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Synthesis of α,ω-Long Chain Disubstituted Sexithiophenes

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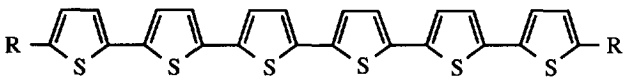
Abstract: The synthesis and electrochemistry of three new symmetrical α,ω-disubstituted sexithiophene derivatives 1-3 substituted by heptadecyl, hexadecyloxymethyl, and *trans*-heptadecenyl groups is described.

INTRODUCTION

Polythiophene and its derivatives, among the family of conjugated conducting polymers, exhibit excellent electrical and optical properties with potential technological applications. A structure engineered synthesis can produce polythiophenes with a wide range of conductivities from insulator (~10^{-10} S.cm^{-1}) to semiconductor and to metals (~10^{3} S.cm^{-1})[1-4]. α-Conjugated thiophene oligomers serve as model compounds in elucidating the mechanism of generation and transport of the charge carriers associated with the electrical conductivity of the corresponding polymer[5]. Bithiophenes and terthiophenes are known to be present in plants belonging to the family Compositae , and exhibit photo enhanced biological activity[6]. The lower oligomers are also used as precursors to electrochemically prepared structured polythiophenes[7]. Among the higher oligomers, the hexamer α-sexithiophene has recently been incorporated successfully into electronic and optical data processing devices[8,9]. α-Sexithiophene and higher oligomers, however, are practically insoluble in organic solvents, and thus are difficult to purify. In addition, sophisticated high temperature vacuum deposition techniques are needed to incorporate them as thin films in devices. The unsubstituted oligothiophenes also suffer from instability as a result of relatively high chemical reactivity at the α-carbons of the terminal thiophene rings[10]. Better solubility of the higher oligomers has been effected by several workers by the introduction of alkyl chains at the β-positions of the thiophene units, but at the expense of a lower degree of conjugation and carrier mobility[11]. This is caused by out of plane twisting of the thiophene rings in the β-substituted systems[12]. In contrast, substitution at the reactive α-positions of the terminal thiophenes results in a chemically stable oligomer[13]. Very recently, several workers have reported the electrochemical and chemical synthesis of α,ω-dialkyl sexithiophenes and their practical utilization in field-effect transistors (FET's)[14] with field-effect mobilities superior to those of polythiophenes and β-substituted oligothiophenes[15]. In the reported chemical preparation of the α,ω-dimethyl[14a, 14b], and the α,ω-dihexyl[14c] sexithiophenes, experimental details of their synthesis have not yet been revealed. The current tremendous interest in α,ω-disubstituted oligomers in the area of molecular electronics has resulted in the fabrication of a fully organic transistor device using as the key component α,ω-dihexylsexithiophene[14d]. High temperature flash evaporation techniques were employed to deposit the thin films of the sexithiophene derivative, which displayed poor solubility in organic solvents. With the aim of obtaining more soluble processable derivatives of α-sexithiophene, the following α,ω-disubstituted derivatives **1-3** with long chain substituents (Figure 1) have now been synthesized. Compound **3** represents the first vinylic sexithiophene derivative prepared.



1. R : $C_{17}H_{35}$

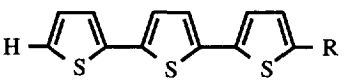
2. R : $CH_2OC_{16}H_{33}$

3. R : $CH{=}CHC_{15}H_{31}$ (trans)

Figure 1. New α,ω-long chain disubstituted sexithiophene derivatives.

RESULTS AND DISCUSSION

The first approach to the new sexithiophenes was by the oxidative coupling of appropriate terthiophenes. In this regard, the monosubstituted terthiophenes **4-6** were first synthesized (Figure 2).



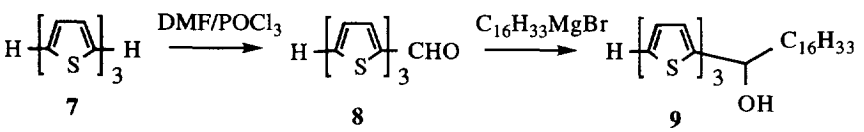
4. R : $C_{17}H_{35}$

5. R : $CH_2OC_{16}H_{33}$

6. R : $CH{=}CHC_{15}H_{31}$ (trans)

Figure 2. Monosubstituted α-terthiophene derivatives.

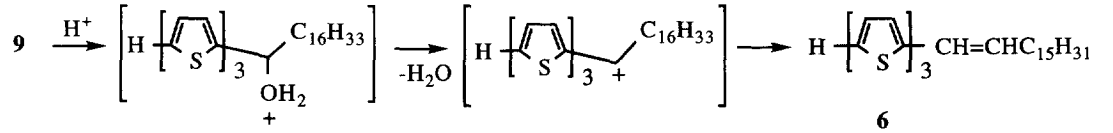
Initial attempts to obtain the octadecyl analog of **4** by selective monolithiation of α-terthiophene[16] **7** using nBuLi, followed by quenching with octadecyl bromide, gave an inseparable mixture of monoalkylated and dialkylated derivatives along with the starting material. A successful route to the monosubstituted α-terthiophenes involved starting from the known 5-formylterthiophene **8**[17]. Vilsmeier-Haack formylation of α-terthiophene by a modified literature procedure[17], using $DMF/POCl_3$ in CH_2Cl_2, furnished **8** in 96% yield. Addition of heptadecylmagnesium bromide to the formyl derivative **8** gave, in near quantitative yields, the secondary benzylic alcohol **9** (Scheme 1).



Scheme 1. Synthesis of the secondary alcohol **9**.

