X = H \leq Br < CN < CO_2H < CHO$, as has been observed for benzene derivatives of a push–pull type such as para-substituted aniline and anisole.[11] This result suggests that in the spectra of mono- (**1**—**5**) and bithiophenes (**6**—**10**) the hexyl side-chain acts as a push part, i.e., as an electron-donative substituent. On the other hand, in the spectra of quater- (**11**—**15**) and octithiophenes (**16**—**20**) the electronic interaction occurs between the electron-withdrawing substituents and the IBU to achieve the push–pull character which is responsible for the observed bathochromic shift for the IBU itself. This suggests that the IBU acts as the electron-donor moiety, as illustrated in Chart 7.

Electronic absorption spectra of thienoquinonoid compounds **21**, **22**, and **23** are shown in Fig. 1. The absorption bands in all spectra are similar in shape and shift to the longer wavelength with enhancement of the

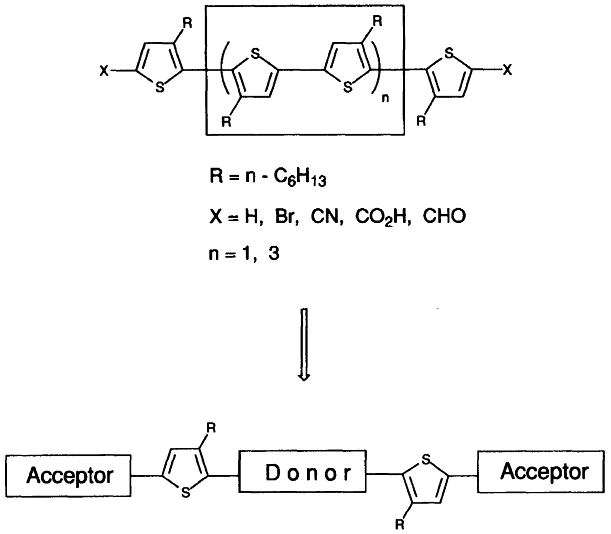


Chart 7.

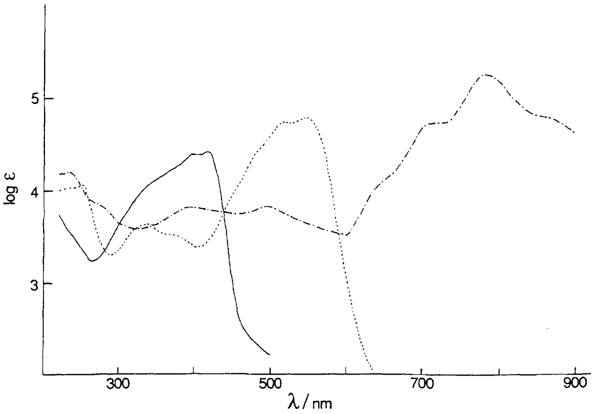


Fig. 1. Electronic absorption spectra of the compounds **21** (——), **22** (- - -), and **23** (- - -) in THF.

intensities in the order of **21** < **22** < **23**, indicating that the electronic structures are similar among compounds **21**—**23** and are the extended quinonoid systems with conjugation. Since little difference is observed in the electronic spectra between the 3-hexyl derivative and the non-alkylated one (between **21** and **33**, or between **22** and **34**) (Chart 4) (See Experimental),[9] we conclude that the existence of the hexyl substituent at 3-position of the thiophene ring serves for alignment of the 3-hexylthiophene moieties in a transoid disposition without distortion of their electronic structures.

Solvent Effects in Electronic Absorption Spectra. To continue the studies on nonlinear optical properties of oligo(3-hexylthiophene)s in H–H orientation,[1] we examined the solvent effect (solvatochromism)[12] in the electronic absorption spectra for series of unsubstituted oligothiophenes (**1**, **6**, **11**, and **16**), dicyano compounds (**3**, **8**, **13**, and **18**), and thienoquinonoids (**21**, **22**, and **23**).

The shifts from the longest wavelength absorption maximum in hexane to those in other solvents were plotted against the dielectric constants (DC)[13] of solvents. Solvents used were hexane (DC=1.9), THF (7.6), dichloromethane (8.9), acetone (20.7), ethanol (24.6), DMF (36.7), and acetonitrile (37.5). The absorption curves were unchanged in all solvents. The results in each series of compounds are shown in Fig. 2 in which (a) is for unsubstituted oligothiophenes, (b) is for dicyano compounds, and (c) is for thienoquinonoids.

The results plotted in Fig. 2 widely scatter without linear dependence, revealing that the longest wavelength absorption maxima of the oligothiophene derivatives shift either to the shorter or the longer wavelengths by changing solvents. Also, the variation in shift is greater in the planar thienoquinonoid series (c) than those in the other series of oligothiophene derivatives (a) and (b). As exemplified in the case of compound **22**, a large bathochromic shift ($\Delta\lambda$=22 nm) is observed by changing the solvent from hexane to DMF. However, it is apparent that in all series of compounds the shifts of the absorption maxima do not correlate with the DC values of the solvents used, as mentioned above. For example, the absorption maximum of **22** in DMF is nearly the same as that in dichloromethane, although the DC is very different for these two solvents. On the the other hand, the shifts of **22** are very different for DMF ($\Delta\lambda$=22 nm) and for acetonitrile ($\Delta\lambda$=9 nm), although the DC is almost the same for these two solvents.

The observed result that the shifts do not correlate with the DC prompted us to use the donor number (DN) of solvents instead of the DC. Since the donor number represents the extent of the electron-donating property for the electron-accepting substances, the solvent with the large DN would stabilize the acceptor molecule more by forming the intermolecular charge-transfer (CT) complex.[14] The shifts from the wavelength of the absorption maximum in acetonitrile with DN of 14.1 to those in other solvents were plotted against the DN. The results for each series of compounds (a), (b), and (c) are shown in Fig. 3. Solvents used are acetone (DN=17.0), THF (20.0), ethanol (20.0), and DMF (26.6).

As can be seen from Fig. 3, the shifts of the maxima seem to be related to the DN of solvent. Both series of the unsubstituted oligothiophenes (a) and the thienoquinonoids (c) exhibit the bathochromic shift with increasing DN. This behavior might reflect the facts that these oligothiophene derivatives (a) and (c) have the electron-accepting properties and that the intermolecular CT interactions between these compounds and solvents increase with an increase of DN.

On the other hand, the trend does not hold for the series of α,ω-dicyano compounds (b). The maxima of the thiophene (**3**) and the octithiophene (**18**) shift to the longer wavelength similarly to those of compounds (a) and (c), while those of the bithiophene (**8**) and the quaterthiophene (**13**) shift to the shorter wavelength

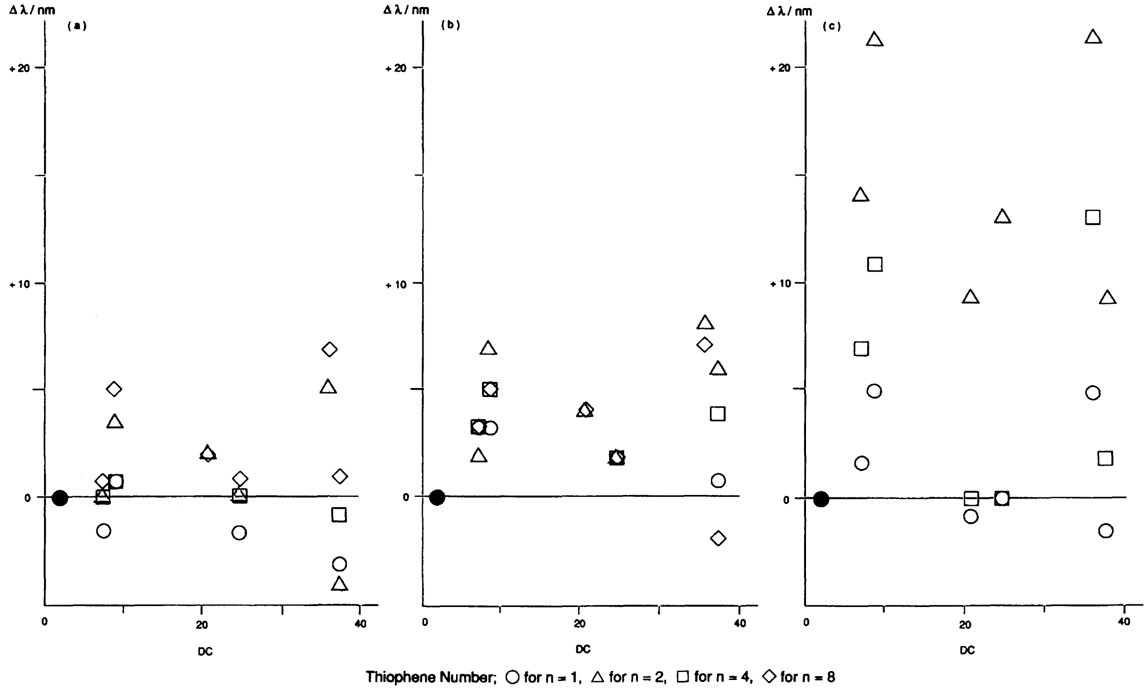


Fig. 2. Plots of the shift (Δλ/nm) from the absorption maximum (black circle) in hexane against dielectric constants (DC) of solvents. (a) Unsubstituted oligo(3-hexylthiophene)s (**1**, **6**, **11**, and **16**). (b) α,ω-Dicyanides (**3**, **8**, **13**, and **18**). (c) Thienoquinonoids (**21**, **22**, and **23**).

