Synthesis of Binaphthyl−Oligothiophene Copolymers with Emissions of Different Colors: Systematically Tuning the Photoluminescence of Conjugated Polymers

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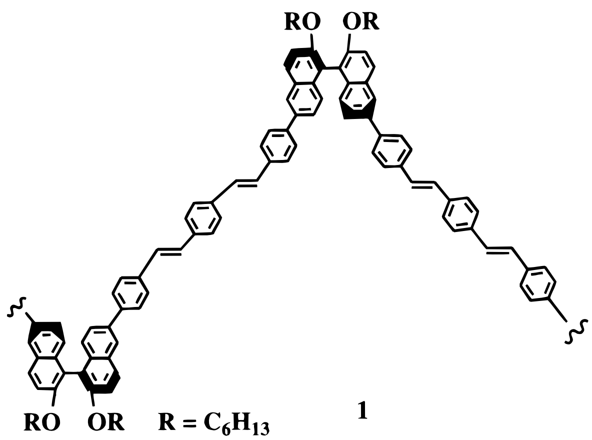
ABSTRACT: Copolymers of 1,1′-binaphthyl and oligothiophenes have been synthesized by using the Suzuki coupling reaction. These polymers are soluble in organic solvents such as chloroform and THF. The higher molecular weight polymers have shown high thermal stability. These binaphthyl−thiophene copolymers have well-defined conjugation that is independent of their polymer chain length. With the increase of the number of thiophene units in the repeating unit, both the absorption and emission wavelengths of these polymers undergo a red shift. Materials that can emit different intense colors have been obtained. This study demonstrates that the luminescence properties of binaphthyl-based conjugated polymers can be systematically tuned.

Introduction

Conjugated polymers have been studied extensively in the past 2 decades.[1,2] These materials have exhibited a number of important and potentially very useful properties such as high doped conductivity, electroluminescence, and optical nonlinearity. Recently, we have used the optically active 1,1′-binaphthyls to construct chiral conjugated polymers[3] such as **1**,[4] **2**,[5] and **3**.[6] These polymers are soluble in organic solvents, which makes them easy to process. They have shown strong fluorescence and are potentially useful for polarized photo- and electroluminescences. Compounds **4**,[7] **5**,[5] and **6**[6] have been prepared as the repeating units of the binaphthyl-based polymers. Spectroscopic study shows that both the absorption and emission wavelengths of these repeating units are very close to those of their



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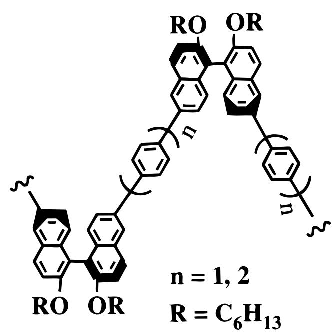

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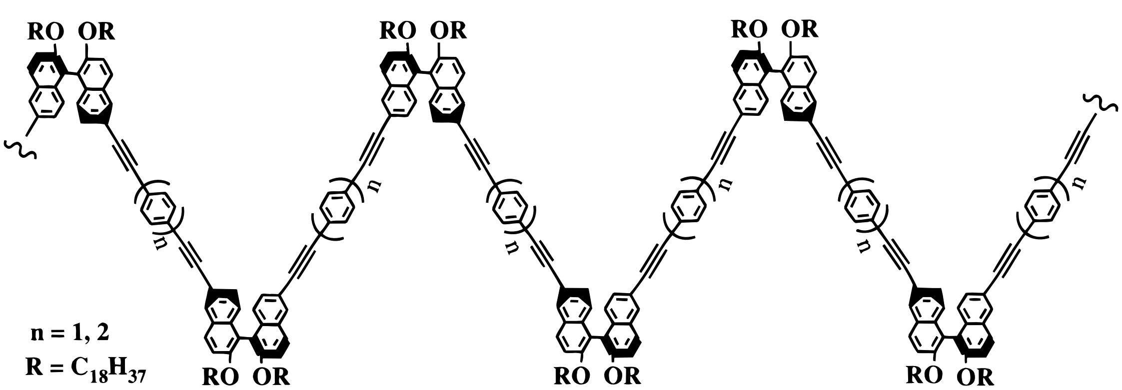

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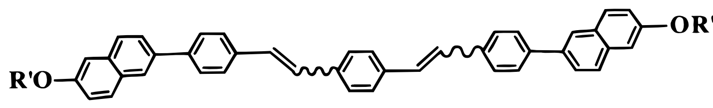

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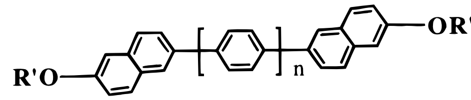
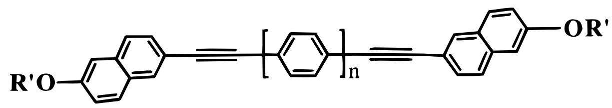


n = 1, 2

5

R' = -$CH_2C(CH_3)_3$



n = 1, 2

6

corresponding polymers. This demonstrates that the conjugation of the binaphthyl-based polymers is mostly determined by the conjugation within their repeating units and there is almost no extended conjugation between each adjacent repeating unit in the main chain. The conjugation of these polymers is thus independent of their chain lengths. Therefore, it is possible to systematically adjust the conjugation of the binaphthyl-based polymers by incorporating linkers of different conjugation lengths between the binaphthyl units in the polymer chain. In this way, the photo- and electroluminescent properties of these polymers can be systematically tuned.

Polymers **1**−**3** are all strong blue-light-emitting materials with emissions below 500 nm and absorptions below 390 nm. Because oligothiophenes have shown low band gap, high stability, and interesting optical and electrical properties, we have carried out the copolymerization of binaphthyl molecules with oligothiophenes in order to prepare polymers that can emit light of a broad range of colors. The use of silanylene[8] and *m*-phenylene units[9] to synthesize copolymers with thiophenes has been reported recently, and the photo- and electroluminescence properties of these polymers are systematically tuned by using different oligothiophene linkers. In this paper, we report the synthesis and characterization of the binaphthyl−oligothiophene copolymers that exhibit emissions of different colors.

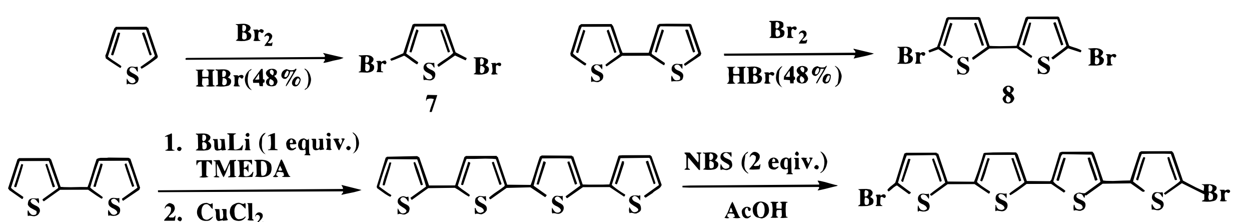
Results and Discussion

1. Synthesis of Oligothiophene Monomers. Oligothiophene monomers containing one, two, and four thiophene units are prepared by following the literature procedure.[10−12] As shown in Scheme 1, bromination of thiophene or 2,2′-bithiophene gives **7**[10] or **8**,[10,11] respectively. Treatment of 2,2′-bithiophene with *n*-BuLi followed by $CuCl_2$ generates the tetrathiophene **9**,[12] which is then converted to **10** upon reaction with 2 equiv of NBS.[11]