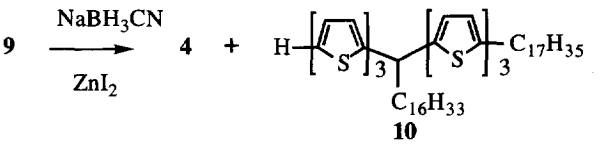
Reduction of **9** using conventional methods was expected to furnish **4**. Various literature methods for the reduction of secondary benzylic alcohols to alkanes ($NaBH_4/CF_3CO_2H$[18]; Et_3SiH/CF_3CO_2H[19]) resulted in inseparable mixtures containing the olefin **6**. The olefin was identified by comparing the proton NMR with that of a sample of **6** prepared by acid catalyzed dehydration of **9**. The intermediate in the reaction, shown in Scheme 2, is presumably the resonance stabilized carbocation. The subsequent elimination of a proton adjacent

to the carbocation, leading to the formation of **6** apparently competes with the hydride transfer reaction required for the formation of **4**. Reduction of **9** with Me_3SiI/CH_3CN[20] also gave an inseparable mixture of products.



Scheme 2. Formation of the olefin **6** by the acid catalyzed dehydration of **9**.

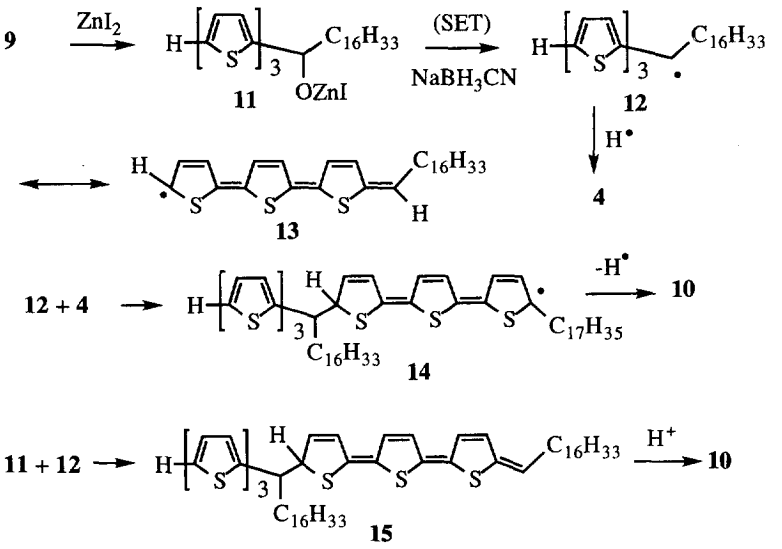
A recent method for the reduction of secondary benzylic type alcohols to alkanes employing $NaBH_3CN/ZnI_2$[21] in 1,2-dichloroethane proceeded smoothly at room temperature and converted the alcohol **9** to the desired 5-heptadecyl-α-terthiophene **4** in excellent yields. The synthetic steps involved in the formation of **4** represent an efficient high yielding route to the preparation of 5-alkyl substituted-α-terthiophenes in comparison to a recently reported method for the preparation of the hexyl analog of **4**[14c]. Reduction of **9** with $NaBH_3CN/ZnI_2$ at refluxing temperatures, however, resulted in the formation of a significant amount of the unexpected dimer **10** along with **4** (Scheme 3). The structure of **10** was elucidated and confirmed by spectral and elemental analysis.



Conditions	Yields of reaction (%)	
	4	**10**
rt, 12 h	96.5	-
reflux, 12 h	49.6	21.6

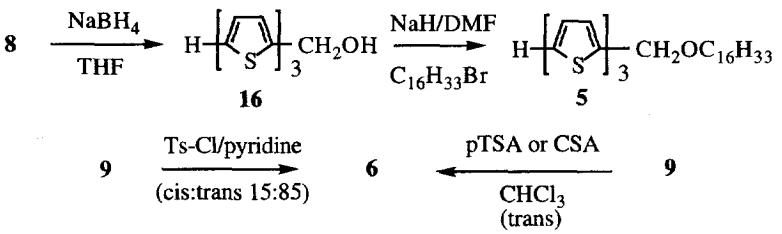
Scheme 3. Products formed by the reduction of **9** with $NaBH_3CN/ZnI_2$.

The formation of **10** suggests the involvement of a thermally favored single electron transfer (SET) mechanism. The probable mechanism for the formation of the **4** and the dimer **10** at higher temperatures are shown in Scheme 4. The ZnI_2 first reacts with the alcohol **9** forming the zinc alkoxide **11**. A single electron transfer by the cyanoborohydride ion would result in the benzylic type radical **12**, a resonance form of which is the delocalized radical **13**. The radical **12** can then pick up a hydrogen from the reducing agent, affording the desired alkane **4**. Alternatively, it can add to the free α position of the reduced compound **4**, generating the dimeric radical **14** which then spontaneously affords **10** after hydrogen abstraction. Alternatively, the addition of the benzylic type radical **12** to the alkoxide **11** results in the formation of the high energy quinonoid intermediate **15**, which subsequently undergoes an acid-catalyzed isomerization to form the dimer **10**. An SET mechanism has been proposed previously as an explanation for the formation of dimeric products in the deoxygenation of simpler substrates by the $ZnI_2/NaBH_3CN$ reagent[21].



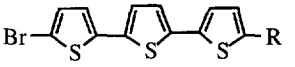
Scheme 4. Plausible mechanisms for the formation of **4** and **10** by the high temperature reduction of **9** with $NaBH_3CN/ZnI_2$.

The hexadecyloxymethyl substituted terthiophene derivative **5** was obtained in good yield by the O-alkylation of 5-hydroxymethyl-α-terthiophene[17] **16** using NaH/DMF and hexadecyl bromide. Attempts to obtain the trans olefin **6** by treatment of **9** with tosyl chloride in pyridine resulted in an inseparable cis:trans (15:85) mixture of olefins as determined by proton NMR. However, the sulfonic acid catalyzed dehydration of **9** gave, albeit in low yield, only the desired trans olefin **6**. No dimeric products were obtained from these reactions. The steps involved in the synthesis of **5** and **6** are outlined in Scheme 5.



Scheme 5. Synthesis of the alkoxymethyl substituted terthiophene derivative **5** and the olefinic derivative **6**.

Oxidative coupling of **4** using $FeCl_3$ as an oxidant in benzene medium gave the corresponding sexithiophene derivative **1** in 55% yield after rigorous purification. However, the same procedure applied to **5** and **6** gave only intractable solids. An organometallic methodology employing the coupling of a bromo compound by the in situ generation of Ni(0) complex was then employed to obtain the derived sexithiophene derivatives[22]. For this purpose, the following α-bromo substituted derivatives **17-19** shown in Figure 3 were prepared.