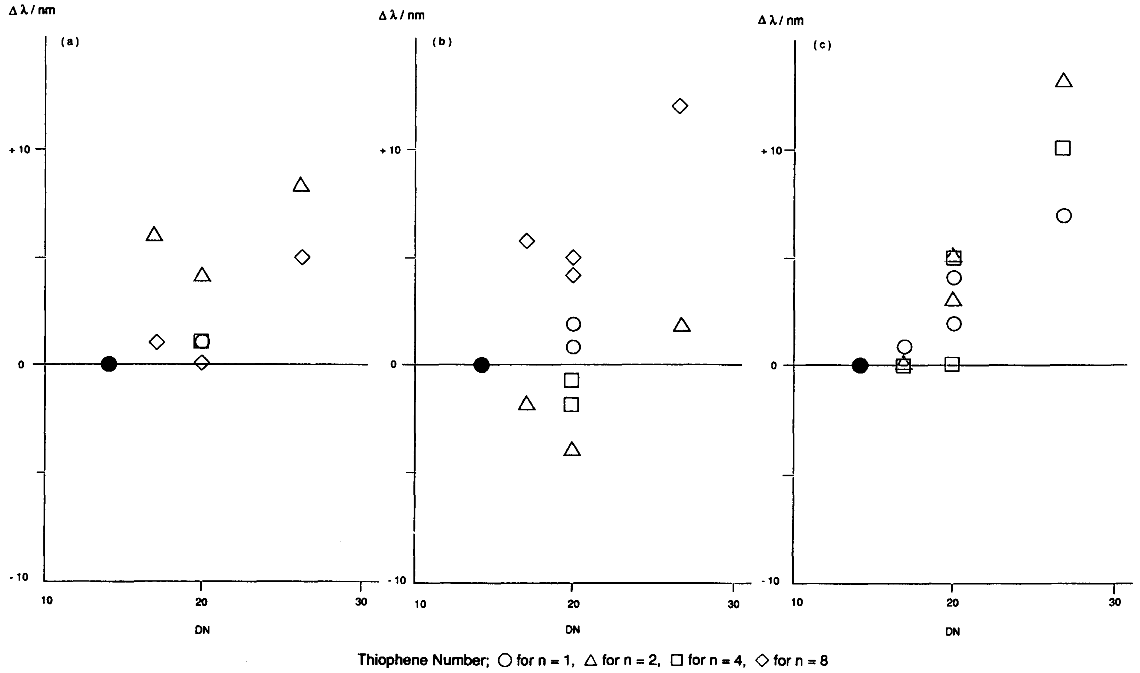


Fig. 3. Plots of the shift (Δλ/nm) from the absorption maximum (black circle) in acetonitrile against donor numbers (DN) of solvents. (a) Unsubstituted oligo(3-hexylthiophene)s (**1**, **6**, **11**, and **16**). (b) α,ω-Dicyanides (**3**, **8**, **13**, and **18**). (c) Thienoquinonoids (**21**, **22**, and **23**).

with increasing DN. This suggests that the property of the interaction with solvents in the case of the compounds (b) is different from the intermolecular CT interaction in the cases of compounds (a) and (c).

Thus, we suggest that the oligothiophene derivatives (a) and (c) undergo stabilization by the intermolecular CT interaction and that the thienoquinonoid compounds (c) with high planarity and conjugation exhibit stronger interactions with solvents than the oligothiophenes (a).

Redox Properties of Oligothiophene Derivatives. The electrochemical property of the oligothiophene cyano derivatives was studied by cyclic voltammetry. Their half-wave reduction potentials are listed in Table 2, together with those of the closely related compounds **33** and **34**.[9)]

Recently it was reported that the didodecylsexithiophene with conjugation is reduced at the redox potentials of −2.27 and −2.40 V, forming the radical anion and the dianion, respectively.[15)] In the oligothiophenes **6** (n=2) and **11** (n=4), however, redox potentials could not be determined clearly; the irreversible reactions over the range between −1.00 and −2.50 V suggest the instability of the reduction products. On the other hand, the corresponding oligothiophenes **8** and **13** bearing the cyano substituent at the terminals showed the reversible redox behavior, although some irreversible reactions also competed with the electron transfer cycles at a small rate. In compounds **8** and **13**, two redox waves were observed in the potential region between −1.70 and −2.00 V, suggesting that the cyano substituent enhances the electron-accepting ability of the molecule and the stability of the reduction product. The reduction potentials are almost the same for these bi- (**8**) and quaterthiophenes (**13**) and the fashion of the electron transfer processes is also similar. This suggests that the cyano function not only lowers the LUMO level of the molecules but also takes part in the electron-accepting processes.

Reduction of the thienoquinonoids **21**—**23** would be expected to proceed via two one-electron transfer processes, as represented for the case of **22** in Scheme 5. The first step is assigned to one electron transfer to form the radical anion $\mathbf{22}^{-\bullet}$ and the second step is to form the corresponding dianion $\mathbf{22}^{2-}$. The compounds **21** (n=1) and **23** (n=4) exhibited two reversible redox waves, while the compound **22** (n=2) was reduced via a single two-electron transfer process, affording only one reversible wave at various sweep rates.

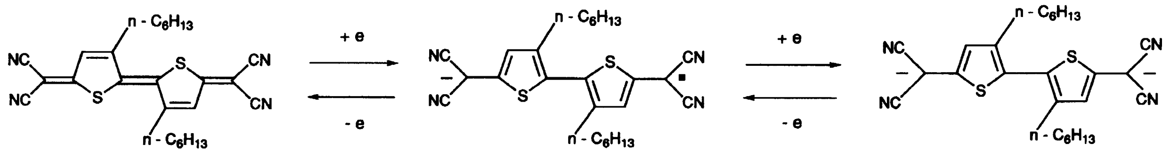
Table 2. Half-Wave Reduction Potentials[a)] of Compounds **8**, **13**, **21**—**23**, **33**, and **34**

	$E^1_{1/2}$/V	$E^2_{1/2}$/V	$\Delta E\ (E^1_{1/2}-E^2_{1/2})$/V
8	−1.76	−1.88	
13	−1.83	−1.95	
21	−0.06	−0.57	0.51
22	−0.34	−0.34	0.00
23	−0.07	−0.18	0.11
33[b)]	+0.07	−0.54	0.61
34[b)]	−0.03	−0.26	0.23

a) The redox potentials were measured at the scan rate 100 mV s^{-1} in dichloromethane containing 0.1 M tetrabutylammonium perchlorate by use of an Ag/AgCl standard electrode and a platinum working electrode. Under these conditions, the ferrocene radical cation (Fc$^+$) is reduced to generate the ferrocene (Fc) at +0.15 V. b) See Ref. 9.