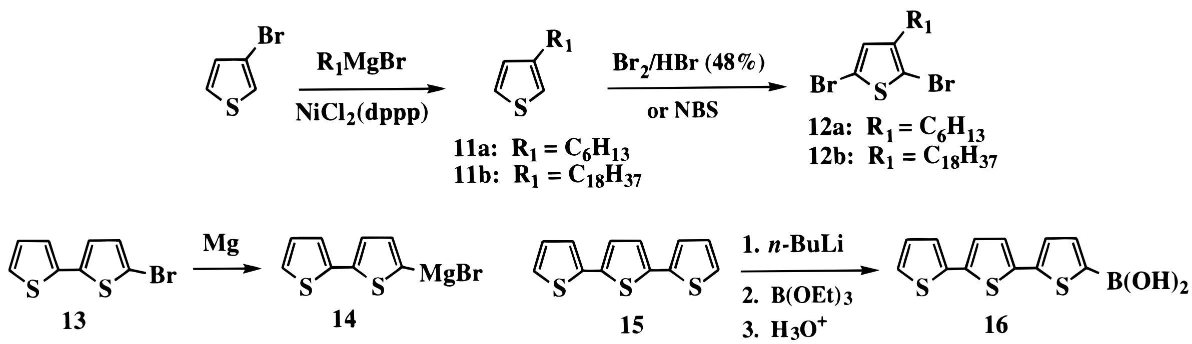
The tetrathiophene dibromide monomer **10** has a very low solubility in organic solvents. To make higher oligothiophenes, we have introduced flexible alkyl groups to increase their solubility. Scheme 2 shows the synthesis of the mono-, di-, and terthiophene reagents to be used for the preparation of higher thiophene oligomers. In the presence of $Ni^{II}Cl_2$(dppp) [dppp = 1,3-bis(diphenylphosphino)propane] catalyst, the coupling of 3-bromothiophene with a alkyl Grignard reagent, either hexylmagnesium bromide or octadecylmagnesium bromide, generates **11a** or **11b**.[13] Reaction of **11a** and **11b** with either bromine/HBr (48%) or NBS generates **12a** and **12b**.[10,14] A bithiophene Grignard reagent **14** is prepared from a bithiophene bromide **13**. Treatment of terthiophene **15**[11] with *n*-butyllithium followed by reaction with triethyl borate and 1 N HCl gives a terthiophene boronic acid **16**.

The nickel(II)-catalyzed cross-coupling of **12a**[14] with 2 equiv of **14** forms a pentathiophene **17** (Scheme 3).[13,15]

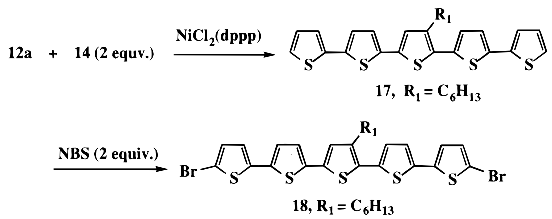
Scheme 1



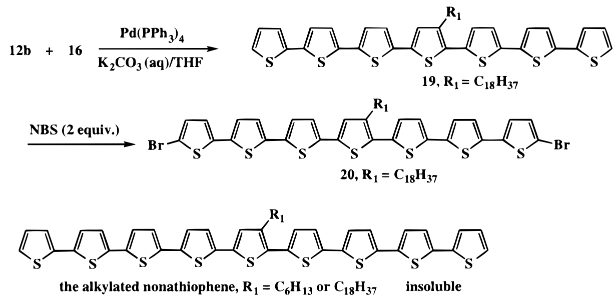
Scheme 2



Scheme 3



Scheme 4



The reaction of **17** with 2 equiv of NBS gives a pentathiophene dibromide monomer **18**.[11] Both **17** and **18** are soluble in chloroform and THF.

The Suzuki coupling of **16** with **12b** gives an octadecyl-substituted heptathiophene molecule **19** (Scheme 4).[16] Bromination of **19** with NBS forms **20**. The heptathiophenes **19** and **20** are soluble in chloroform and benzene at temperatures above 60 °C. However, the nonathiophene made from the coupling of **18** with **14** is not soluble no matter whether the hexyl or octadecyl R1 group is introduced.

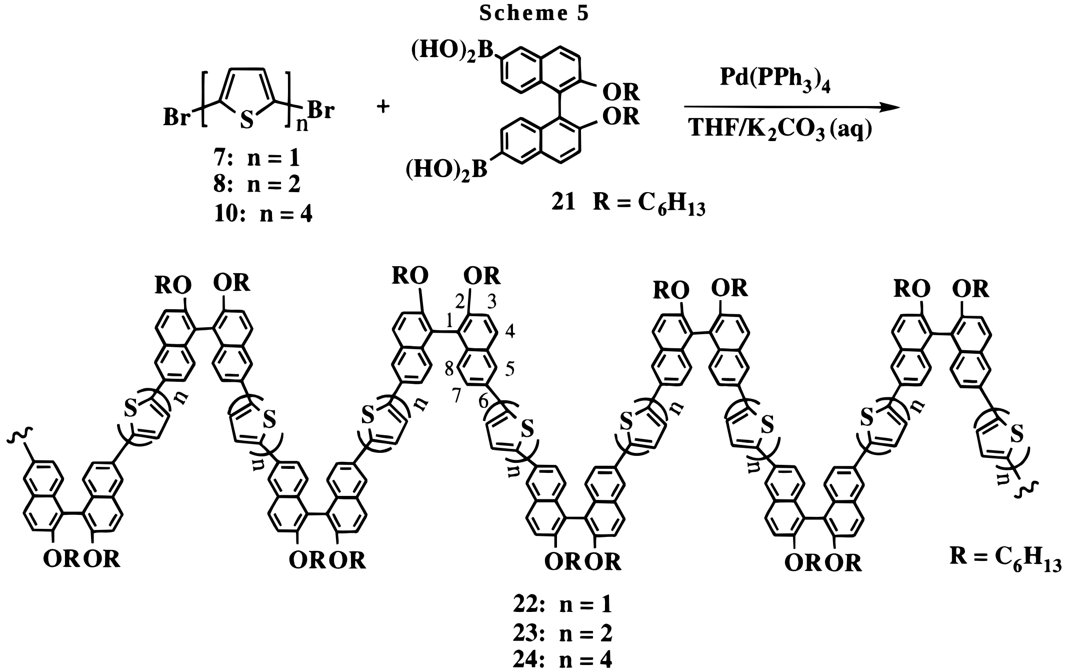
2. Synthesis of Binaphthyl−Oligothiophene Copolymers. In the presence of $Pd(PPh_3)_4$ (5 mol %), a 1:1 mixture of the monothiophene dibromide **7** and a binaphthyldiboronic acid **21**[4] undergoes the Suzuki coupling[16] in THF and 1 M K_2CO_3 (aqueous) to produce a binaphthyl−thiophene copolymer **22** (Scheme 5). This polymer is isolated as a greenish-yellow solid in 93% yield. Gel permeation chromatography (GPC) analysis shows that the molecular weight of **22** is M_w = 35 500 and M_n = 13 900 (PDI = 2.6). All of the GPC data in this paper are obtained by using polystyrene standards. Polymer **22** is soluble in organic solvents such as methylene chloride, chloroform, and THF. In the same way, **8** is coupled with **21** to give polymer **23** as a yellow solid in 97% yield. GPC shows that its molecular weight is M_w = 30 300 and M_n = 18 100 (PDI = 1.7). When the tetrathiophene monomer **10** is used to couple with **21**, a much lower molecular weight polymer **24** is obtained due to the low solubility of **10** in the reaction mixture. GPC shows its molecular weight is M_w = 5500 and M_n = 5100 (PDI = 1.1). This polymer is isolated as an orange solid in 88% yield.

Unlike **10**, the alkylated pentathiophene monomer **18** is very soluble in organic solvents. When **18** is polymerized with **21**, polymer **25** is obtained in 94% yield. This polymer is a red solid and soluble in chloroform and THF. GPC analysis shows that its molecular weight is M_w = 28 000 and M_n = 17 400 (PDI = 1.6), much higher than the binaphthyl−tetrathiophene copolymer **24**.

When the heptathiophene monomer **20** is coupled with **21** using THF as the solvent, because of the low solubility of **20**, only very low oligomers are obtained. To improve the polymerization, we have changed the solvent from THF to benzene for the Suzuki coupling reaction and have increased the polymerization temperature to 85 °C (bath temperature). Under this condition, polymer **26** is produced. Its molecular weight is M_w = 6000 and M_n = 2300 (PDI = 2.6) as shown by GPC analysis. This polymer is soluble in THF and hot chlorobenzene. It is isolated as a dark-red solid in 54% yield. The lower yield of **26** is due to the formation of insoluble and probably higher molecular weight materials.