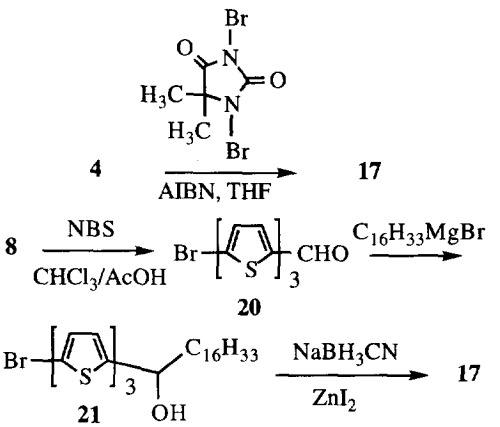
17 R : $C_{17}H_{35}$

18 R : $CH_2OC_{16}H_{33}$

19 R : $CH{=}CHC_{15}H_{31}$ (trans)

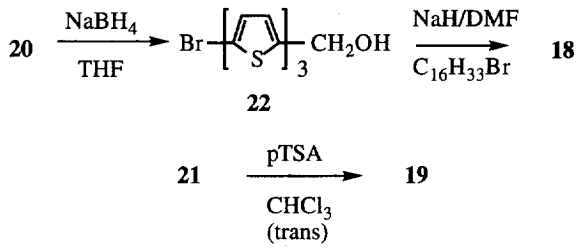
Figure 3. 5-Bromo-5"-substituted α-terthiophenes.

The bromo derivative **17** was obtained by two different routes. Bromide **17** was conveniently prepared by the bromination of **4** with 1,3-dibromo-5,5-dimethylhydantoin in excellent yields. Alternatively, the formyl terthiophene **8** was brominated with NBS, and to the resulting bromo aldehyde **20** was added hexadecylmagnesium bromide, affording the bromo alcohol derivative **21**. Reduction of **21** with $NaBH_3CN/ZnI_2$ in refluxing 1,2-dichloroethane yielded exclusively the bromo compound **17**. No dimeric structure was obtained during the reduction of **21**. Apparently, the presence of a bromine in the potential radical coupling position blocks any dimer formation (Scheme 6).



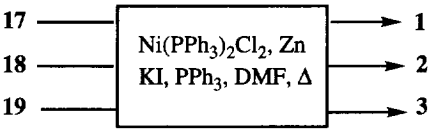
Scheme 6. Synthesis of 5-bromo-5"-heptadecyl terthiophene **17**.

The bromo ether derivative **18** was synthesized by reducing the bromo aldehyde **20** with $NaBH_4$ followed by O-alkylation of the resulting alcohol **22** with NaH/DMF and hexadecyl bromide. The olefinic precursor **19** was obtained exclusively as the trans isomer by the acid catalyzed dehydration of the corresponding bromo alcohol **21** (Scheme 7).



Scheme 7. Synthesis of 5-bromo-5"-substituted terthiophene derivatives **18** and **19**.

Coupling of the bromo terthiophenes **17-19** by reductive Ni(0) coupling reaction afforded the desired sexithiophene derivatives **1-3** in moderate to excellent yields.



Scheme 8. Synthesis of disubstituted sexithiophene derivatives **1-3**.

Physical and Electrochemical Study of the Oligothiophenes:

The 5-substituted-α-terthiophene derivatives **4-6** exhibited irreversible redox behavior as seen by cyclic voltammetric experiments. With repeated scan cycles, new anodic and cathodic peaks appear, presumably due to dimeric products resulting from radical coupling reactions. However, no insoluble dimerization products were detected on the anode during the electrochemical oxidation of **4-6**, suggesting the formation of β-coupled soluble dimers. The dimeric side product **10** surprisingly showed two quasi reversible redox waves, quite stable to repeated cyclic scans. The oxidation potential of the ether **5** was higher than those of the alkanes **4** and **10**, while the vinylic derivative **6** displayed the lowest potential. This result can be explained as due to an increase in the conjugation of the vinylic substituted derivative **6** in comparison to the alkyl and the ether derivatives, leading to a greater ease of oxidation. The oxidation potentials (vs SCE) and the wavelengths of the absorption maxima are summarized in Table 1.

Table 1. Redox Potentials (V vs SCE) and Absorption Maxima of the α Monosubstituted Terthiophenes.

Compound	Redox potentials (V vs SCE)		λ_{Max} (nm)/ log ε in $CHCl_3$
	E_{pa}^1/E_{pc}^1	E_{pa}^2/E_{pc}^2	
4	1.08 / -	-	361.5 (4.61)
5	1.13 / -	-	358.8 (4.38)
6	0.96 / -	-	383.8 (4.53)
10	1.04 / 0.91	1.18 / 1.11	369.5 (4.84)

The α,ω-sexithiophene derivatives **1-3**, unlike the α-terthiophenes **4-6**, showed the presence of two stable reversible redox waves. In the cyclic voltammograms, the first redox potential corresponds to the formation of the radical cation and the second represents the dicationic state. The excellent stability of **1-3** to repeated redox cycling can be attributed to be due to effective delocalization of the cation radical and the dication, facilitated by the blocking of the reactive α-positions of the terminal thiophene rings in the oligomers. The ease of oxidation follows the same trend seen in the case of the monosubstituted terthiophene derivatives **4-6** (Table 2) and correlates with the ultraviolet absorption maxima, the unsaturated sexithiophene derivative **3** showing both the longest absorption maxima and the lowest oxidation potential.

Table 2. Redox Potentials (V vs SCE) and Visible Absorption Data and Solubility of the α,ω–Disubstituted Sexithiophenes.