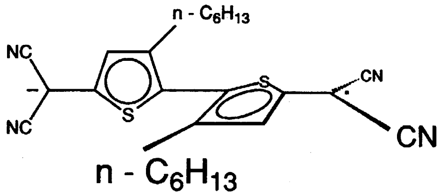
Table 2 shows that the planar thienoquinonoids are reduced at much lower potentials than the oligothiophene cyano derivatives. However, compounds **21** and **22** are reduced with more difficulty in every step than the corresponding non-alkylated compounds **33** and **34**,[9)] presumably reflecting the electron-donating property of the hexyl substituent. Since the first redox potentials ($E^1_{1/2}$) are almost the same for **21** and **23** but are lower than that of **22**, their radical anions $\mathbf{21}^{-\bullet}$ and $\mathbf{23}^{-\bullet}$ are more stable than $\mathbf{22}^{-\bullet}$. On the other hand, the second redox potential ($E^2_{1/2}$) for the dianion formation decreases with increasing number of thiophene rings. These results are explained by consideration of the magnitude of both the on-site Coulomb repulsion and the resonance stabilization of the reduction products. If only the effect of the on-site Coulomb repulsion is taken into account for the formation of the dianion, the thienoquinonoids might be reduced more readily with decreasing $\Delta E\ (E^1_{1/2}-E^2_{1/2})$ value; **21** (0.51)>**23** (0.11)>**22** (0.00). This is not true for the series of compounds **21**—**23**. Therefore, we conclude that the resonance effect plays a role for the stabilization of the reduction products in a series of thienoquinonoids in H–H orientation.

In the case of bithienoquinonoid **22**, contribution of the resonance effect for the stability of the radical anion $\mathbf{22}^{-\bullet}$ would be small, owing to the steric hindrance between the bulky alkyl chain and the sulfur atom of the adjacent thiophene ring, leading to a twisted structure of $\mathbf{22}^{-\bullet}$ (Chart 8), as observed in the bithiophene **6**. However in the case of the quater system **23** with one IBU, the electron-donative property of IBU, as shown in Chart 7, may contribute for the stability of $\mathbf{23}^{-\bullet}$, presumably by the intramolecular CT interaction between IBU and electron deficient radical site at the terminal. In the case of **22**, the energy difference between the radical anion ($\mathbf{22}^{-\bullet}$) and the dianion ($\mathbf{22}^{2-}$) is so small that little energy must be required for the formation of



22 $\mathbf{22}^{-\bullet}$ $\mathbf{22}^{2-}$

Scheme 5.



22$^{\cdot-}$

Chart 8.

the dianion from the radical anion. Thus the compound **22** exhibits a favorable reduction via a single two-electron transfer process. The fact that the bithiophene **34**[9] corresponding to **22** shows two pairs of reversible redox waves clearly indicates that the resonance effect contributes to the stability of the radical anion $\mathbf{34}^{-\bullet}$.

In summary, we found that electronic absorption maxima of the oligo(3-hexylthiophene) derivatives in H–H orientation shift to the longer wavelength with increasing numbers of the thiophene rings, with increasing electron-withdrawing ability of the substituent at the terminal positions, and with increasing molecular planarity. The finding in the electronic properties also relates to the behavior of the third-order hyperpolarizabilities $\langle\gamma\rangle$ observed for the compounds: **8** (n=2); 10×10^{-36}, **13** (n=4); 220×10^{-36}, and **18** (n=8); 956×10^{-36} esu for the cyano derivatives, and for the compounds: **11** (X=H); 68×10^{-36}, **12** (X=Br); 190×10^{-36}, and **15** (X=CHO); 300×10^{-36} esu for the quaterthiophenes.[1] The planar conjugated macrocycles showed the large hyperpolarizabilities $\langle\gamma\rangle$;[16] the quaterthienoquinonoid **23** also exhibited the large $\langle\gamma\rangle$, 19000×10^{-36} esu by a factor of ca. 100 as compared with the dicyanoquaterthiophene **13** with thiophene rings of the same number as **23**.

The electron acceptabilities observed for the oligothiophene derivatives increase by introduction of cyano substituent at the terminals and with increasing molecular planarity. The electron-accepting property of these compounds also relates to the behavior of their third-order hyperpolarizabilities $\langle\gamma\rangle$, as has been described above. Thus, the effect of intermolecular CT interaction which arises from the electron acceptabilities of the compounds discussed in this study enhances the third-order nonlinear optical property, similarly to that reported for the second-order nonlinear optical property.[17]

Experimental

The melting points were determined on a hot-stage apparatus and are uncorrected. IR spectra were measured on a JASCO 7300 spectrophotometer as KBr disks, unless otherwise stated; only significant absorptions are reported. Electronic spectra were determined in THF on a Shimadzu UV-2200A spectrophotometer (sh=shoulder). ^{1}H NMR spectra were measured in $CDCl_3$ solution on a JEOL FX-90 Q (90 MHz) spectrophotometer and were recorded in δ-values with TMS as an internal standard. The coupling constants (J) are given in Hz. Mass spectra were recorded with a Hitachi RM-50 or a JEOL JMS-O1SG-2 spectrophotometer operating at 75 eV using a direct inlet system. Cyclic voltammetry was performed on a BAS CV-27. Silica gel (Daiso gel 1001W or Merck 60) and alumina (Merck, Act II—III) were used for column chromatography. Dichloromethane was distilled over calcium hydride before use. THF was distilled from sodium benzophenone ketyl 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 solvent. 3-Hexylthiophene (**1**) was used as the starting material; it was purchased from Tokyo Kasei Chemicals Co., Ltd. Ether refers to diethyl ether.

2-Bromo-3-hexylthiophene (24):[18] To a solution of 3-hexylthiophene (**1**) (2.0 g, 12.0 mmol) in a mixture of chloroform and acetic acid (50 : 50 v/v, 20 cm^3) portions of NBS (4.0 g, 12.6 mmol) were added at 0 °C over 30 min. After being stirred for 30 min, the mixture was diluted with water and extracted with chloroform. The extracts were washed first with aqueous 2 M KOH (1 M=1 mol dm^{-3}) and then with water, and then dried. The residue obtained after removal of the solvent was chromatographed on silica gel (3.2×5 cm) with hexane to give the monobromide **24** (2.6 g, 88%): Colorless oil; Mass m/z 246 and 248 (M^+ and M^++2, based on ^{79}Br); IR (neat) 2950, 2920, and 2850 cm^{-1} (CH); ^{1}H NMR δ=7.05 (1H, d, J=5.6 Hz, ThH), 6.71 (1H, d, J=5.6 Hz, ThH), 2.54 (2H, t, J=7.6 Hz, $\underline{CH_2}$–C_5H_{11}), 1.80—1.10 (8H, m, CH_2–($\underline{CH_2}$)$_4$–CH_3), 0.88 (3H, m, CH_3); UV λ_{max} 238 nm (ε 7450). Found: C, 48.29; H, 6.07%. Calcd for $C_{10}H_{15}BrS$: C, 48.59; H, 6.12%.

Other monobromides **25** and **26** were prepared by employing the same procedure as that used for the monobromide **24**.

5-Bromo-3,3′-dihexyl-2,2′-bithiophene (25): 55% Yield from the bithiophene **6** (1.80 g, 5.39 mmol) (see below) and NBS (1.16 g, 6.52 mmol); Pale yellow oil; Mass m/z 412 and 414 (M^+ and M^++2, based on ^{79}Br); IR (neat) 2960, 2930, and 2860 cm^{-1} (CH); ^{1}H NMR 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=6.6 Hz, $\underline{CH_2}$–C_5H_{11}), 2.41 (2H, t, J=5.9 Hz, $\underline{CH_2}$–C_5H_{11}), 1.54—0.78 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 243 (ε 12200), 266 nm (sh, 8700). Found: C, 58.30; H, 7.14%. Calcd for $C_{20}H_{29}BrS_2$: C, 58.09; H, 7.07%.

The later fractions afforded the dibromide **7** (853 mg, 32%) (see below).

5-Bromo-3,3′,3″,3‴-tetrahexyl-2,2′ : 5′,5″ : 2″,2‴-quaterthiophene (26): 62% Yield from the quaterthiophene **11** (200 mg, 0.30 mmol) (see below) and NBS (55 mg, 0.31 mmol); Pale yellow oil; Mass m/z 744 and 746 (M^+ and M^++2, based on ^{79}Br); IR (neat) 2950, 2925, and 2855 cm^{-1} (CH); ^{1}H NMR 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}), 1.68—0.79 (44H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 230 (ε 20600), 341 nm (25000). Found: C, 64.69; H, 7.74%. Calcd for $C_{40}H_{57}BrS_4$: C, 64.39; H, 7.70%.

The later fractions gave 5,5‴-dibromo- 3,3′,3″,3‴- tetrahexyl-2,2′ : 5′,5″ : 2″,2‴-quaterthiophene (**12**) (37 mg, 15%

yield) (see below).