3. Spectroscopic Study of the Binaphthyl−Thiophene Copolymers. Polymer **22** gives a very well-resolved ^{1}H NMR spectrum in chloroform-*d* (Figure 1a). The singlet at δ 8.07 in the ^{1}H NMR spectrum is assigned to H-5 of the binaphthyl unit. Another singlet at δ 7.29 is attributed to the protons on the thiophene units. Four other doublets in the aromatic region are due to the four remaining protons on the binaphthyl

Scheme 5



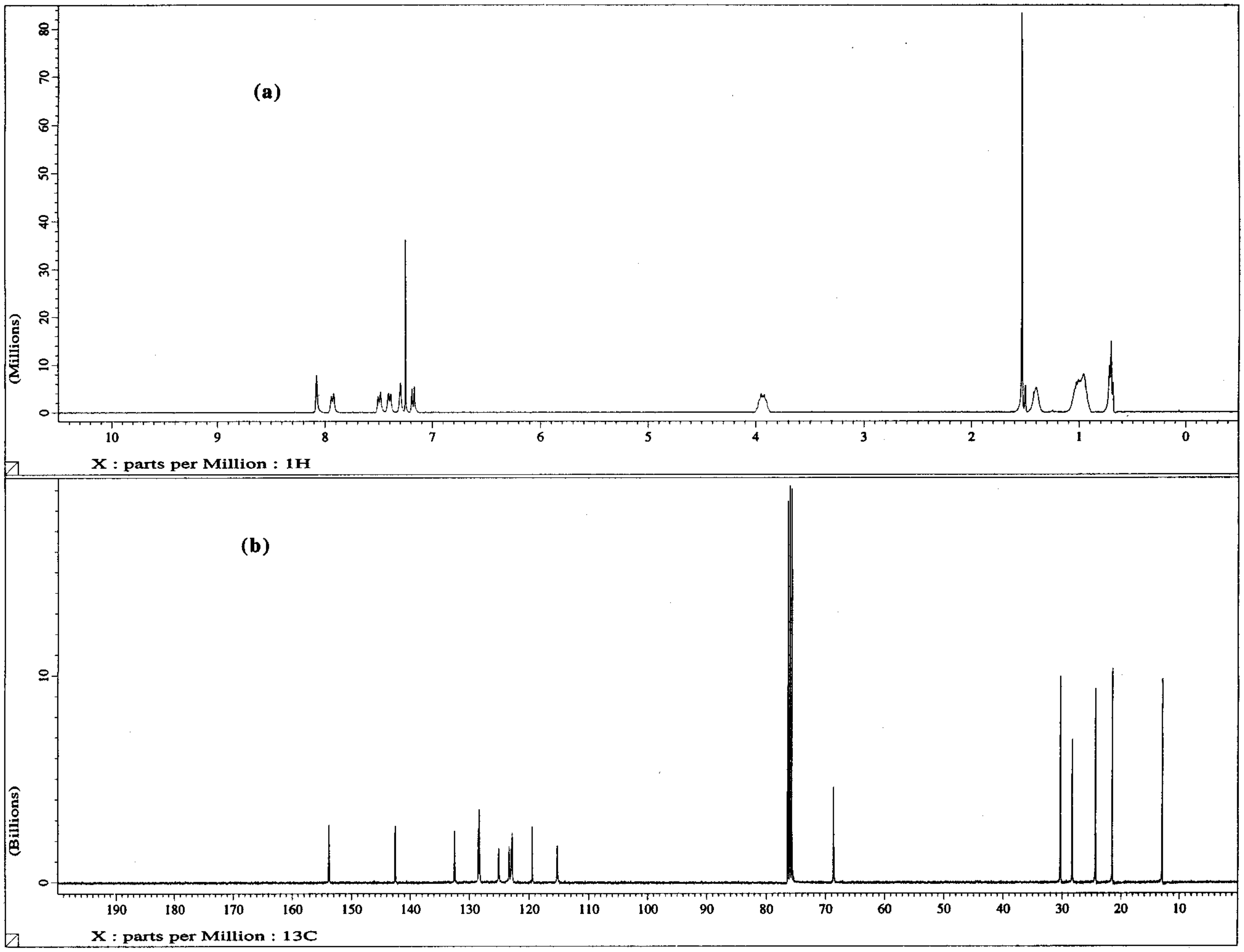
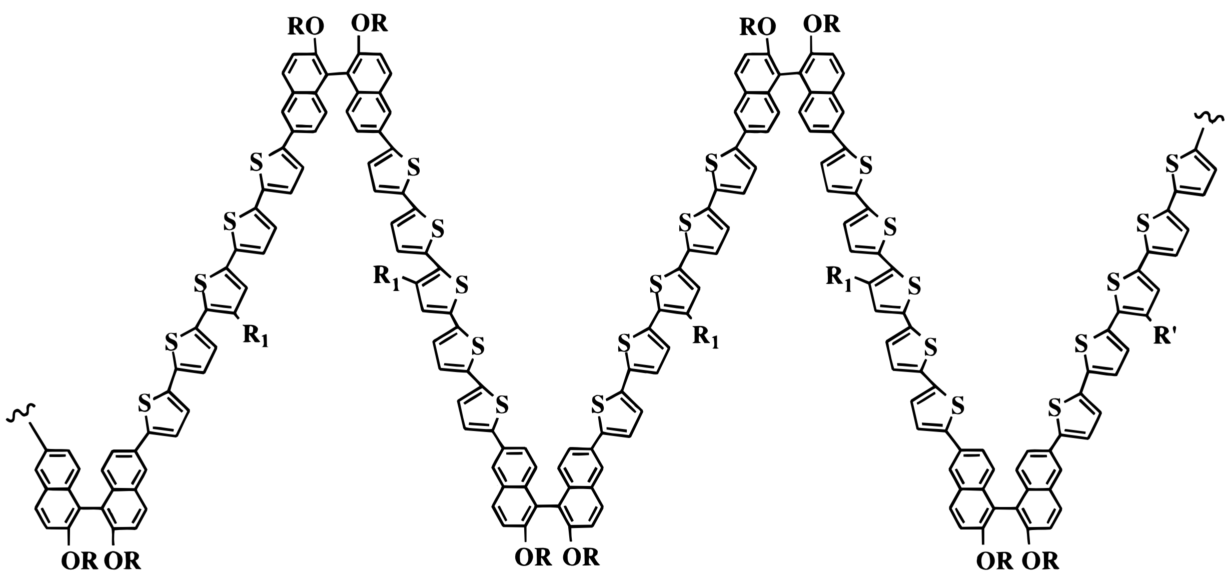
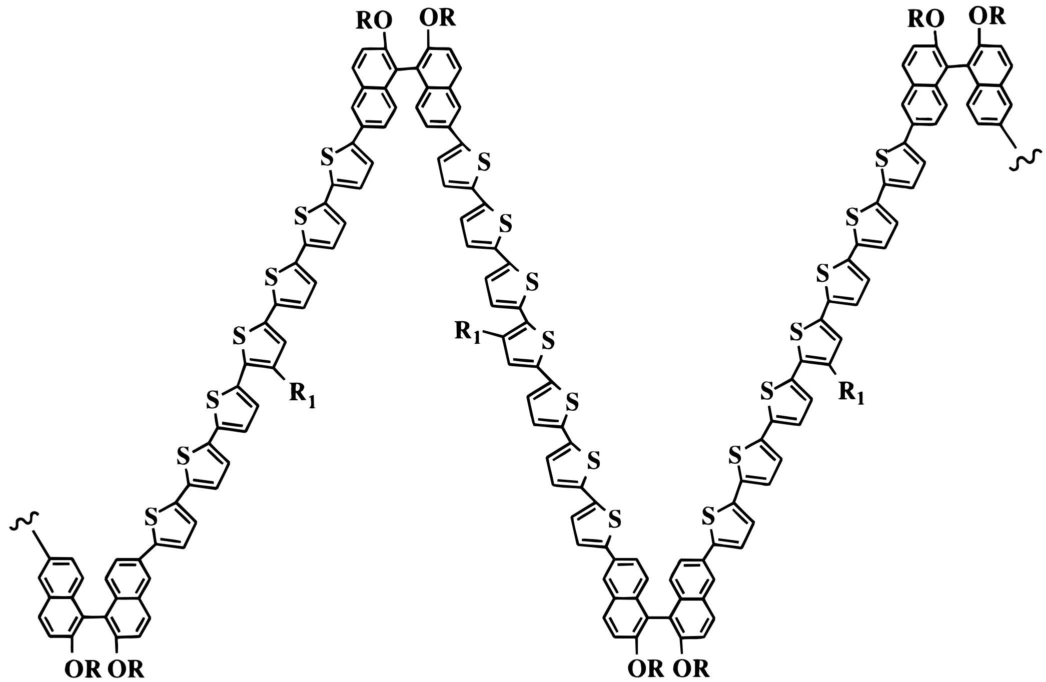


Figure 1. (a) ^{1}H NMR spectrum of **22** in $CDCl_3$. (b) ^{13}C NMR spectrum of **22** in $CDCl_3$.