Compound	Redox potentials (V vs SCE)		λ_{Max} (nm)/ log ε in $CHCl_3$	Solubility at rt mg/L in $CHCl_3$
	E_{pa}^1/E_{pc}^1	E_{pa}^2/E_{pc}^2		
1	0.88 / 0.81	1.05 / 0.98	442.0 (4.77)	3.6
2	0.92 / 0.85	1.13 / 1.01	437.2 (4.44)	5.2
3	0.84 / 0.78	0.96 / 0.92	452.8 (5.17)	4.7

Contrary to our expectations, the new sexithiophenes did not show a much greater solubility in organic solvents than the parent intractable α-sexithiophene (Table 2). The oligomers were sparingly soluble in hot boiling THF, benzene, CCl_4, $CHCl_3$, and 1,2-dichloroethane in comparison to the almost insoluble α-sexithiophene. Strong π-π intermolecular interactions between the oligomeric thiophene units, combined with intermolecular hydrophobic interactions would appear to cause the low solubility of these highly linear molecules.

In conclusion, we have achieved the synthesis of several long-chain α,ω–disubstituted sexithiophenes. Like the parent α-sexithiophene, these redox stable α,ω-disubstituted sexithiophenes displayed surprisingly poor room temperature solubility in a number of organic solvents.

EXPERIMENTAL

General:

Melting point determinations are uncorrected. All electrochemical experiments were performed in a single compartment cell with a platinum disk working electrode, a platinum wire auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode. For each study, a 0.1 M solution of the supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAHFP) in 1,2-dichloroethane (HPLC grade) was employed.

5-Formyl-2,2':5',2''-terthiophene (8):

Into a loosely capped Erlenmeyer flask containing a solution of DMF (1.2 mL, 15 mmol) and dry CH_2Cl_2 (5 mL) at 0 °C, $POCl_3$ (1.4 mL, 15 mmol) was added dropwise with intermittent stirring. The mixture was removed from the ice bath and warmed to around 40 °C until a clear pale yellow solution was obtained. The Vilsmeier reagent thus prepared was added dropwise into a flask containing a solution of 2,2':5',2''-terthiophene[16], **7** (2.5 g, 10 mmol) in 15 mL of dry CH_2Cl_2 at 0°C. After standing for 12 h at rt, the CH_2Cl_2

was evaporated, cold aq. NaOH (1 M) was added (pH of 8-9) and the mixture was heated on a steam bath for 2h. Filtration, washing with water and drying gave a yellow powder. Silica flash chromatography (hexanes-CH_2Cl_2 1:1) yielded 2.67g (96%) of **8** in the form of yellow crystals, mp 134 °C (lit.[17] mp 135-136.5 °C). UV-vis ($CHCl_3$) λ_{Max} (nm): 401.7 (log ε = 4.40).

*5-(1-Hydroxyheptadecyl)-2,2':5',2''-terthiophene (**9**):*

In a flame dried 500 mL loosely capped roundbottom flask containing Mg turnings (1.59 g, 65 mmol) and 75 mL of dry Et_2O was added 1,2-dibromoethane (0.7 mL, 7.6 mmol) and the mixture was warmed gently until constant bubbling was observed at rt. Hexadecyl bromide (13.26 g, 43 mmol) was added producing a vigorous reaction to form the alkyl Grignard reagent. The mixture was refluxed for 1 h followed by the addition of **8** (3 g, 11 mmol) in one portion with Et_2O (20 mL), and the course of reaction was monitored by UV-vis spectroscopy. After refluxing for 1.5 h, the reaction mixture was cooled to rt and 200 mL of cold sat. NH_4Cl solution was added. After stirring for 30 min, the yellow precipitate was extracted into hexanes:Et_2O (1:1). The organic layer was washed with water, dried over anhyd Na_2SO_4, and evaporated to give a yellow waxy solid. Addition of 250 mL of hexane and stirring in a sonicator for 2 h, filtration and washing with hexanes yielded 5 g (92%) of spectroscopically pure **9** in the form of a yellow powder. Recrystallization from hexanes:benzene mixtures afforded an analytically pure sample, mp 96 °C. ^{1}NMR (360 MHz, $CDCl_3$), δ (ppm): 7.21 (dd, 1H, J=5.1, 0.9Hz), 7.16 (dd, 1H, J=3.4, 0.9Hz), 7.06 (d, 1H, J=3.8Hz), 6.99-7.04 (m, 3H), 6.86 (d, 1H, J=3.6Hz), 4.87 (t, 1H, J = 6.6Hz), 1.94-2.03 (bs, 1H), 1.78-1.93 (m, 2H), 1.20-1.50 (m, 28H), 0.88 (t, 3H, J=6.6Hz). UV-vis ($CHCl_3$) λ_{Max} (nm): 361.5 (log ε = 4.40). IR (KBr) cm^{-1}: 3420(b), 2940, 2860, 1470, 1430, 1065, 840, 800, 690. MS(m/e): 502 (3), 484 (100), 287 (66), 274 (19), 261 (45), 209 (12), 127 (9). Anal. Calcd. C, 69.32%; H, 8.37%. Found C, 69.37%; H, 8.40%.

*5-Heptadecyl-2,2':5',2''-terthiophene (**4**) and Dimer (**10**):*

To a stirred solution of **3** (4.5 g, 9.0 mmol) in 275 mL of dry 1,2-dichloroethane was added zinc iodide (4.29 g, 13 mmol) and sodium cyanoborohydride (4.23 g, 67 mmol). The reaction mixture was refluxed for 12h with a dry tube attachment, then filtered through Celite, and washed with dichloromethane. The concentrated filtrate was adsorbed onto basic Al_2O_3 and flash chromatographed (basic Al_2O_3) eluting with hexanes and hexanes:CH_2Cl_2 mixtures, yielding spectrally pure **4** (2.16 g, 50%) and **10** (0.94 g, 22%). Recrystallization from hexanes:benzene mixture afforded analytical grade **4**, mp 75-76 °C and **10**, mp 75-77 °C in the form of yellow crystals. Carrying out the same reaction at rt on a 2.5 g scale afforded **4** exclusively in 97% yield.