2,5-Dibromo-3-hexylthiophene (2):$^{19)}$ To a solution of 3-hexylthiophene (**1**) (480 mg, 2.86 mmol) in a mixture of chloroform and acetic acid (50 : 50 v/v, 15 cm^3) was added NBS (1.02 g, 5.72 mmol) in portions during 10 min at 30 °C. The mixture was refluxed with stirring for 30 min. After being diluted with water, the mixture was extracted with chloroform. The extracts were washed with aqueous 2 M KOH and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (3.5×25 cm) with hexane to give the dibromide **2** (585 mg, 95%): Colorless oil; Mass *m*/*z* 324, 326, and 328 (M$^+$, M$^+$+2, and M$^+$+4, based on ^{79}Br); IR (neat) 2960, 2930, and 2860 cm^{-1} (CH); ^{1}H NMR δ=6.77 (1H, s, ThH), 2.58 (2H, t, *J*=7.3 Hz, $\underline{CH}_2$–C_5H_{11}), 1.60—0.82 (11H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 241 (ε 8600), 257 nm (sh, 7350). Found: C, 36.79; H, 4.38%. Calcd for $C_{10}H_{14}Br_2S$: C, 36.83; H, 4.33%.

All other dibromides **7**, **31**, **12**, and **17** were also prepared by employing the same procedure as that used for the dibromide **2**.

5,5′-Dibromo-3,3′-dihexyl-2,2′-bithiophene (7): 95% Yield from the bithiophene **6** (1.00 g, 2.99 mmol) (see below) and NBS (1.07 g, 6.00 mmol); Colorless oil; Mass *m*/*z* 490, 492, and 494 (M$^+$, M$^+$+2, and M$^+$+4, based on ^{79}Br); IR (neat) 2950, 2925, and 2855 cm^{-1} (CH); ^{1}H NMR δ=6.90 (2H, s, ThH), 2.44 (4H, t, *J*=6.6 Hz, $\underline{CH}_2$–C_5H_{11}), 1.52—0.66 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 244 (ε 12500), 272 nm (sh, 9600). Found: C, 48.70; H, 5.85%. Calcd for $C_{20}H_{28}Br_2S_2$: C, 48.79; H, 5.73%.

5,5′-Dibromo-3,3′-didodecyl-2,2′-bithiophene (31): 95% Yield from the bithiophene **30** (590 mg, 1.17 mmol) (see below) and NBS (418 mg, 2.35 mmol); Colorless oil; Mass *m*/*z* 658, 660, and 662 (M$^+$, M$^+$+2, and M$^+$+4, based on ^{79}Br); IR (neat) 2950, 2920, and 2850 cm^{-1} (CH); ^{1}H NMR δ=6.90 (2H, s, ThH), 2.43 (4H, t, *J*=7 Hz, $\underline{CH}_2$–$C_{11}H_{23}$), 1.55—1.25 (40H, m, CH_2–$(\underline{CH}_2)_{10}$–CH_3), 0.88 (6H, t, *J*=5 Hz, CH_3); UV λ_{max} 247 (ε 11700), 278 nm (sh, 8900). Found: C, 58.34; H, 7.66%. Calcd for $C_{32}H_{52}Br_2S_2$: C, 58.17; H, 7.93%.

5,5′′′-Dibromo-3,3′,3′′,3′′′-tetrahexyl-2,2′ : 5′,5′′ : 2′′,2′′′-quaterthiophene (12): 97% Yield from the quaterthiophene **11** (476 mg, 0.71 mmol) (see below) and NBS (254 mg, 1.43 mmol); Pale yellow microcrystals (from ethanol), mp 59—60 °C; Mass *m*/*z* 822, 824, and 826 (M$^+$, M$^+$+2, and M$^+$+4, based on ^{79}Br); IR 2950, 2920, and 2845 cm^{-1} (CH); ^{1}H NMR δ=7.00 (2H, s, ThH), 6.93 (2H, s, ThH), 2.48—2.40 (8H, m, $\underline{CH}_2$–C_5H_{11}), 1.56—0.80 (44H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 238 (ε 20200), 343 nm (23300). Found: C, 58.00; H, 6.75%. Calcd for $C_{40}H_{56}Br_2S_4$: C, 58.24; H, 6.84%.

5,5′′′′′′′-Dibromo-3,3′,3′′,3′′′,3′′′′,3′′′′′,3′′′′′′,3′′′′′′′-octahexyl-2,2′ : 5′,5′′ : 2′′,2′′′ : 5′′′,5′′′′ : 2′′′′,2′′′′′ : 5′′′′′,5′′′′′′:2′′′′′′,2′′′′′′′-octithiophene (17): 91% Yield from the octithiophene **16** (176 mg, 0.13 mmol) (see below) and NBS (48 mg, 0.27 mmol); Pale yellow microcrystals (from hexane), mp 76—77 °C; Mass *m*/*z* 1486, 1488, and 1490 (M$^+$, M$^+$+2, and M$^+$+4, based on ^{79}Br); IR 2950, 2920, and 2855 cm^{-1} (CH); ^{1}H NMR δ=7.03 (6H, br s, ThH), 6.91 (2H, s, ThH), 2.55—2.41 (16H, m, $\underline{CH}_2$–C_5H_{11}), 1.66—0.54 (88H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 252 (ε 29300), 367 nm (58100). Found: C, 64.05; H, 7.40%. Calcd for $C_{80}H_{112}Br_2S_8$: C, 64.48; H, 7.58%.

3,3′-Dihexyl-2,2′-bithiophene (6) and Its H–T Isomer: To a solution of the bromide **24** (1.0 g, 4.0 mmol) in THF (28 cm^3) were added drops of butyllithium (1.6 mol dm^{-3}; 2.8 cm^3, 4.5 mmol) in hexane below −70 °C over 10 min under Ar atmosphere. After the mixture was stirred for 20 min, Fe(acac)$_3$ (1.4 g, 4.0 mmol) was added in portions over 30 min at −70 °C. After being stirred for 2 h at −70 °C, the mixture was diluted with water (30 cm^3), neutralized with 3 M HCl, and extracted with dichloromethane. The extracts were washed with brine. The residue obtained after removal of the solvent was chromatographed on silica gel (3.2×6 cm) with hexane to afford a mixture (650 mg) of the H–H bithiophene **6**, the H–T isomer of **6**, and 3-hexylthiophene (**1**). Distillation of the liquid, bp 50 °C/532 Pa (1 mmHg=133 Pa), gave the reduction product **1** (225 mg), leaving the mixture of bithiophenes (425 mg, 63%) in a flask. The isomeric mixture was again chromatographed on silica gel (3.2×44 cm) with hexane to afford **6** (352 mg), a mixture (57 mg) of H–H and H–T isomers in an almost 1 : 1 ratio, and the H–T isomer (10 mg) in order. H–H bithiophene **6**: Colorless oil; Mass *m*/*z* 334 (M$^+$); IR (neat) 2950, 2920, and 2850 cm^{-1} (CH); ^{1}H NMR 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–$\underline{C_5H_{11}}$); UV λ_{max} 244 (ε 14000), 272 nm (sh, 7700). Found: C, 71.51; H, 9.23%. Calcd for $C_{20}H_{30}S_2$: C, 71.79; H, 9.04%.

3,3′-Dihexyl-2,5′-bithiophene (H–T Isomer of 6): Colorless oil; Mass *m*/*z* 334 (M$^+$); IR (neat) 2950, 2920, and 2850 cm^{-1} (CH); ^{1}H NMR 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}), 1.70—0.82 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV λ_{max} 253 (ε 8390), 297 nm (9630). Found: C, 71.82; H, 9.22%. Calcd for $C_{20}H_{30}S_2$: C, 71.79; H, 9.04%.

3,3′-Didodecyl-2,2′-bithiophene (30) and Its H–T Isomer: The reaction was carried out employing the same procedure as that for the compound **24** using 2-bromo-3-dodecylthiophene (**29**)$^{18)}$ (1.0 g, 3.0 mmol), butyllithium (1.6 mol dm^{-3}; 2.27 cm^3, 3.9 mmol), and Fe(acac)$_3$ (1.07 g, 3.02 mmol) to give the H–H bithiophene **30** (533 mg, 70%), a mixture of the H–H and H–T bithiophenes (135 mg 4 : 1), and the H–T isomer of **30** (36 mg, 4.8%) in order.