25
R and $R_1 = C_6H_{13}$

units. The methylene protons adjacent to the oxygen atom in the hexyloxy group are observed as a multiplet at δ 3.92. The remaining alkyl protons are observed at δ 0.7−1.5. The ^{13}C NMR of this polymer is also well-resolved (Figure 1b). The well-resolved NMR spectra of this polymer are quite unusual, because **22** is made of racemic binaphthyl monomer and it should have a polymer backbone with randomly distributed *R* and *S* binaphthyl units. This indicates that there is very little interference between the adjacent chiral binaphthyl units for the NMR signals. Polymers **23**−**26** also exhibit similar NMR signals as **22**.



26
R and $R_1 = C_6H_{13}$

We have studied the UV absorption and fluorescence spectroscopic properties of the oligothiophene molecules and the binaphthyl−thiophene copolymers. Table 1 summarizes the absorption and fluorescence spectral data of the oliogothiophenes. A very large red shift (∼200 nm) for the longest wavelength absorption is observed from thiophene to the heptathiophene molecule **19**.

Table 2 summarizes the UV and fluorescence spectral data of the binaphthyl−thiophene copolymers in methylene chloride solution. The emission spectra of these polymers are taken by excitation at their longest wavelength absorption maximums. As shown in the table, with the increase of the number of thiophene rings in the polymer repeating units, both the absorption and emission wavelengths are increasing systematically. However, due to the alkyl substituent in the pentathiophene unit of **25**, the planarity of the polymer repeating unit has been disrupted and the UV absorptions of **25** do not show the expected red shift. Nevertheless, the fluorescence signals of **25** do undergo a red shift from those of **24**. From the monothiophene polymer **22** to the heptathiophene polymer **26**, the luminescences of these binaphthyl-based conjugated materials undergo a systematic red shift. Figure 2 is the UV absorption spectra of polymers **22**−**26**, and Figure 3 is their fluorescence spectra.

The fluorescence quantum yields of the binaphthyl−oligothiophene copolymers in methylene chloride solution are estimated by using 9-anthracenecarboxylic acid as the reference. The quantum yield of 9-anthracenecarboxylic acid in acetonitrile is 0.26.[17] This molecule has absorptions at $\lambda_{max} = 344$, 361, and 381 nm and an emission at 465 nm. Therefore, 9-anthracenecarboxylic acid is only good as a reference for the one thiophene and two thiophene copolymers **22** and **23**, but not good for polymers **24**−**26** due to quite different absorption and emission wavelengths. The data measured for polymers **24**−**26** are thus only provided as references.

Since the binaphthyl−oligothiophene copolymers are not soluble in acetonitrile, their measurements were carried out in methylene chloride. The quantum yield of the reference 9-anthracenecarboxylic acid in methylene chloride was obtained as 0.442 according to the following equation:[18]

$$\phi_F = \phi_{F,ref}\left(\frac{A_{ref}}{A}\right)\left(\frac{n_D}{n_{D,ref}}\right)^2\left(\frac{a}{a_{ref}}\right)$$

In this equation, $\phi_{F,ref}$ is the quantum yield of the reference. A_{ref} is the absorbance of the reference. $n_{D,ref}$ is the refraction index of the solvent of the reference. a_{ref} is the intergration of the area under the fluorescence signal of the reference.

In the measurement of the polymer fluorescence quantum yields, the concentrations of the polymers in methylene chloride are in the range of 10^{-7}−10^{-6} M, with the absorbances below 0.1. By using the quantum yield of the reference in methylene chloride and the following equation, the quantum yields of the polymers have been obtained:

$$\phi_F = \phi_{F,ref}\left(\frac{A_{ref}}{A}\right)\left(\frac{a}{a_{ref}}\right)$$

When the excitation wavelength is set at 380 nm, the estimated quantum yields for polymers **22**, **23**, **24**, **25**,

Table 1. UV Absorption Wavelengths of the Oligothiophenes

oligothiophene	thiophene	2,2′-bithiophene	**9**	**17**	**19**
λ_{max}, nm	246	248, 306	254, 394	254, 406	210, 218, 234, 336, 438

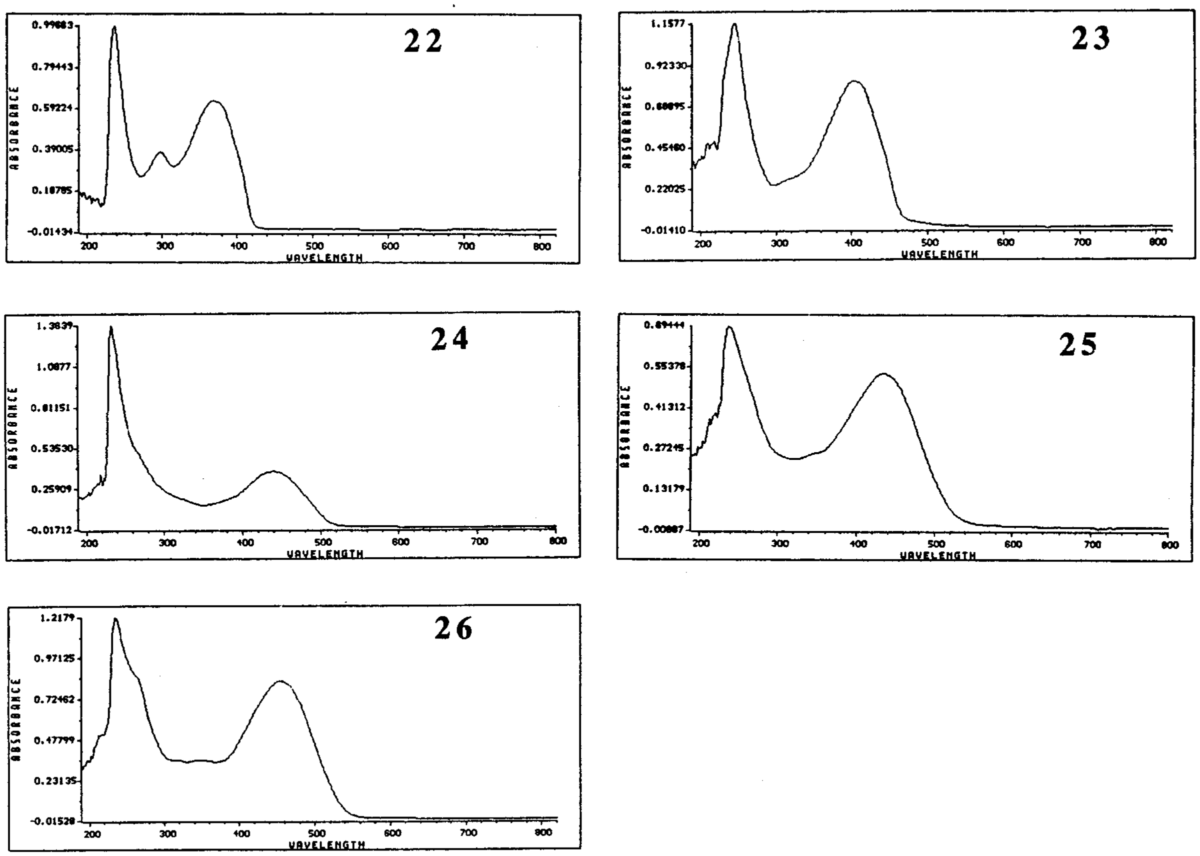


Figure 2. UV spectra of polymers **22**−**26** in methylene chloride.