(4) ^{1}H NMR (360 MHz, $CDCl_3$), δ (ppm): 7.20 (dd, 1H, J=5.1, 0.9Hz), 7.15 (dd, 1H, J=3.8, 0.9 Hz), 7.05 (d, 1H, J=3.8Hz), 6.93-7.03 (m, 3H), 6.68 (d, 1H, J=3.3Hz), 2.79 (t, 2H, J=7.5Hz), 1.69 (p, 2H, J=7.0Hz), 1.17-1.50 (m, 28H), 0.89 (t, 3H, J=6.5Hz). UV-vis ($CHCl_3$) λ_{Max} (nm): 361.5 (log ε = 4.61). MS(m/e): 486 (73), 261 (100), 190 (63), 157 (13), 124 (8). Anal. Calcd. C, 71.61%; H, 8.64%. Found C, 71.63%; H, 8.67%.

(10) ^{1}H NMR (360MHz, $CDCl_3$), δ (ppm): 7.20 (dd, 1H, J=5.0, 0.8Hz), 7.15 (dd, 1H, J=4.0, 0.8Hz), 7.05 (d, 1H, J=3.7Hz), 6.93-7.03 (m, 7H), 6.81 (t, 2H, J = 2.6Hz), 6.66 (d, 1H, J=3.4Hz), 4.32 (t, 1H, J = 7.3Hz), 2.78 (t, 2H, J=7.65Hz), 2.09 (q, 2H, J=6.06Hz), 1.60-1.73 (m, 2H), 1.15-1.47 (m, 56H), 0.88 (t, 6H, J=6.64Hz). UV-vis ($CHCl_3$) λ_{Max} (nm): 369.9 (log ε = 4.84). MS(m/e): 970 (28), 745 (26), 486 (61), 261 (100), 155 (49), 123 (72). Anal. Calcd. C, 71.75%; H, 8.45%. Found C, 71.64%; H, 8.49%.

*5-Hydroxymethyl-2,2':5',2''-terthiophene (**16**):*

To a stirred solution of **8** (1.0 g, 3.6 mmol) in 50 mL of dry THF was added sodium borohydride (0.1 g, 2.5 mmol) under N_2 at rt. After 4 h, the THF was evaporated, dilute acid (1 M HCl) was added (pH ~ 6), and the mixture was stirred in a sonicator for 1 h. The yellow ppt was filtered, washed with water, and dried

yielding 0.94 g (93.3%) of **16**, mp 148 °C. lit.[17] mp 150 - 151 °C. UV-vis ($CHCl_3$) λ_{Max} (nm): 359.7 (log ε = 4.33).

5-Hexadecyloxymethyl-2,2':5',2''-terthiophene (5):

To a sodium hydride dispersion (50% in paraffin) (0.82 g, 17 mmol), washed twice with dry hexanes, was added a solution of **16** (1.9 g, 6.8 mmol) in 30 mL of dry DMF. The reaction mixture was stirred for 20 min at rt, followed by addition of hexadecyl bromide (2.51 g, 8.2 mmol). After 5 h, 200 mL of water was added and the mixture was stirred for 5h. The resulting yellow precipitate was filtered, washed with water and dried, yielding a yellow powder which was further purified by silica flash chromatography eluting with hexanes:CH_2Cl_2 (6:1, 4:1, 1:1) and CH_2Cl_2, yielding 2.48 g (7%) of **5**. Recrystallization from hexanes:benzene gave an analytically pure sample, mp 72 °C. ^1H NMR (360MHz, $CDCl_3$), δ (ppm): 7.22 (dd, 1H, J=5.1, 1.0Hz), 7.17 (dd, 1H, J= .4, 1.0Hz), 7.01-7.08 (m, 4H), 6.89 (d, 1H, J=3.4Hz), 4.63 (s, 2H), 3.50 (t, 2H, J=6.6Hz), 1.62 (p, 2H, J=7.2Hz), 1.26-1.35 (m, 26H), 0.89 (t, 3H, J=6.6Hz). UV-vis ($CHCl_3$) λ_{Max} (nm): 358.8 (log ε = 4.38). MS(m/e): 502 (57), 276 (15), 262 (100), 248 (17), 229 (9), 203 (6), 180 (21), 111 (19). Anal. Calcd. C, 69.32%; H, 8.37%. Found C, 69.23%; H, 8.45%.

5-(Heptadec-1-enyl)-2,2':5',2''-terthiophene (6):

Procedure A: To a stirred solution of **9** (0.7 g, 1.4 mmol) in 20 mL of $CHCl_3$ was added a catalytic amount of *p*-toluenesulfonic acid (pTSA) (0.14 g) and the mixture was kept in the dark at rt for 32 h. To the reaction mixture was added water, and the product was extracted into $CHCl_3$. The organic layer was washed with dilute aq Na_2CO_3 and water, dried over anhyd Na_2SO_4 and evaporated. Purification by neutral Al_2O_3 chromatography eluting with hexanes:CH_2Cl_2 (12:1), followed by recrystallization from hexanes:benzene mixtures afforded 0.2 g (30%) of **6** (exclusively trans) as yellow microcrystals, mp = 85 °C. Using the same procedure with camphor sulfonic acid (CSA) instead of pTSA gave 25% of **6** (trans). ^1H NMR (360MHz, $CDCl_3$), δ (ppm): 7.21 (dd, 1H, J=5.1, 0.8Hz), 7.16 (dd, 1H, J = 3.7, 0.9Hz), 7.06 (d, 1H, J=3.7Hz), 7.02-7.04 (m, 2H), 7.00 (d, 1H, J = 3.9Hz), 6.76 (d, 1H, J=3.7Hz), 6.45 (d, 0.15H, J=15.6Hz), 6.00-6.11 (m, 1H), 2.18 (q, 2H, J=6.9Hz), 1.45 (p, 2H, J=6.9Hz), 1.23-1.35 (m, 24H), 0.88 (t, 3H, J=6.8Hz). UV-vis ($CHCl_3$) λ_{Max} (nm): 383.8 (log ε = 4.53). IR (KBr) cm^{-1}: 2940, 2860, 1480, 1230, 1070, 960, 840, 800, 700. MS(m/e): 484 (100), 287 (57), 261 (35), 209 (7). Anal. Calcd. C, 71.90%; H, 8.27%. Found C, 71.78%; H, 8.25%.