30: Colorless oil; Mass *m*/*z* 502 (M$^+$); IR (neat) 2950, 2900, and 2840 cm^{-1} (CH); ^{1}H NMR δ=7.26 (2H, d, *J*=5 Hz, ThH), 6.95 (2H, d, *J*=5 Hz, ThH), 2.50 (4H, t, *J*=7 Hz, $\underline{CH}_2$–$C_{11}H_{23}$), 1.6—1.3 (40H, m, CH_2–$(\underline{CH}_2)_{10}$–CH_3), 0.88 (6H, t, *J*=6 Hz, CH_3); UV λ_{max} 247 (ε 11300), 274 nm (sh, 5650). Found: C, 76.44; H, 10.53%. Calcd for $C_{32}H_{54}S_2$: C, 76.42; H, 10.82%.

3,3′-Didodecyl-2,5′-bithiophene (H–T Isomer of 30): Colorless oil; Mass *m*/*z* 502 (M$^+$); IR (neat) 2950, 2925, and 2850 cm^{-1} (CH); ^{1}H NMR δ=7.12 (1H, d, *J*=6 Hz, ThH), 6.93 (1H, s, ThH), 6.90 (1H, d, *J*=6 Hz, ThH), 6.87 (1H, d, *J*=6 Hz, ThH), 2.73 (2H, t, *J*=7.8 Hz, $\underline{CH}_2$–$C_{11}H_{23}$), 2.59 (2H, t, *J*=7.7 Hz, $\underline{CH}_2$–$C_{11}H_{23}$), 1.64—1.58 (4H, m, CH_2–$\underline{CH}_2$–$C_{10}H_{21}$), 1.33—1.23 (36H, m, $(CH_2)_2$–$(\underline{CH}_2)_9$–CH_3), 0.88 (6H, t, *J*=6.6 Hz, CH_3); UV λ_{max} 253 (ε 7200), 298 nm (8500). Found: C, 76.46; H, 10.66%. Calcd for $C_{32}H_{54}S_2$: C, 76.42; H, 10.82%.

3,3′,3′′,3′′′-Tetrahexyl-2,2′ : 5′,5′′ : 2′′,2′′′-quaterthiophene (11): To a solution of the bromide **25** (600 mg, 1.45 mmol) in THF (20 cm^3) drops of butyllithium (1.6

mol dm^{-3}; 1.0 cm^3, 1.59 mmol) in hexane were added below −80 °C over 10 min under Ar atmosphere. After the mixture was stirred for 10 min at −80 °C, Fe(acac)$_3$ (512 mg, 1.45 mmol) was added in portions over 15 min. After being stirred for 30 min at −80 °C, the mixture was diluted with water (30 cm^3), neutralized with 3 M HCl (40 cm^3), and extracted with dichloromethane. The extracts were washed with brine. The residue obtained after removal of the solvent was chromatographed on silica gel (3.2×60 cm) with hexane to give the quaterthiophene **11** (292 mg, 60%): Colorless oil; Mass *m/z* 666 (M$^+$); IR (neat) 2950, 2925, and 2855 cm^{-1} (CH); ^{1}H NMR δ=7.29 (2H, d, J=5.3 Hz, ThH), 7.02 (2H, s, ThH), 6.96 (2H, d, J=5.3 Hz, ThH), 2.56 (4H, t, J=7.0 Hz, $\underline{CH_2}$–C_5H_{11}), 2.47 (4H, t, J=7.0 Hz, $\underline{CH_2}$–C_5H_{11}), 1.55—0.66 (44H, m, CH_2–$\underline{C_5H_{11}}$); UV $\lambda_{\max}$ 224 (ε 15800), 337 nm (17600). Found: C, 72.27; H, 8.71%. Calcd for $C_{40}H_{58}S_4$: C, 72.01; H, 8.76%.

3,3′,3″,3‴,3⁗,3′′′′′,3′′′′′′,3′′′′′′′-Octahexyl-2,2′:5′,5″:2″,2‴:5‴,5⁗:2⁗,2′′′′′:5′′′′′,5′′′′′′:2′′′′′′,2′′′′′′′-octithiophene (16): To a solution of the bromide **26** (300 mg, 0.41 mmol) in THF (9 cm^3) drops of butyllithium (1.6 mol dm^{-3}; 0.3 cm^3, 0.48 mmol) in hexane were added below −80 °C over 10 min under Ar atmosphere. After the mixture was stirred for 10 min at −80 °C, Fe(acac)$_3$ (143 mg, 0.41 mmol) was added in portions during 10 min. After being stirred for 30 min at −80 °C, the mixture was diluted with water and neutralized with 3 M HCl. After being extracted with dichloromethane, the extracts were washed with brine and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (3.2×25 cm) with hexane to give the octithiophene **16** (120 mg, 45%): Pale yellow leaflets (from methanol), mp 57—58 °C; Mass *m/z* 665 (M$^+$/2); IR 2945, 2910, and 2845 cm^{-1} (CH); ^{1}H NMR δ=7.30 (2H, d, J=5.3 Hz, ThH), 7.04 (6H, br s, ThH), 6.97 (2H, d, J=5.3 Hz, ThH), 2.62—2.47 (16H, m, $\underline{CH_2}$–C_5H_{11}), 1.74—0.66 (88H, m, CH_2–$\underline{C_5H_{11}}$); UV $\lambda_{\max}$ 367 nm (ε 55700). Found: C, 71.12; H, 8.65%. Calcd for $C_{80}H_{114}S_8$: C, 71.12; H, 8.62%.

3,3′,3″-Trihexyl-2,2′:5′,2″-terthiophene (28): To a solution of the bromide **24** (100 mg, 0.405 mmol) and the bromide **25** (167 mg, 0.405 mmol) in THF (7 cm^3) drops of butyllithium (1.6 mol dm^{-3}; 0.56 cm^3, 0.89 mmol) in hexane were added below −80 °C over 10 min under Ar atmosphere. After the mixture was stirred for 30 min at −80 °C, Fe(acac)$_3$ (315 mg, 0.89 mmol) was added in portions over 15 min below −80 °C. After being stirred for 30 min at −80 °C, the mixture was diluted with water and neutralized with 3 M HCl. After being extracted with dichloromethane, the extracts were washed with brine and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (3.2×25 cm) with hexane to give 3-hexylthiophene (**1**) (10 mg) from the initial fractions. The later fractions eluted with hexane gave the bithiophene **6** (68 mg, 50%), the terthiophene **28** (87 mg, 43%), and the quaterthiophene **11** (55 mg, 20%) in order.

28: Colorless oil; Mass *m/z* 500 (M$^+$); IR(neat) 2950, 2925, and 2860 cm^{-1} (CH); ^{1}H NMR δ=7.30 (1H, d, J=5.2 Hz, ThH), 7.15 (1H, d, J=5.2 Hz, ThH), 6.97 (1H, s, ThH), 6.97 (1H, d, J=5.2 Hz, ThH), 2.77 (2H, t, J=8.2 Hz, $\underline{CH_2}$–C_5H_{11}), 2.51 (2H, t, J=8.0 Hz, $\underline{CH_2}$–C_5H_{11}), 2.46 (2H, t, J=8.0 Hz, $\underline{CH_2}$–C_5H_{11}), 1.64—1.22 (24H, m, CH_2–$(\underline{CH_2})_4$–CH_3), 0.90—0.83 (9H, m, CH_3); UV $\lambda_{\max}$ 247 (ε 10500), 316 nm (12600). Found: C, 72.15; H, 9.05%. Calcd for $C_{30}H_{44}S_3$: C, 71.94; H, 8.85%.

3,3′,3″,3‴,3⁗,3′′′′′-Hexahexyl-2,2′:5′,5″:2″,2‴:5‴,5⁗:2⁗,2′′′′′-sexithiophene (27): Cross coupling of the bromide **25** (55 mg, 0.13 mmol) and the bromide **26** (100 mg, 0.13 mmol) was carried out by employing the same procedure as that of **24** and **25**. Column chromatography of the product on silica gel with hexane afforded the bithiophene **6** (14 mg, 31%), the quaterthiophene **11** (16 mg, 18%), the sexithiophene **27** (35 mg, 26%), and the octithiophene **16** (26 mg, 15%) in order.