Table 2. UV and Fluorescence Spectral Data of the Binaphthyl−Thiophene Copolymers

polymer	no. of thiophenes per repeat unit	color of polymer	UV λ_{max}, nm	fluorescence λ_{emi}, nm
22	1	yellow−green	236	421
			298	446
			368	475 (sh)
23	2	yellow	246	463
			406	498
24	4	orange	232	515
			270 (sh)	549 (sh)
			440	
25	5	bright red	236	530
			348 (sh)	568 (sh)
			434	
26	7	dark red	234	545
			264 (sh)	583
			454	631 (sh)

and **26** are 0.54, 0.26, 0.23, 0.054, and 0.065, respectively. When the excitation wavelengths for polymers **24**, **25**, and **26** are changed from 380 nm to their longest wavelength absorption maxmiums, their estimated quantum yields are 0.19, 0.23, and 0.072, respectively.

4. Thermogravimetric Analysis of the Binaphthyl−Thiophene Copolymers. Thermogravimetric analyses (TGA) for polymers **22**−**26** have been carried out. Figure 4 is the TGA plot of **22** under N_2 at a heating rate of 10 °C/min. As shown in the plot, the onset decomposition temperature of **22** is 383 °C (5% weight loss). There is about 32% weight loss before 475 °C. This is probably due to the fragmentation of the hexyl groups of **22**. After the loss of the alkyl groups on the binaphthyl units, the decomposition of **22** becomes very slow. Only about 10% weight loss is observed between 475 and 800 °C. This thermal decomposition pattern of **22** is very similar to what we have observed earlier for other binaphthyl-based chiral conjugated polymers such as **2** and **3**.

The TGA plot of polymer **23** is similar to that of **22**. The onset decomposition temperature of **23** is 393 °C. Before 460 °C, **23** probably loses its hexyl groups (28% of the polymer mass). From 460 to 800 °C, this polymer loses an additional 12% mass. Polymer **24** is much less stable compared to **22** and **23**, probably because of its low molecular weight. It shows 5% weight loss at 240 °C. When heated to 800 °C, a total 54% weight loss of **24** is observed.

The pentathiophene−binaphthyl polymer **25** exhibits similar thermal stability as **22** and **23**. The onset decomposition temperature of **25** is 389 °C. The major weight loss of this polymer, ca. 33% of the polymer mass, occurs before 485 °C. From 485 to 800 °C, the decomposition becomes very slow and only ca. 10% weight loss is observed. The low molecular weight polymer **26** has a much lower thermal stability. This polymer shows an onset decomposition temperature at 339 °C. Polymer **26** also has a two-stage decomposition pattern from 339 to 470 °C and from 470 to 800 °C. However, unlike **22**, **23**, and **25**, the decomposition rates of **26** in these two temperature ranges are similarly fast. A total mass loss of 63% is observed when heated to 800 °C.

Summary

In summary, we have demonstrated that the conjugation of the binaphthyl-based polymers can be systematically tuned by incorporating different lengths of oligothiophene units. Materials that can emit different intense colors have been obtained. These polymers are

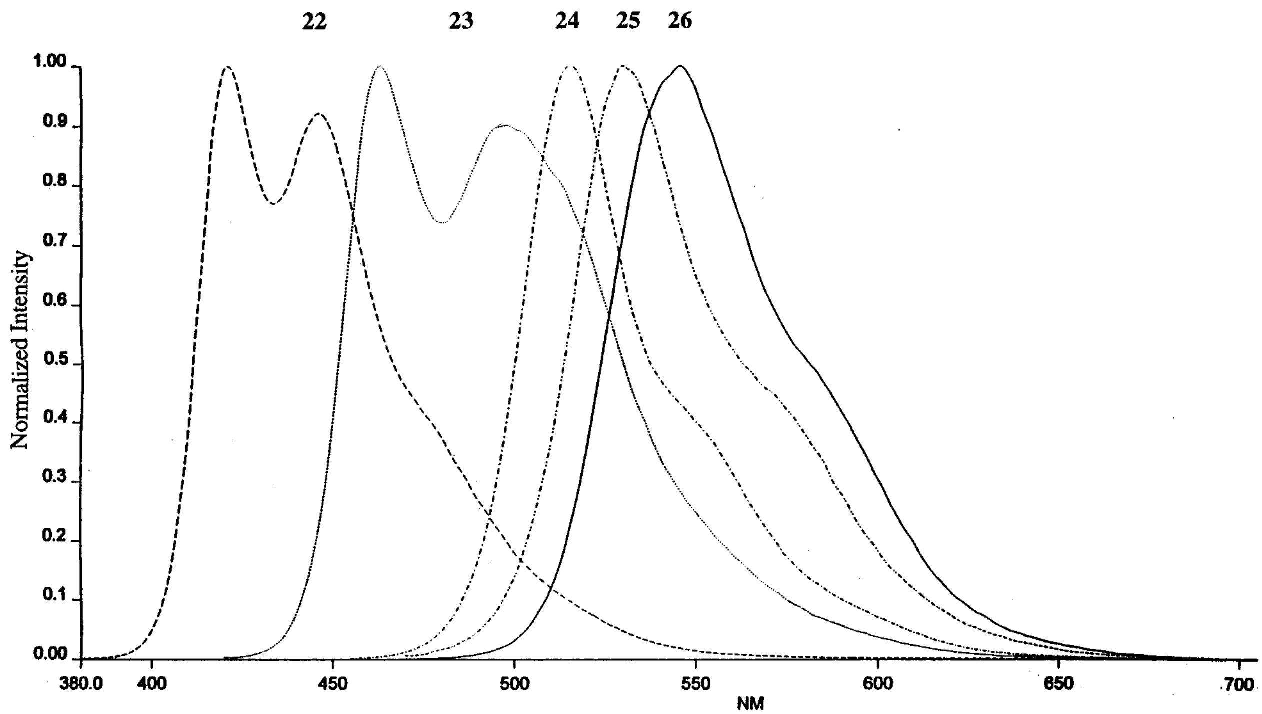


Figure 3. Fluorescence spectra of polymers **22**−**26** in methylene chloride.

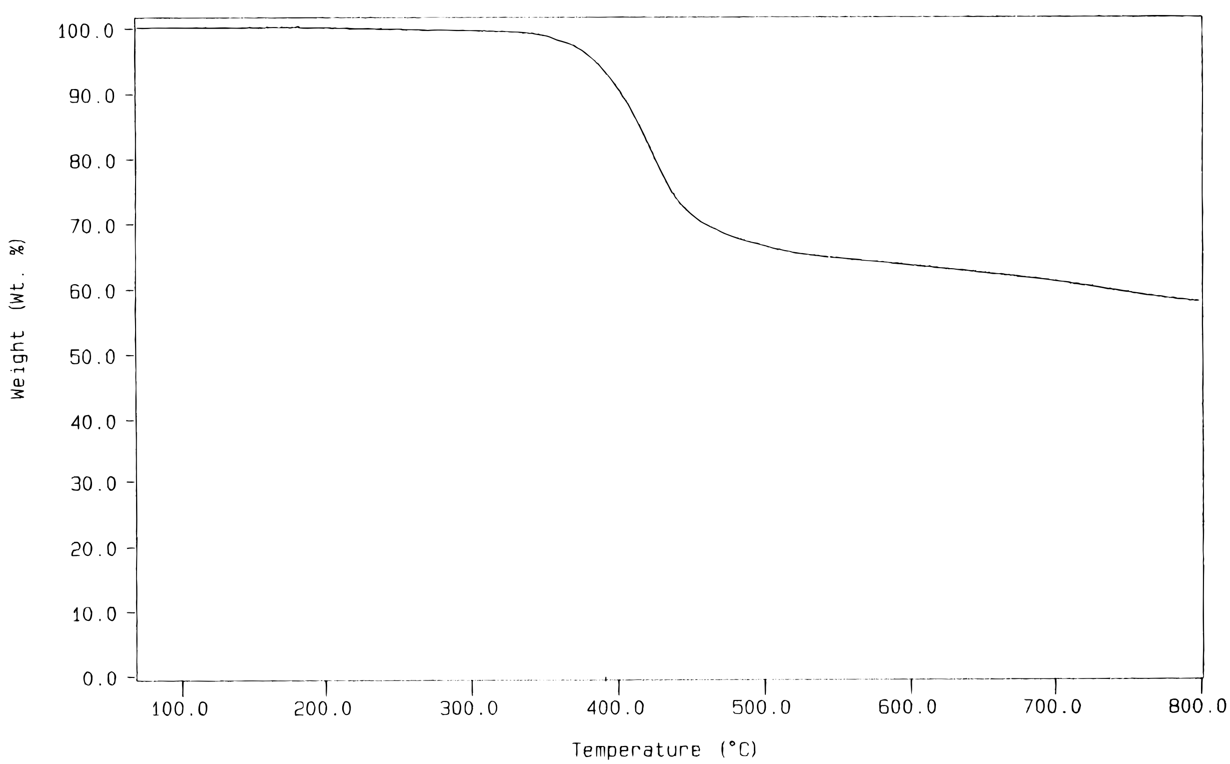


Figure 4. TGA plot of polymer **22**.

potentially useful for LED displays with tunable colors. The TGA study of these polymers demonstrates that the thiophene−binaphthyl polymers with higher molecular weights are thermally stable materials.