Procedure B: To a solution of **9** (125.5 mg, 0.25 mmol) in 3 mL of pyridine was added *p*-toluenesulfonyl chloride (Ts-Cl) (52.4 mg, 0.28 mmol), and the mixture was heated at 85 °C for 12 h. After evaporation of the pyridine, water was added and the mixture was extracted with CH_2Cl_2. The organic layer was washed with water, dried over anhyd Na_2SO_4, evaporated and purified by flash chromatography (basic Al_2O_3) eluting with hexanes:CH_2Cl_2 (12:1) yielding 0.07 g (58%) of **6** (cis : trans = 15 : 85) as yellow microcrystals. Recrystallization from hexanes:benzene mixtures gave an analytically pure sample, mp 83 °C. ^1H NMR (360MHz, $CDCl_3$), δ(ppm): 7.21(dd, 1.5H, J = 5.0, 0.8Hz), 7.16 (dd, 1H, J=3.3, 0.7Hz), 6.98-7.09 (m, 4.6H), 6.87 (d, 0.15H, J=3.7Hz), 6.76 (d, 1H, J=3.6Hz), 6.48 (d, 0.15H, J=10.8Hz), 6.45 (d, 1H, J=15.6Hz), 6.00-6.11 (m, 1H), 5.55-5.65 (m, 0.15H), 2.44 (q, 0.3H, J=7.0Hz), 2.18 (q, 2H, J=7.0Hz), 1.41-1.50 (m, 2.3H), 1.23-1.35 (m, 28H), 0.89 (t, 3.5H, J=6.7Hz). UV-vis ($CHCl_3$) λ_{Max} (nm): 379.8 (log ε = 4.52). IR (KBr) cm^{-1}: 2940, 2860, 1470, 1070, 960, 840, 800, 690. MS(m/e): 484 (100), 287 (39), 261 (31), 249 (18), 149 (21), 134 (32). Anal. Calcd. C, 71.90%; H, 8.27%. Found C, 71.92%; H, 8.33%.

5-Bromo-5''-formyl-2,2':5',2''-terthiophene (20):

To a stirred solution of **8** (2.5 g, 9.1 mmol) in 250 mL of CH_2Cl_2/glacial AcOH (1:1) was added N-bromosuccinimide (1.60 g, 9.1 mmol) at rt. After 24 h the resultant yellow precipitate was filtered, washed with water (pH = 7), and dried yielding **20** (2.49 g, 77%) in the form of yellow powder. The filtrate was washed

with water and the organic layer, after drying over anhyd Na_2SO_4, and evaporation, gave another fraction of **20** (0.63 g, 20%), in the form of tan-brown powder. The two fractions were combined and recrystallized from hexanes:CH_2Cl_2 mixtures affording analytically pure **20** in the form of brown yellow needles, mp 158 °C. ^1H NMR (360MHz, $CDCl_3$), δ (ppm): 9.87 (s, 1H), 7.67 (d, 1H, J=3.9Hz), 7.25 (d, 1H, J=4.0Hz), 7.24 (d, 1H, J=4.0Hz), 7.06 (d, 1H, J=3.9Hz), 7.00 (d, 7H, J=3.9Hz), 6.97 (d, 1H, J=3.8Hz). UV-vis ($CHCl_3$) λ_{Max} (nm): 402.9 (log ε = 4.42). IR (KBr) cm^{-1}: 2800, 1660, 1450, 1240, 1230, 1060, 980, 860, 800, 750, 670. MS(m/e): 356 (100), 275(11), 231 (38), 203 (16), 145 (16), 123 (12). Anal. Calcd. C, 43.94%; H, 1.99%; Br, 22.49; S. 27.07. Found C, 44.05%; H, 2.07%; Br, 22.57%; S, 27.17%.

5-Bromo-5''-(1-hydroxyheptadecyl)-2,2':5',2''-terthiophene (21):

In a flame dried 250 mL roundbottom flask containing Mg turnings (1.23 g, 51 mmol) and 120 mL of anhyd Et_2O was added 1,2-dibromoethane (0.5 mL, 5.9 mmol), and the mixture was warmed to approx 40 °C till constant bubbling was observed at rt. Hexadecyl bromide (7.73 g, 25 mmol) was added, upon which a vigorous reaction ensued to form the alkyl Grignard reagent. The mixture was refluxed for 1 h followed by the addition of **20** (3 g, 8.5 mmol) in one portion with Et_2O (20 mL). The course of the reaction was monitored by UV-vis spectroscopy. After refluxing for 1.5 h, the reaction mixture was cooled to rt and 200 mL of cold sat. NH_4Cl solution was added. After stirring for 30 min, the yellow precipitate was extracted with hexanes:Et_2O (1:1). The organic layer, after washings with water, drying over anhyd Na_2SO_4, and evaporation gave a yellow waxy solid. Addition of 250 mL of hexane and stirring in a sonicator for 2 h, filtration and washing with hexanes yielded 4.72 g (96%) of spectroscopically pure **21** in the form of a yellow powder. Recrystallization from hexanes:benzene mixtures afforded a pure sample, mp 120 °C. ^1H NMR (360MHz, $CDCl_3$), δ (ppm): 6.99-7.05 (m, 3H), 6.97 (d, 1H, J=3.9Hz), 6.91 (d, 1H, J=3.9Hz), 6.87 (d, 1H, J=3.7Hz), 4.88 (m, 2H), 1.96 (d, 7H, J=4.1Hz), 1.72-1.89 (m, 2H), 1.20-1.42 (bs, 26H), 0.88 (t, 3H, J=6.7Hz). UV-vis ($CHCl_3$) λ_{Max} (nm): 366.0 (log ε = 4.56). IR (KBr) cm^{-1}: 3440(b), 2935, 2860, 1470, 1430, 1070, 850, 800, 720. MS(m/e): 581 (4), 564 (100), 484 (46), 367 (72), 341 (58), 287 (47). HRMS for (M^+ - H_2O) $C_{29}H_{39}BrS_3$ Calcd. 564.13762. Found 564.136246.