27: Yellow microcrystals (from hexane–benzene), mp 33—34 °C; Mass *m/z* 998 (M$^+$); IR 2955, 2925, and 2855 cm^{-1} (CH); ^{1}H NMR δ=7.30 (2H, d, J=5.0 Hz, ThH), 7.15 (4H, br s, ThH), 6.97 (2H, d, J=5.0 Hz, ThH), 6.97 (1H, d, J=5.2 Hz, ThH), 2.62—2.39 (12H, m, $\underline{CH_2}$–C_5H_{11}), 1.80—1.10 (48H, m, CH_2–$(\underline{CH_2})_4$–CH_3), 0.86 (18H, t, J=6 Hz, CH_3); UV $\lambda_{\max}$ 363 nm (ε 39800). Found: C, 72.21; H, 8.77%. Calcd for $C_{60}H_{86}S_6$: C, 72.08; H, 8.67%.

2,5-Dicyano-3-hexylthiophene (3): A mixture of the dibromide **2** (100 mg, 0.2 mmol) and copper(I) cyanide (110 mg, 1.12 mmol) in *N*-methyl-2-pyrrolidone (NMP; 3 cm^3) was refluxed for 1 h. The mixture was poured into a 25% aqueous ammonia (20 cm^3). The mixture was extracted with benzene and the extracts were washed with brine. The residue obtained after removal of the solvent was chromatographed on silica gel (2.2×7 cm) with 40% benzene in hexane to afford the dicyanide **3** (40 mg, 59%): Colorless oil; Mass *m/z* 218 (M$^+$); IR (neat) 2950, 2923, 2850 (CH), and 2230 cm^{-1} (CN); ^{1}H NMR δ=7.47 (1H, s, ThH), 2.81 (2H, t, J=8 Hz, $\underline{CH_2}$–C_5H_{11}), 1.69—1.61 (2H, m, CH_2–$\underline{CH_2}$–C_4H_9), 1.33—1.32 (6H, m, C_2H_4–$(\underline{CH_2})_3$–CH_3), 0.90 (3H, t, J=7 Hz, CH_3); UV $\lambda_{\max}$ 269 (ε 15000), 277 nm (sh, 12800). Found: C, 66.29; H, 6.50; N, 12.50%. Calcd for $C_{12}H_{14}N_2S$: C, 66.02; H, 6.46; N, 12.83%.

Conversion of other dibromides **7**, **12**, and **17** to the corresponding dicyanides **8**, **13**, and **18**, respectively, was carried out by employing the same procedure as that used for the dibromide **2**.

5,5′-Dicyano-3,3′-dihexyl-2,2′-bithiophene (8): 67% Yield from the dibromide **7** (100 mg, 0.20 mmol), CuCN (72 mg, 0.72 mmol), and NMP (3 cm^3); Pale yellow oil; Mass *m/z* 384 (M$^+$); IR (neat) 2950, 2920, 2860 (CH), and 2220 cm^{-1} (CN); ^{1}H NMR δ=7.51 (2H, s, ThH), 2.50 (4H, t, J=8 Hz, $\underline{CH_2}$–C_5H_{11}), 1.80—1.10 (16H, m, CH_2–$(\underline{CH_2})_4$–CH_3), 0.87 (6H, m, CH_3); UV $\lambda_{\max}$ 235 (ε 10100), 249 (10300), 288 nm (14450). Found: C, 68.79; H, 7.40; N, 7.11%. Calcd for $C_{22}H_{28}N_2S_2$: C, 68.70; H, 7.34; N, 7.28%.

5,5‴-Dicyano-3,3′,3″,3‴-tetrahexyl-2,2′:5′,5″:2″,2‴-quaterthiophene (13): 76% Yield from the dibromide **12** (616 mg, 0.75 mmol), CuCN (269 mg, 2.69 mmol), and NMP (20 cm^3); Pale yellow microcrystals (from hexane), mp 85—86 °C; Mass *m/z* 716 (M$^+$); IR 2950, 2930, 2850 (CH), and 2215 cm^{-1} (CN); ^{1}H NMR δ=7.49 (2H, s, ThH), 7.06 (2H, s, ThH), 2.55 (4H, t, J=8 Hz, $\underline{CH_2}$–C_5H_{11}), 2.47 (4H, t, J=8 Hz, $\underline{CH_2}$–C_5H_{11}), 1.58—1.55 (8H, m, CH_2–$\underline{CH_2}$–C_4H_9), 1.25 (24H, m, C_2H_4–$(\underline{CH_2})_3$–CH_3), 0.86 (12H, m, CH_3); UV $\lambda_{\max}$ 245 (ε 19400), 268 (17300), 348 nm (27200). Found: C, 70.62; H, 7.88; N, 3.62%. Calcd for $C_{42}H_{56}N_2S_4$: C, 70.34; H, 7.87; N, 3.91%.

5,5′′′′′′′-Dicyano-3,3′,3″,3‴,3⁗,3′′′′′,3′′′′′′,3′′′′′′′-octahexyl-2,2′:5′,5″:2″,2‴:5‴,5⁗:2⁗,2′′′′′:5′′′′′,

5'''''' : 2'''''',2'''''''-octithiophene (18): 70% Yield from the octithiophene **17** (250 mg, 0.17 mmol), CuCN (120 mg, 1.21 mmol), and NMP (10 cm^3); Pale yellow microcrystals (from hexane), mp 83—84 °C; Mass *m/z* 1381 (M$^+$+1); IR 2950, 2920, 2850 (CH), and 2220 cm^{-1} (CN); ^{1}H NMR δ=7.49 (2H, s, ThH), 7.05 (6H, br s, ThH), 2.70—2.40 (16H, m, $\underline{\text{CH}_2}$–C_5H_{11}), 1.80—1.10 (64H, m, CH_2–($\underline{\text{CH}_2}$)$_4$–CH_3), 0.87 (24H, t, *J*=6 Hz, CH_3); UV λ_{max} 249 (ε 29300), 261 (30000), 371 nm (57400). Found: C, 70.95; H, 8.24; N, 1.85%. Calcd for $C_{82}H_{112}N_2S_8$: C, 71.23; H, 8.16; N, 2.03%.

3-Hexylthiophene-2,5-dicarboxylic Acid (4): To a solution of the dibromide **2** (500 mg, 1.53 mmol) in THF (5 cm^3) drops of butyllithium (1.6 mol dm^{-3}; 2.30 cm^3, 3.68 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 (2.2×5 cm) with a mixture of ether and dichloromethane (1 : 10) to afford the acid **4** (315 mg, 80%): Colorless microcrystals (from hexane–ether), mp 217—218 °C; Mass *m/z* 256 (M$^+$); IR 3000 (br OH) and 1680 cm^{-1} (CO); ^{1}H NMR δ=7.54 (1H, s, ThH), 2.97 (2H, t, *J*=8 Hz, $\underline{\text{CH}_2}$–C_5H_{11}), 1.80—1.10 (8H, m, CH_2–($\underline{\text{CH}_2}$)$_4$–CH_3), 0.87 (3H, t, *J*=7 Hz, CH_3); UV λ_{max} 215 (ε 8050), 273 nm (14500). Found: C, 56.34; H, 6.41%. Calcd for $C_{12}H_{16}O_4S$: C, 56.23; H, 6.29%.

Conversion of other bromides **7**, **12**, and **17** to the corresponding carboxylic acids **9**, **14**, and **19**, respectively, was carried out by employing the same procedure as that used for the bromide **2**.

3, 3'- Dihexyl- 2, 2'- bithiophene- 5, 5'- dicarboxylic Acid (9): 50% Yield from the dibromide **7** (200 mg, 0.40 mmol) and butyllithium (1.6 mol dm^{-3}; 0.56 cm^3, 0.90 mmol); Colorless needles (from hexane–ether), mp 168—169 °C; Mass *m/z* 422 (M$^+$); IR 3000 (br OH), 2960, 2930, 2860 (CH), and 1675 cm^{-1} (CO); ^{1}H NMR δ=7.63 (2H, s, ThH), 2.52 (4H, t, *J*=7 Hz, $\underline{\text{CH}_2}$–C_5H_{11}), 1.80—1.10 (16H, m, CH_2–($\underline{\text{CH}_2}$)$_4$–CH_3), 0.85 (6H, t, *J*=6 Hz, CH_3); UV λ_{max} 297 nm (ε 15500). Found: C, 62.32; H, 7.15%. Calcd for $C_{22}H_{30}O_4S_2$: C, 62.52; H, 7.16%.