Experimental Section

General Data. NMR spectra were recorded on JEOL 270-MHz and 400-MHz spectrometers. Infrared spectra were recorded on a 2020/Galaxy Series FT-IR spectrometer by preparing KBr pellets of the materials. Elemental analyses were carried out by using a Perkin-Elmer 2400 Series II CHN S/O analyzer. Routine EI mass spectra were obtained by using a Hewlett-Packard 5890 Series II GC/DIP MS. FAB and electron spray mass spectra were carried out by the UC Riverside mass spectroscopy facility. Gel permeation chromatography (GPC) utilized a Waters 510 HPLC pump, a Waters 410 differential refractometer, and Ultrastyragel Linear GPC columns. UV−vis spectra were recorded on Hewlett-Packard 8451A and 8452A diode array spectrophotometers. Emission spectra were taken using a Perkin-Elmer Model LS50B luminescence spectrometer. Thermogravimetric analyses were carried out by using a Perkin-Elmer TGA 7 analyzer.

Thiophene, 3-bromothiophene, triethyl borate, and *N*-bromosuccinimide (NBS) were purchased from Aldrich and used directly. [1,3-bis(diphenylphosphino)propane]nickel(II) chloride and tetrakis(triphenylphosphine)palladium(0) were purchased from Stream and used directly. Tetramethylethylenediamine (TMEDA), diethyl ether, THF, and benzene were dried over sodium/benzophenone and freshly distilled before use.

Preparation and Characterization of 3″-Hexyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-pentathiophene (17). Under N_2, a diethyl ether solution (3 mL) of the bithiophene bromide **13** (500 mg, 2.0 mmol) was added dropwise to a dry flask containing Mg (67 mg, 2.8 mmol) in diethyl ether (1 mL). After the solution was heated at reflux for 11 h, the resulting Grignard reagent **14** was added to a mixture of **12a** (326 mg, 1.0 mmol) and $NiCl_2$(dppp) (5.4 mg, 0.01 mmol) in diethyl ether (10 mL) at 0 °C. The reaction mixture was then heated at reflux for 24 h. After the mixture cooled at 0 °C, 1 N HCl (20 mL) was added to quench the reaction and the aqueous layer was extracted with diethyl ether (3 × 10 mL). The combined organic solution was then washed sequentially with water, saturated $NaHCO_3$ solution, water, and brine and was dried over Na_2SO_4. After filtration, the solvent was removed with rotary evaporation. The residue was purified by flash chromatography on silica gel with hexane to give **17** as a bright orange solid in 63% yield (312 mg). The product emits bright yellow color on a TLC plate under UV light. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J = 7.0 Hz, 3H, CH_3), 1.32 [m, 6H, (CH_2)$_3$CH$_3$], 1.67 [br p, J = 7.6 Hz, 2H, CH_2(CH$_2$)$_3$CH$_3$], 2.75 [t, J = 7.9 Hz, 2H, ArCH_2(CH$_2$)$_4$CH$_3$], 7.02 (m, 4H), 7.07 (m, 2H), 7.11 (d, J = 3.7 Hz, 1H), 7.17 (m, 2H), 7.22 (m, 2H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 14.20, 22.71, 29.34, 29.59, 30.54, 31.75, 123.77, 123.83, 124.12, 124.28, 124.31, 124.46 (small), 124.47, 124.58, 124.59, 124.63 (small), 126.42, 126.65, 127.97, 127.99, 129.60, 134.90, 134.91, 135.93 (small), 136.00, 136.31, 136.39 (small), 137.18, 137.22, 137.23, 140.60 (the small peaks may be due to isomers or impurities). MS (DIP) m/z M$^+$ (496). HRMS (FAB) analysis has been carried out for **17** where R1 is an octadecyl group. HRMS Calcd for $C_{38}H_{48}S_5$: m/z 664.2360. Obsd: m/z 664.2365.

Preparation and Characterization of 5,5⁗-Dibromo-3″-hexyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-pentathiophene (18). To a solution of **17** (110 mg, 0.22 mmol) in chloroform (10 mL) and acetic acid (10 mL) was added NBS (79 mg, 0.44 mmol). The reaction solution was stirred at room temperature for 1 h and then at 60 °C for 4 h. After completion of the reaction, chloroform (50 mL) was added and the solution was washed with 2.2 M KOH solution, water, and brine. It was then dried over Na_2SO_4. After filtration and removal of the solvent, **18** was obtained as a bright red solid in 83% yield (120 mg). FT-IR (KBr, cm^{-1}) 2924 (m), 2868 (m), 1498 (m), 1429 (m), 1384 (m), 972 (w), 842 (w), 788 (s). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J = 6.9 Hz, 3H, CH_3), 1.32 [m, 6H, (CH_2)$_3$CH$_3$], 1.67 [p, J = 7.6 Hz, 2H, CH_2(CH$_2$)$_3$CH$_3$], 2.73 (t, J = 8.0 Hz, 2H, ArCH_2(CH$_2$)$_4$CH$_3$], 6.90 (m, 2H), 6.96 (m, 2H), 6.99 (m, 3H), 7.04 (m, 2H). MS (DIP) m/e M$^+$ (654). HRMS (FAB) analysis has been carried out for **18** where R1 is an octadecyl group. HRMS Calcd for $C_{38}H_{46}Br_2S_5$: m/z 820.0570. Obsd: m/z 820.0541.

Preparation and Characterization of 3-Octadecylthiophene (11b). (a) Preparation of the Octadecyl Grignard Reagent. Under N_2, to a dry 100-mL flask containing Mg (1.1 g), THF (20 mL) was added to cover the magnesium surface. Then, a THF (20 mL) solution of 1-bromooctadecane (redistilled and dried before use) (7.4 g, 22.2 mmol) containing an initiator $ClCH_2CH_2Cl$ (1 mL) was added dropwise. After the addition, the reaction mixture was heated at reflux for 1 h. At this point, most of the magnesium disappeared and the formation of the Grignard reagent was followed by quenching a small portion of the reaction mixture and then checking its ^{1}H NMR spectrum. **(b) Preparation of 11b.** To a dry 100-mL flask charged with 3-bromothiophene (3 g, 18.4 mmol), $NiCl_2$(dppp) (0.10 g, 0.184 mmol), and THF (50 mL), the Grignard reagent was added slowly through an additional funnel. The resulting brown mixture was heated at reflux overnight and was then quenched with 1 N HCl at 0 °C. After extraction with diethyl ether (3 × 30 mL), the organic solution was washed with water and dried over Na_2SO_4. The solvent was then removed with rotary evaporation. Purification of the residue by distillation at 210 °C (0.25 Torr) and then flash chromatography (silica gel, hexane) gave **11b** as a white solid in 87.5% yield (5.42 g). UV−vis λ_{max} (CH_2Cl_2, nm) 250. FT-IR (KBr, cm^{-1}) 2918 (s), 2849 (s), 1471 (m), 1384 (w), 1221 (w), 1182 (w), 1080 (w), 862 (w), 773 (s), 729 (w), 632 (w). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, J = 6.8 Hz, 3H, CH$_3$), 1.27 (br m, 30H), 1.61 (p, J = 7.1 Hz, 2H), 2.63 (t, J = 8.0 Hz, 2H, ArCH_2), 6.92 (m, 2H), 7.22(m, 1H). Anal. Calcd for $C_{22}H_{40}S$: C, 78.50; H, 11.98. Found: C, 78.66; H, 12.04. HRMS (FAB) Calcd for $C_{22}H_{40}S$: m/z 337.2928. Obsd: m/z 337.2942.