5-Bromo-5''-heptadecyl-2,2':5',2''-terthiophene (17):

Procedure A. To a suspension of **21** (0.18 g, 0.31 mmol) in 10 mL of 1,2-dichloroethane was added zinc iodide (0.15 g, 0.47 mmol) and sodium cyanoborohydride (0.15 g, 2.3 mmol). The reaction mixture was refluxed for 1h. Water was added and the produce was extracted with dichloromethane. The organic layer was washed with water, dried over anhyd Na_2SO_4, and evaporated yielding 0.13 g (75%) of spectroscopically pure **17** in the form of a yellow powder. Recrystallization from hexanes:benzene mixture afforded analytically pure **17**, mp 104-105 °C.

Procedure B. To a stirred solution of **4** (1 g, 2.06 mmol) in 20 mL of dry THF containing 0.1g of AIBN was added 1,3-dibromo-5,5-dimethylhydantoin (0.29 g, 1.03 mmol) at -78 °C. After 24 h, addition of ice water resulted in a yellow precipitate. Filtration, washing with water, and drying yielded 1.08 g (93%) of spectrally pure **17** in the form of yellow powder. Recrystallization from hexanes:benzene afforded an analytical sample of **17**, mp 104-105 °C. ^1H NMR (360MHz, $CDCl_3$), δ (ppm): 6.95-7.00 (m, 4H), 6.89 (d, 1H, J=3.9Hz), 6.68 (d, 1H, J=3.7Hz), 2.78 (t, 2H, J=7.6Hz), 1.68 (p, 2H, J=7.2Hz), 1.31-1.41 (m, 2H), 1.21-1.30 (bs, 26H), 0.88 (t, 3H, J=7.6Hz). UV-vis ($CHCl_3$) λ_{Max} (nm): 367.8 (log ε = 4.38). MS(m/e): 566 (52), 486 (36), 350 (100), 261 (36), 180 (29), 152 (47). Anal. Calcd. C, 61.59%; H, 7.26%. Found C, 61.65%; H, 7.31%.

5-Bromo-5''-hydroxymethyl-2,2':5',2''-terthiophene (22):

To a stirred solution of **20** (0.1 g, 0.28 mmol) in 5 mL of dry THF was added sodium borohydride (11 mg, 0.28 mmol) at rt. After 12 h, the THF was evaporated, water was added, and the mixture was stirred

for 2 h. The resultant yellow ppt was filtered, washed repeatedly with water, and dried yielding spectroscopically pure **22** in quantitative yield. Recrystallization from hexanes:ethyl acetate mixture afforded an analytically pure sample of **22** in the form of yellow needles, mp 165 °C (dec.). ^{1}H NMR (360MHz, $CDCl_3$), δ (ppm): 7.04 (d, 1H, J=3.8Hz), 7.03 (d, 1H, J=3.5Hz), 7.01 (d, 1H, J=3.6Hz), 6.98 (d, 1H, J=3.6Hz), 6.92 d, 1H, J=3.4Hz), 6.91 (d, 1H, J=3.8Hz), 4.81 (s, 2H). UV-vis ($CHCl_3$) λ_{Max} (nm): 358.5 (log ε = 4.39). IR(KBr) cm^{-1}: 3320(b), 2920, 2880, 1430, 1200, 1040, 1000, 970, 845, 800, 650. MS(m/e): 358 (100), 356 (98), 341 (71), 216 (18), 203 (20), 171 (13), 145 (12). Anal. Calcd. C, 43.70%; H, 2.54%; Br, 22.36; S. 26.92. Found C, 43.79%; H, 2.50%; Br, 22.43%; S, 27.00%.

5-Bromo-5''-hexadecyloxymethyl-2,2':5',2''-terthiophene (18):

To a sodium hydride dispersion (50% in paraffin) (0.27 g, 5.6 mmol), washed twice with dry hexanes, was added a solution of **22** (1 g, 2.8 mmol) in 40 mL of dry DMF. The reaction mixture was stirred for 30 min. at rt, followed by the addition of hexadecyl bromide (0.86 g, 2.8 mmol). After 10h., the reaction mixture was diluted with 200 mL of water and stirred for 3 h. The organic layer was passed through a short SiO_2 column, eluting with CH_2Cl_2. Evaporation of the organic layer and addition of methanol yielded 1g (63%) of **18** in the form of pale yellow powder. Recrystallization from hexanes:benzene mixture afforded an analytical sample of **18**, mp 101 °C. ^{1}H NMR (360MHz, $CDCl_3$), δ (ppm): 7.03 (d, 1H, J=3.9Hz), 7.02 (d, 1H, J=3.8Hz), 7.00 (d, 1H, J=3.6Hz), 6.97 (d, 1H, J=3.8Hz), 6.90 (d, 1H, J=3.9Hz), 6.87 (d, 1H, J=3.4Hz), 4.62 (s, 2H), 3.49 (t, 2H, J=6.5Hz), 1.6 (p, 2H, J=7.7Hz), 1.20-1.39 (m, 26H), 0.88 (t, 3H, J=6.8Hz). UV-vis ($CHCl_3$) λ_{Max} (nm): 364.5 (log ε = 4.33). MS(m/e): 582 (61), 502 (24), 341 (100), 261(60), 217 (24), 135 (56), 111 (66). Anal. Calcd. C, 59.90%; H, 7.06%. Found C, 59.99%; H, 7.11%.

5-Bromo-5''(heptadec-1-enyl)-2,2':5',2''-terthiophene (19):

To a stirred solution of **21** (1 g, 1.7 mmol) in 100 mL of $CHCl_3$ was added a catalytic amount of *p*-toluenesulfonic acid (pTSA) (0.2 g) and the mixture was kept at rt for 16 h. To the reaction mixture was added water, followed by extraction with $CHCl_3$. The organic layer was washed with dilute aq Na_2CO_3, then water, dried over anhyd Na_2SO_4 and evaporated. Purification by SiO_2 chromatography eluting with hexanes:CH_2Cl_2 (12:1), followed by recrystallization from hexanes:benzene mixture afforded 0.71 g (73%) of **19** (exclusively trans) as yellow microcrystals, mp = 127-130 °C. ^{1}H NMR (360MHz, $CDCl_3$), δ (ppm): 6.98-7.03 (m, 3H), 6.89 (d, 1H, J=3.8Hz), 6.75 (d, 1H, J=3.7Hz), 6.44 (d, 1H, J=15.7Hz), 6.01-6.12 (m, 1H), 2.18 (q, 2H, J=7.0Hz), 1.45 (p, 2H, J=6.8Hz), 1.19-1.37 (m, 24H), 0.88 (t, 3H, J=6.7Hz). UV-vis ($CHCl_3$) λ_{Max} (nm): 381.0 (log ε = 4.33). IR(KBr) cm^{-1}: 2940, 2860, 1470, 1435, 1070, 955, 860, 800, 720. MS(m/e): 564 (72), 484 (100), 354 (31), 287 (32), 261 (64), 149 (25). Anal. Calcd. C, 61.81%; H, 6.93%. Found C, 61.61%; H, 6.95%.