3,3',3'',3'''-Tetrahexyl-2,2' : 5',5'' : 2'',2'''-quaterthiophene-5,5'''-dicarboxylic Acid (14): 34% Yield from the dibromide **12** (259 mg, 0.31 mmol) and butyllithium (1.6 mol dm^{-3}; 2.30 cm^3, 3.68 mmol); Pale yellow microcrystals (from hexane–ether), mp 178–179 °C; Mass *m/z* 754 (M$^+$); IR 3000 (br OH), 2950, 2925, 2850 (CH), and 1680 cm^{-1} (CO); ^{1}H NMR δ=7.64 (2H, s, ThH), 7.06 (2H, s, ThH), 2.52 (8H, m, $\underline{\text{CH}_2}$–C_5H_{11}), 1.80—1.10 (32H, m, CH_2–($\underline{\text{CH}_2}$)$_4$–CH_3), 0.86 (12H, m, CH_3); UV λ_{max} 250 (ε 16700), 351 nm (21900). Found: C, 66.76; H, 7.88%. Calcd for $C_{42}H_{58}O_4S_4$: C, 66.80; H, 7.74%.

3, 3', 3'', 3''', 3'''', 3''''', 3'''''', 3'''''''- Octahexyl- 2, 2' : 5', 5'' : 2'',2''' : 5''',5'''' : 2'''',2''''' : 5''''',5'''''' : 2'''''',2'''''''-octithiophene-5,5'''''''-dicarboxylic Acid (19): This compound was prepared by the same procedure as that for the preparation of the compound **4**, except for the purification procedure, using the dibromide **17** (238 mg, 0.16 mmol) and butyllithium (1.6 mol dm^{-3}; 0.23 cm^3, 0.37 mmol). After the mixture was poured into aqueous K_2CO_3 and this combination was shaken with ether twice, the aqueous phase was acidified with 1 M HCl to give the acid **19** (65 mg, 30%) as precipitates: Yellow microcrystals (from hexane–ether), mp 84—86 °C; IR 3000 (br OH), 2955, 2926, 2856 (CH), and 1672 cm^{-1} (CO); ^{1}H NMR δ=7.76 (2H, s, ThH), 7.05 (6H, s, ThH), 2.52 (16H, m, $\underline{\text{CH}_2}$–C_5H_{11}), 1.80—1.10 (64H, m, CH_2–($\underline{\text{CH}_2}$)$_4$–CH_3), 0.87 (24H, m, CH_3); UV λ_{max} 257 (ε 30100), 373 nm (55000). Found: C, 68.96; H, 7.87%. Calcd for $C_{82}H_{114}O_8S_4$: C, 69.35; H, 8.09%.

3-Hexylthiophene-2,5-dicarbaldehyde (5): (A) To a solution of the dibromide **2** (100 mg, 0.31 mmol) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA; 78 mg, 0.68 mmol) in THF (5 cm^3) drops of butyllithium (1.6 mol dm^{-3}; 0.42 cm^3, 0.68 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 (224 mg, 3.07 mmol) was added over 10 min at −80 °C. The mixture was stirred for 5 h at room temperature, was poured into 1 M HCl at −10 °C with continued vigorous stirring, and then neutralized by addition of saturated aqueous $NaHCO_3$. 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 (2.8×10 cm) with a mixture of dichloromethane and benzene (1 : 10) to afford the dialdehyde **5** (37 mg, 55%): Colorless oil; Mass *m/z* 224 (M$^+$); IR (neat) 2950, 2910, 2845 (CH), and 1670 cm^{-1} (CO); ^{1}H NMR δ=10.14 (1H, s, CHO), 9.97 (1H, s, CHO), 7.67 (1H, s, ThH), 3.02 (2H, t, *J*=8 Hz, $\underline{\text{CH}_2}$–C_5H_{11}), 1.90—1.10 (8H, m, CH_2–($\underline{\text{CH}_2}$)$_4$–CH_3), 0.89 (3H, t, *J*=5 Hz, CH_3); UV λ_{max} 294 (ε 14300), 313 nm (sh, 10900). Found: C, 64.46; H, 7.25%. Calcd for $C_{12}H_{16}O_2S$: C, 64.25; H, 7.19%.

(B) To a mixture of 3-hexylthiophene (**1**) (100 mg, 0.59 mmol) and TMEDA (152 mg, 1.31 mmol) in THF (3 cm^3) drops of butyllithium (1.6 mol dm^{-3}; 0.86 cm^3, 1.31 mmol) in hexane were added during 10 min at room temperature under Ar atmosphere. After this mixture was stirred for 30 min at 70 °C, a further amount of THF (3 cm^3) was added. The resulting solution was cooled to −40 °C and then DMF (261 mg, 3.56 mmol) was added over 10 min. The mixture was stirred for 5 h at room temperature. Work-up similar to that in method (A) gave the dialdehyde **5** (57 mg, 43%).

Because the yield of the dialdehyde **5** using the method (A) is higher than that using the method (B), the method (A) was adopted for the preparation of other dialdehydes (**10**, **15**, and **20**).

3,3'-Dihexyl-2,2'-bithiophene-5,5'-dicarbaldehyde (10): 78% Yield from the dibromide **7** (500 mg, 1.02 mmol), TMEDA (250 mg, 2.16 mmol), butyllithium (1.6 mol dm^{-3}; 1.52 cm^3, 2.44 mmol), and DMF (447 mg, 6.12 mmol); Colorless oil; Mass *m/z* 390 (M$^+$); IR (neat) 2950, 2930, 2850 (CH), and 1670 cm^{-1} (CO); ^{1}H NMR δ=9.89 (2H, s, CHO), 7.67 (2H, s, ThH), 2.57 (4H, t, *J*=8 Hz, $\underline{\text{CH}_2}$–C_5H_{11}), 1.60—1.20 (16H, m, CH_2–($\underline{\text{CH}_2}$)$_4$–CH_3), 0.86 (6H, m, CH_3); UV λ_{max} 263 (ε 11700), 317 nm (16600). Found: C, 67.94; H, 7.58%. Calcd for $C_{22}H_{30}O_2S_2$: C, 67.64; H, 7.74%.

3,3',3'',3'''-Tetrahexyl-2,2' : 5',5'' : 2'',2'''-quaterthiophene-5,5'''-dicarbaldehyde (15): 50% Yield from the dibromide **12** (200 mg, 0.24 mmol), TMEDA (61 mg, 0.51 mmol), butyllithium (1.6 mol dm^{-3}; 0.38 cm^3, 0.61 mmol), and DMF (175 mg, 2.40 mmol); Yellow microcrystals (from hexane), mp 52—53 °C; Mass *m*/*z* 722 (M^+); IR 2950, 2930, 2850 (CH), and 1675 cm^{-1} (CO); ^{1}H NMR δ=9.87 (2H, s, CHO), 7.65 (2H, s, ThH), 7.07 (2H, s, ThH), 2.61 (4H, t, *J*=7 Hz, $\underline{CH_2}$–C_5H_{11}), 2.52 (4H, t, *J*=8 Hz, $\underline{CH_2}$–C_5H_{11}), 1.80—1.10 (32H, m, CH_2–($\underline{CH_2}$)$_4$–CH_3), 0.86 (12H, m, CH_3); UV λ_{max} 264 (ε 20500), 365 nm (26200). Found: C, 69.64; H, 7.99%. Calcd for $C_{42}H_{58}O_2S_4$: C, 69.75; H, 8.08%.

$3,3',3'',3''',3'''',3''''',3''''''$-Octahexyl-$2,2':5',5'':2'',2''':5''',5'''':2'''',2''''':5''''',5'''''':2'''''',2'''''''$-octithiophene-$5,5'''''''$-dicarbaldehyde (20): 32% Yield from the dibromide **17** (270 mg, 0.18 mmol), TMEDA (44 mg, 0.38 mmol), butyllithium (1.6 mol dm^{-3}; 0.23 cm^3, 0.36 mmol), and DMF (131 mg, 1.80 mmol); Yellow microcrystals (from hexane), mp 39—40 °C; Mass *m*/*z* 722 (M^+); IR 2955, 2925, 2855 (CH), and 1675 cm^{-1} (CO); ^{1}H NMR δ=9.87 (2H, s, CHO), 7.65 (2H, s, ThH), 7.06 (6H, br s, ThH), 2.75—2.40 (16H, m, $\underline{CH_2}$–C_5H_{11}), 1.80—1.10 (64H, m, CH_2–($\underline{CH_2}$)$_4$–CH_3), 0.86 (24H, m, CH_3); UV λ_{max} 260 (ε 37100), 379 nm (59200). Found: C, 70.22; H, 8.66%. Calcd for $C_{82}H_{114}O_2S_8$: C, 70.94; H, 8.28%.