Preparation of 2,5-Dibromo-3-hexylthiophene (12a). To a mixture of 3-hexylthiophene (4.6 mmol), 48% HBr (3 mL), and diethyl ether (12 mL) was added Br_2 (0.5 mL, 9.7 mmol) via a syringe at −10 °C. After 2.5 h, the temperature was raised to 0 °C and water was added. The aqueous layer was then extracted with CH_2Cl_2, and the combined organic layer was washed with Na_2SO_3 solution and brine. After the solution was dried over Na_2SO_4, the solvent was removed. The crude product was loaded on top of a silica gel column and eluted with hexane to give **12a** as a colorless oil, 80% yield (1.2 g). The spectroscopic data of **12a** are consistent with the literature data.[14]

Preparation and Characterization of 2,5-Dibromo-3-octadecylthiophene (12b). A mixture of **11b** (2.0 g, 5.95 mmol) and NBS (2.62 g, 14.72 mmol) in chloroform (40 mL) and acetic acid (40 mL) was stirred at room temperature for 2 h and then at 35 °C for 9 h. After the mixture was cooled to room temperature, chloroform (40 mL) was added followed by the addition of KOH (2.2 M) solution until the mixture was basic. The organic phase was separated and was washed with water and brine. After the solution was dried over Na_2SO_4, the solvent was removed with rotary evaporation and the residue was purified by column chromatography (silica gel, hexane) to give **12b** as a white solid in 83% yield (2.43 g). FT-IR (KBr, cm^{-1}) 2951 (s), 2893 (s), 1471 (m), 1425 (w), 1383 (w), 1190 (w), 1001 (w), 808 (w), 715 (m), 470 (w). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, J = 9.7 Hz, 3H, CH_3), 1.28 (br, 30H, (CH_2)$_{15}$CH$_3$), 1.52 [m, 2H, CH_2(CH$_2$)$_{15}$CH$_3$], 2.48 [t, J = 11.4 Hz, 2H, ArCH_2(CH$_2$)$_{16}$CH$_3$], 6.76 (s, 1H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 14.23, 22.80, 29.19−29.80 (multiple peaks), 32.03, 107.99, 110.37, 131.02, 143.07. HRMS (FAB) Calcd for $C_{22}H_{38}Br_2S$: m/z 492.1060. Obsd: m/z 492.1051.

Preparation and Characterization of Terthienyl-2-boronic Acid (16). To a THF solution (5 mL) of terthiophene (**15**; 1.03 g, 4.15 mmol)[11] was added *n*-butyllithium (1.7 mL, 2.5 M solution in hexane, 4.25 mmol) dropwise at −78 °C (dry ice/acetone bath). After the solution was stirred at −78 °C for 1 h, the reaction solution was warmed to room temperature and was transferred to an addition funnel. It was added dropwise into a solution of triethyl borate (686 mg, 4.70 mmol) in 10 mL of THF at −78 °C. The resulting mixture was allowed to warm to room temperature and stirred for 1 h. After the mixture was cooled to 0 °C, it was quenched with 1 N HCl (20 mL). The organic layer was separated, and the aqueous layer was extracted with diethyl ether (2 × 20 mL). The combined organic solution was neutralized with saturated $NaHCO_3$ and was washed with brine. After the solution was dried over Na_2SO_4, the solvent was removed and the residue was purified by flash column chromatography (silica gel, using 1:9 EtOAc/hexane to remove the starting material and 98:2 EtOAc/EtOH for the product) to give **16** in 55% yield (470 mg). The starting material **15** (310 mg) was also recovered. Characterization of **16**. FT-IR (KBr, cm^{-1}) 3423 (m), 1502 (w), 1450 (w), 1440 (w), 1346 (s), 1070 (w), 835 (w), 796 (m), 692 (m). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.09 (t, J = 4.0 Hz, 1H), 7.28 (m, 2H), 7.34 (m, 2H), 7.53 (d, J = 5.1 Hz, 1H), 7.60 (d, J = 2.9 Hz, 1H), 8.34 (s, 2H, BOH$_2$). **Esterification of 16.** To further characterize this compound, the boronic acid **16** was converted to the corresponding boronic ester. To a flask containing **16** (636 mg, 2.18 mmol), neopentyl glycol (227 mg, 2.18 mmol), and dry benzene (30 mL), a Dean−Stark trap filled with dry benzene (20 mL) was mounted. The reaction solution was then heated at reflux for a day. After removal of the solvent with rotary evaporation, the residue was purified by flash column chromatography (silica gel, ethyl acetate/hexane). Recrystallization from ethyl acetate and hexane gave the boronic ester of **16** as a green solid in 94.2% yield (740 mg). UV−vis λ_{max} (CH_2Cl_2, nm) 260, 368. FT-IR (KBr, cm^{-1}) 3130 (m), 3078 (w), 2955 (s), 2899 (m), 2872 (m), 1481 (s), 1444 (s), 1415 (s), 1338 (m), 1303 (s), 1105 (m), 868 (w), 837 (m), 787 (m), 704 (m), 651 (m), 497 (w) 457 (w). ^1H NMR (400 MHz, $CDCl_3$) δ 1.03 (s, 6H), 3.76 (s, 4H), 7.00 (dd, J = 4.8, 5.1 Hz, 1H), 7.08 (d, J = 3.8 Hz, 2H), 7.13 (d, J = 3.8 Hz, 1H), 7.17 (br d, J = 3.5 Hz, 1H), 7.21 (d, J = 3.7 Hz, 2H), 7.46 (d, J = 3.5 Hz, 1H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 21.99, 32.17, 72.50, 123.84, 124.50, 124.62, 124.82, 124.89, 127.98, 136.44, 136.55, 136.62, 137.19, 142.77. Anal. Calcd for $C_{17}H_{17}BO_2S_3$: C, 56.67; H, 4.76. Found: C, 56.48; H, 4.65.

Preparation and Characterization of 3′′′-Octadecanyl-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′:5′′′′,2′′′′′:5′′′′′,2′′′′′′-heptathiophene (19). Under N_2, to a heterogeneous mixture of **16** (660 mg, 2.26 mmol) and **12b** (350 mg, 0.71 mmol) in THF (20 mL) and K_2CO_3 (10 mL, 1 M aqueous solution) was added a THF solution (20 mL) of $Pd(PPh_3)_4$ (110 mg, 0.095 mmol). The resulting mixture was heated at reflux, and the color of it changed from green to dark red in 3 h. After 10 h, the formation of a red precipitate was observed. The reaction mixture was then cooled to room temperature and filtered. The solid was transferred to a flask and stirred in HCl (10 mL, 1 N) for 30 min. After filtration, the solid was washed with water (2 × 20 mL), acetone, CH_2Cl_2, and methanol until the filtrate was colorless. The red solid was dried under vacuum and was redissolved in hot chloroform under nitrogen. After the solution was cooled to room temperature, a solid was formed and was washed with acetone to give **19** as a bright red solid in 68% yield (400 mg). FT-IR (KBr, cm^{-1}) 2918 (s), 2850 (s), 1465 (4 weak bands), 1261 (w), 1068 (w), 792 (s), 688 (m). ^1H NMR (400 MHz, benzene-d_6, 70 °C) δ 0.87 (br, 3H), 1.32 (br, 30 H), 1.63 (br t, J = 7.8 Hz, 2H), 2.74 (br, 2H), 6.66 (m, 2H), 6.74 (dm, J_d = 5.4 Hz, 2H), 6.85 (m, 5H), 6.89 (d, J = 3.5 Hz, 1H), 6.91 (d, J = 3.5 Hz, 1H), 6.95 (d, J = 3.5 Hz, 1H), 6.98 (m, 2H), 7.00 (s, 1H). HRMS (FAB) Calcd for $C_{46}H_{52}S_7$: *m/z* 828.2114. Obsd: *m/z* 828.2112.