5,5''''''-Diheptadecyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2'''''':hexathiophene or α,ω-Diheptadecylsexithiophene (1):

Procedure A. To a stirred solution of **4** (0.4 g, 0.82 mmol) in 25 mL of dry benzene was added anhyd $FeCl_3$ (0.85 g, 5.2 mmol). An immediate color change from pale yellow to dark blue was observed. After 10 min., the benzene was evaporated, the mixture was diluted with 1:1 water/methanol, and the oxidized product was reduced with aq. 40% hydrazine. Stirring in the sonicator for 1 h followed by filtration, washing with water, methanol, CH_2Cl_2, Et_2O, and drying gave a red solid. Purification was achieved by dissolving the solid in large amount of boiling benzene followed by hot filtration. Compound **1** precipitated at rt in the form of an orange red solid. Filtration, washing with benzene and drying yielded 0.22 g (55%) of the pure product, mp 265 °C.

Procedure B. Into a flame dried three-necked flask equipped with a reflux condenser and flushed with N_2, was added zinc (57.9 mg, 0.89 mmol), triphenylphosphine (464 mg, 1.8 mmol), potassium iodide (14.7 mg, 0.09 mmol), $Ni(PPh_3)_2Cl_2$ (579 mg, 0.89 mmol), and 6 mL of dry oxygen-free DMF. The stirred mixture was heated for 1 h at 60 °C under N_2 to form the Ni(0) reagent. During this time the initial deep blue suspension turned to green-yellow, and finally to red-brown. A solution of **17** (0.5 g, 0.89 mmol) in 20 mL of dry oxygen-free THF was syringed in, and the reaction mixture was stirred under N_2 at 60 °C for 24 h. Cooling the reaction mixture, and pouring into water gave a precipitate which was filtered, washed with methanol and acetone (to remove triphenylphosphine, and other terthiophene by-products), again with methanol and dried, yielding a deep red solid. The precipitate was extracted using a soxhlet extraction unit with CCl_4. The extract, on cooling to rt afforded orange red crystals, which after filtration, washing with CCl_4, and drying afforded 0.24 g (56%) of **1**, mp 265 °C. MS(m/e): 971 (100), 745 (15), 485 (8), 372 (6). UV-vis (hot $CHCl_3$) λ_{Max} (nm): 442.0 (log ε = 4.77). IR(KBr) cm^{-1}: 2940, 2860, 1480, 1470, 1450, 1080, 840, 800, 720. HRMS for $C_{58}H_{82}S_6$ Calcd. 970.474084; Found 970.473557.

5,5''''-Dihexadecyloxymethyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2'''''-hexathiophene or α,ω-Dihexadecyloxymethylsexithiophene (2):

Into a flame dried three-necked flask equipped with a reflux condenser and flushed with N_2, was added zinc (56.3 mg, 0.86 mmol), triphenylphosphine (451 mg, 1.7 mmol), potassium iodide (14 mg, 0.09 mmol), $Ni(PPh_3)_2Cl_2$ (563 mg, 0.86 mmol), and 6 mL of dry oxygen-free DMF. The stirred mixture was heated for 1 h at 60 °C under N_2. A solution of **18** (0.5 g, 0.86 mmol) in 12 mL of dry oxygen-free THF was syringed in, and the reaction mixture was stirred under N_2 at 60 °C for 24 h. Following the same workup conditions as used in the preparation of **1** (Procedure B), 0.35 g (81%) of **2** was obtained in the form of orange crystals, mp 236 °C. MS(m/e): 1003 (3), 762 (7), 522 (100), 261 (17). UV-vis (hot $CHCl_3$) λ_{Max} (nm): 437.2 (log ε = 4.44). IR(KBr) cm^{-1}: 2940, 2860, 1480, 1470, 1450, 1370, 1110, 840, 800, 720. HRMS for $C_{58}H_{82}O_2S_6$ Calcd. 1002.463913; Found 1002.463837.

5,5''''-Diheptadec-1-enyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2'''''-hexathiophene or α,ω-Dipentadecylvinylsexithiophene (3):

Into a flame dried three-necked flask equipped with a reflux condenser and flushed with N_2, was added zinc (58.1 mg, 0.89 mmol), triphenylphosphine (465 mg, 1.8 mmol), potassium iodide (14.7 mg, 0.09 mmol), $Ni(PPh_3)_2Cl_2$ (581 mg, 0.89 mmol), and 6 mL of dry oxygen-free DMF. The stirred mixture was heated for 1 h at 60 °C under N_2. A solution of **19** (0.5 g, 0.89 mmol) in 20 mL of dry oxygen-free THF was syringed in, and the reaction mixture was stirred under N_2 at 60 °C for 24 h. Following the same workup conditions used in the preparation of **1** (Procedure B), 0.35 g (82%) of **3** was obtained in the form of red microcrystals, mp 285 °C. MS(m/e): 967 (59), 562 (34), 486 (80), 337 (38), 257 (100), 228 (55). UV-vis (hot $CHCl_3$) λ_{Max} (nm): 452.8 (log ε = 5.17). IR(KBr) cm^{-1}: 2940, 2860, 1480, 1470, 1450, 1380, 1080, 960, 850, 800, 720. HRMS for $C_{58}H_{78}S_6$ Calcd. 966.442784; Found 966.440063.

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