2,5-Bis(dicyanomethylene)-3-hexyl-2,5-dihydrothiophene (21): A solution of the dibromide **2** (500 mg, 1.53 mmol), tetracyanoethylene oxide (TCNEO)[7] (1.96 g, 15.3 mmol), and copper(I) chloride (CuCl, 1.06 g, 1.07 mmol) in 1,3-dibromopropane (6 cm^3) was heated with stirring in an oil bath at 160 °C for 8 h. The mixture was concentrated and the residue was chromatographed on silica gel (3.8×10 cm) with a mixture of benzene and hexane (2 : 3) to afford the thienoquinonoid **21** (145 mg, 32%): Deep yellow oil; Mass *m*/*z* 294 (M^+); IR (neat) 3050, 2950, 2920, 2850 (CH), and 2220 cm^{-1} (CN); ^{1}H NMR δ=7.34 (1H, br s, ThH), 2.95 (2H, br t, *J*=7 Hz, $\underline{CH_2}$–C_5H_{11}), 1.71—0.85 (11H, m, CH_2–$\underline{C_5H_{11}}$); UV-visible λ_{max} 398 (ε 24600), 419 nm (26000). Found: C, 64.91; H, 5.09; N, 18.70%. Calcd for $C_{16}H_{14}N_4S$: C, 65.28; H, 4.79; N, 19.03%.

UV-visible Data of Thienoquinonoid 33: UV-visible λ_{max} 330 (ε 6400), 400 (18000), 421 nm (20300).[9]

5,5′-Bis(dicyanomethylene)-3,3′-dihexyl-5,5′-dihydro-$\Delta^{2,2'}$-bithiophene (22): (A) Reaction using TCNEO:[8,9] A solution of the dibromide **7** (600 mg, 1.22 mmol), TCNEO (1.80 g, 12.0 mmol), and CuCl (830 mg, 838 mmol) in 1,3-dibromopropane (20 cm^3) was heated with vigorous stirring at 160 °C for 7 h. The mixture was concentrated and the residue was chromatographed on silica gel (3.2×10 cm) with a mixture of hexane and benzene (1 : 1) to give the bithienoquinonoid **22** (59 mg, 10.5%).

(B) Reaction using sodium dicyanomethanide–bromine water:[9] To a suspension of sodium hydride (115 mg, 60% in oil, 2.28 mmol) in 1,2-dimethoxyethane (8 cm^3) was added malononitrile (91.5 mg, 1.44 mmol) at 0 °C under Ar atmosphere. The mixture was then stirred for 20 min at room temperature. To this solution were added the dibromide **7** (300 mg, 0.60 mmol) and tetrakis(triphenylphosphine)palladium(0) (93.6 mg, 0.60 mmol) successively and the mixture was heated under reflux for 4 h. The mixture was poured into saturated aqueous bromine (40 cm^3) at 0 °C, diluted with cold water (100 cm^3), and then extracted with dichloromethane. The extracts were washed with brine and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (4.8×10 cm) with a mixture of hexane and benzene (1 : 1) to afford the brominated derivative, 4-bromo-5,5′-bis(dicyanomethylene)-3,3′-dihexyl-5,5′-dihydro-$\Delta^{2,2'}$-bithiophene (6.5 mg, 2%), from the initial fractions: Black purple needles (from hexane–benzene), mp 144—145 °C (decomp); Mass *m*/*z* 539 and 541 (M^+ and M^++2, based on ^{79}Br); IR 2930, 2855 (CH), and 2213 cm^{-1} (CN); ^{1}H NMR δ=7.36 (1H, s, ThH), 3.15—2.84 (4H, m, $\underline{CH_2}$–C_5H_{11}), 1.83—0.76 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV-visible λ_{max} 534 (ε 6390), 560 nm (76000). Found: C, 58.11; H, 5.08; N, 10.15%. Calcd for $C_{26}H_{27}BrN_4S_2$: C, 57.88; H, 5.04; N, 10.38%.

The later fractions gave the desired quinonoid compound **22** (130 mg, 46%): Reddish purple needles (from hexane–benzene), mp 193—195 °C (decomp); Mass *m*/*z* 460 (M^+); IR 2900 (br CH) and 2205 cm^{-1} (CN); ^{1}H NMR δ=7.26 (2H, s, ThH), 2.92 (2H, t, *J*=7 Hz, $\underline{CH_2}$–C_5H_{11}), 1.87—0.93 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV-visible λ_{max} 482 (ε 27800), 518 (55300), 549 nm (60800). Found: C, 68.05; H, 6.23; N, 11.88%. Calcd for $C_{26}H_{28}N_4S_2$: C, 67.79; H, 6.13; N, 12.16%.

UV-visible Data of Bithienoquinonoid 34: UV-visible λ_{max} 343 (ε 7000), 525 (65700), 550 nm (73100).[9]

5,5′-Bis(dicyanomethylene)-3,3′-didodecyl-5,5′-dihydro-$\Delta^{2,2'}$-bithiophene (32): This compound was prepared by employing the same procedure as described (method (B)) for the preparation of the quinonoid compound **22**. The reaction of malononitrile (95 mg, 1.44 mmol), sodium hydride (115 mg, 60% in oil, 2.88 mmol), the dibromide **31** (400 mg, 0.61 mmol), and the palladium complex (94 mg, 0.06 mmol) (see above) gave **32** (130 mg, 34%): Purple microcrystals (from hexane–benzene), mp 148—149 °C (decomp); Mass *m*/*z* 628 (M^+); IR 2920, 2850 (CH), and 2220 cm^{-1} (CN); ^{1}H NMR δ=7.26 (2H, s, ThH), 2.92 (4H, t, *J*=7 Hz, $\underline{CH_2}$–C_5H_{11}), 1.87—1.27 (40H, m, CH_2–($\underline{CH_2}$)$_{10}$–CH_3), 0.88 (6H, t, *J*=5 Hz, CH_3); UV-visible λ_{max} 485 (sh, ε 31300), 518 (59000), 547 nm (68000). Found: C, 72.27; H, 8.19; N, 8.69%. Calcd for $C_{38}H_{52}N_4S_2$: C, 72.56; H, 8.33; N, 8.90%.

5,5‴-Bis(dicyanomethylene)-3,3′,3″,3‴-tetrahexyl-5,5‴-dihydro-$\Delta^{2,2':5',5'':2'',2'''}$-quaterthiophene (23): To a suspension of sodium hydride (69.9 mg, 60% in oil, 1.75 mmol) in 1,2-dimethoxyethane (10 cm^3) was added malononitrile (57.7 mg, 0.87 mmol) in one portion at 0 °C under Ar atmosphere. After this mixture was stirred for 30 min at room temperature, the dibromide **12** (300 mg, 0.36 mmol) and the palladium complex (56.2 mg, 0.036 mmol) (see above) were successively added. The mixture was heated under reflux for 6 h. This mixture was poured into saturated bromine in water (40 cm^3) under ice-cooling and then diluted with cold water (100 cm^3); the resulting mixture was extracted with dichloromethane and the extracts were washed with brine. The residue obtained after removal of the solvent was chromatographed on silica gel (4.8×10 cm) with a mixture of benzene and hexane (3 : 2) to give the quaterthienoquinonoid **23** (78 mg, 27%): Pale brown needles (from benzene), mp 182—183 °C (decomp); Mass *m*/*z* 792 and 794 (M^+ and M^++2); IR 2910 (br CH) and 2200 cm^{-1} (CN); ^{1}H NMR δ=7.26 (4H, br s, ThH), 3.2—2.7 (8H, br m, $\underline{CH_2}$–C_5H_{11}), 1.78—0.93 (44H, m, CH_2–$\underline{C_5H_{11}}$); UV-visible λ_{max} 715 (sh, ε 55000), 781 (183000), 860 nm (sh, 63500). Found: C, 69.48; H, 7.09; N, 7.05%. Calcd for $C_{46}H_{56}N_4S_4$: C, 69.65; H, 7.12; N, 7.06%.

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