Preparation and Characterization of 5,5′′′′′′-Dibromo-3′′′-octadecanyl-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′:5′′′′,2′′′′′:5′′′′′,2′′′′′′-heptathiophene (20). In a procedure similar to the preparation of **18**, **20** was prepared from the reaction of **19** with NBS. Recrystallization from benzene afforded **20** as a red solid in 75% yield. FT-IR (KBr, cm^{-1}) 2918 (s), 2849 (s), 1494 (w), 1464 (w), 1427 (w), 1384 (w), 1068 (w), 970 (w), 839 (w), 788 (s), 721 (w), 459 (w). ^1H NMR (400 MHz, benzene-d_6, 70 °C) δ 1.01 (br, 3H), 1.44 (br, 30H), 1.77 (br, 2H), 2.85 [br t, J = 8.1 Hz, 2H, Ar$CH_2(CH_2)_{16}CH_3$], 6.66−6.72 (3 br peaks, 7H), 6.99−7.12 (m, 6H). HRMS (FAB) Calcd for $C_{46}H_{50}Br_2S_7$: *m/z* 984.0324. Obsd: *m/z* 984.0284.

Preparation and Characterization of Polymer 22. The typical polymerization procedure for the preparation of the binaphthyl−thiophene copolymers is as follows: Under N_2, racemic **21** (0.46 mmol) and **7** (0.46 mmol) were dissolved in THF (5 mL). To this solution, an aqueous solution of K_2CO_3 (7 mL, 1 M, degassed with N_2) and a THF solution (3 mL) of $Pd(PPh_3)_4$ (27 mg, 0.024 mmol) were added sequentially. After the resulting mixture was heated at 60 °C for 48 h, it was cooled to room temperature. CH_2Cl_2 (20 mL) was added, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL). The combined CH_2Cl_2 solution was washed with 1 N HCl and brine and was then concentrated by rotary evaporation. The residue was dissolved in a minimum amount of THF and was precipitated with the addition of MeOH. The solid was isolated by filtration. This procedure was repeated twice. The polymer was then dried under vacuum for a day to give **22** as a greenish-yellow solid in 93% yield (230 mg). FT-IR (KBr, cm^{-1}) 3068 (w), 2928 (s), 2862 (s), 1593 (m), 1491 (m), 1465 (m), 1340 (m), 1273 (m), 1091 (w), 1049 (m), 879 (w), 798 (m). ^1H NMR (400 MHz, $CDCl_3$) δ 0.70 (t, J = 6.8 Hz, 6H, CH_3), 0.96 [br, 12 H, $(CH_2)_3$-CH_3], 1.40 (br, 4H, CH_2CH_2O), 3.92 (m, 4H, OCH_2), 7.17 (d, J = 8.6 Hz, 2H), 7.29 (s, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.8 Hz, 2H), 7.92 (d, J = 8.86 Hz, 2H), 8.07 (s, 2H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 12.96, 21.51, 24.37, 28.36, 30.35, 68.67, 115.27, 119,4,6 122.82, 122.96, 123.35, 125.09, 128.33, 128.50, 132.50, 142.58, 153.80. Anal. Calcd for $(C_{36}H_{38}O_2S)_n$: C, 80.90; H, 7.11. Found: C, 79.91; H, 7.11.

Characterization of Polymer 23. In a procedure similar to the preparation of **22**, **23** was obtained from the Suzuki coupling of the bithiophene dibromide **8** with **21** in 97% yield as a yellow solid. FT-IR (KBr, cm^{-1}) 2928 (m), 2868 (m), 1591 (m), 1491 (m), 1465 (m), 1384 (m), 1340 (w), 1271 (m), 1091 (w), 1051 (w), 881 (w), 794 (m). ^1H NMR (400 MHz, $CDCl_3$) δ 0.70 (br t, 6H), 0.97 (br, 12H), 1.41 (br, 4H), 3.93 (m, 4H, OCH_2), 7.05−7.25 (br m, 6H), 7.41 (br d, J = 8.4 Hz, 2H), 7.46 (br d, J = 8.3 Hz, 2H), 7.92 (br, 2H), 8.04 (s, 2H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 14.06, 22.61, 25.45, 29.41, 31.42, 69.70, 116.32, 120.43 123.65, 124.13, 124.34, 124.46, 126.18, 129.19, 129.33, 129.42, 133.61, 136.49, 143.48, 154.93. Anal. Calcd for $(C_{40}H_{40}O_2S_2)_n$: C, 77.92; H, 6.49. Found: C, 76.39; H, 6.65.

Characterization of Polymer 24. In a procedure similar to the preparation of **22**, **24** was obtained from the Suzuki coupling of the tetrathiophene dibromide **10** with **21** in 88% yield as an orange solid. FT-IR (KBr, cm^{-1}) 3065 (w), 2926 (s), 2866 (m), 1591 (m), 1491 (m), 1464 (m), 1310(m), 1248 (m), 1091 (m), 1031 (s), 795 (s), 484 (w). ^1H NMR (400 MHz, $CDCl_3$) δ (br peaks) 0.70 (m), 1.00 (br), 1.40 (br), 3.93 (br), 7.08−7.14 (m), 7.41−7.43 (br), 7.93 (m), 8.04 (s) (a number of small end group signals are observed in the aromatic region due to the low molecular weight). Anal. Calcd for $(C_{48}H_{44}O_2S_4)_n$: C, 73.84; H, 5.64. Found: C, 74.71; H, 6.36.

Characterization of Polymer 25. In a procedure similar to the preparation of **22**, **25** was obtained from the Suzuki coupling of the alkylated pentathiophene dibromide **18** with **21** in 94% yield as a bright red solid. FT-IR (KBr, cm^{-1}) 2926 (m), 2854 (m), 1591 (m), 1491 (w), 1464 (m), 1384 (m), 1338 (w), 1246 (m), 1091 (w), 1049 (m), 792 (m). ^1H NMR (400 MHz, THF-d_8) δ 0.71 (br, 6H, CH_3), 0.88−1.44 (br m, 27H), 2.80 (br m, 2H, thiophene−CH_2), 3.80 (br m, 4H, binaph−OCH_2), 7.10−7.21 (br m, 9H), 7.35 (s, 2H), 7.48 (br d, J = 6.2 Hz, 4H), 7.97 (br d, J = 8.6 Hz, 2H), 8.12 (s, 2H) (small peaks of the end groups are observed in the aromatic region). ^{13}C (100.5 MHz, THF-d_8) δ 13.45, 13.58, 22.50, 22.53, 25.48, 20.29, 29.39, 30.42, 31.41, 31.75, 68.93, 115.79, 120.06, 123.7−123.9 (overlapping peaks), 124.17, 124.40, 124.72, 126.05, 126.50, 126.62, 128.91, 129.30, 129.43, 129.51, 133.69, 134.43, 134.82, 135.54, 135.60, 135.64, 135.70, 136.40, 137.34, 140.51, 143.74, 155.11. Anal. Calcd for $(C_{58}H_{60}O_2S_5)_n$: C, 73.57; H, 6.13. Found: C, 71.38; H, 6.08.

Characterization of Polymer 26. **26** was made from the Suzuki coupling of the alkylated heptathiophene dibromide **20** with **21** in benzene at 85 °C (oil bath temperature). Other reaction conditions were similar to the preparation of **22**. **26** was obtained in 54% yield as a dark red solid. Insoluble materials, probably the high molecular weight polymer, were also obtained. FT-IR (KBr, cm^{-1}) 3063 (w), 2922 (s), 2850 (s), 1591 (m), 1491 (m), 1464 (m), 1338 (w), 1246 (m), 1045 (m), 790 (s), 688 (w). ^1H NMR (400 MHz, THF-d_8, 55 °C) δ 0.71 (br), 0.85 (br), 1.02 (br), 1.15 (br), 2.78 (br, thiophene−CH_2), 3.96 (br, binaph−OCH_2), 6.97−7.47 (br m), 7.90−8.16 (br m) (a number of small end group signals were observed in the aromatic region).

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