# Synthesis of chiral polybinaphthyls with novel conjugated chromophores

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**Abstract**—An efficient strategy has been developed to incorporate new chromophores into chiral binaphthyl polymers. The repeating units of these polymers are made of conjugated structures with strongly electron-donating amino groups at the both ends. These optically active materials contain the highest possible density of chromophores in a polymer chain since every repeating unit in these polymers is a chromophore. They are soluble in common organic solvents and can be easily processed. The spectroscopic properties of these polymers are studied. The structural similarity of the chromophores in these chiral conjugated polymers with those of two-photon absorbing molecules may lead to interesting optical properties. © 2003 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Chiral conjugated polymers are optically active materials made of organic fragments such as aromatic rings and unsaturated carbon or heteroatom bonds that have delocalizable electrons. Depending upon their specific structure and chirality, these materials may or may not have fully extended conjugation along the polymer chain. There are two general types of chirality sources for chiral conjugated polymers: one incorporates inherently chiral units into the polymer main chain and the other contains either chiral side chains or chiral dopants. Both types of materials have received growing research attentions in recent years.[1–6]

Besides their structurally appealing features, these polymers have also exhibited potential applications in areas such as nonlinear optics, polarized light emission, chiral sensing, chiral separation, and asymmetric catalysis.

In our laboratory, we have used optically active binaphthyl molecules to construct a class of main chain chiral conjugated polymers.[7–10] For example, (*R*)-**1** has been synthesized as a chiral nonlinear optical polymer.[10] This polymer contains amino electron donors and nitro acceptors in its dipolar units. Since (*R*)-**1** is made of optically pure binaphthyl units, when the aromatic rings in its conjugated dipolar units are assumed to be coplanar, a helical structure
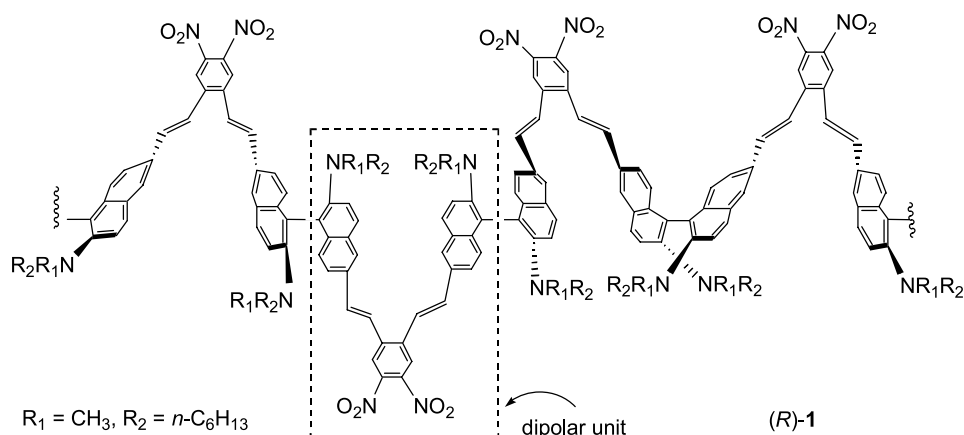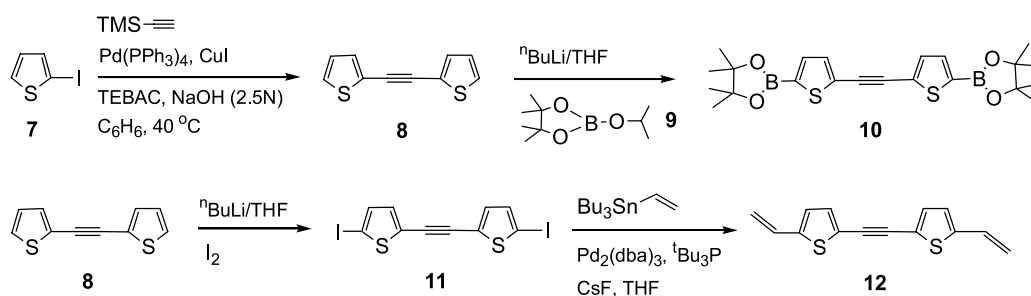


R₁ = CH₃, R₂ = *n*-C₆H₁₃          dipolar unit          (*R*)-**1**
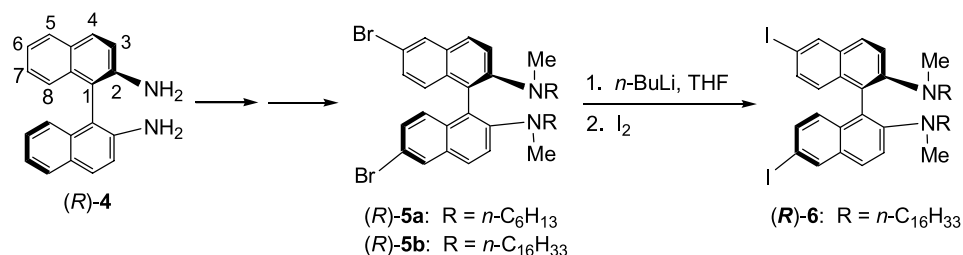
**Scheme 1.** Synthesis of chiral binaphthyl monomers.



**Scheme 2.** Synthesis of conjugated linker monomers.

should be generated. In this case, the dipolar units in this polymer should progressively revolve along the polymer axis like the blades of a propeller. Other conformations of the polymer are also possible because of the rotations around the vinyl–aryl single bonds in the dipolar units of (*R*)-**1**. By collaboration with Persoons, the second-order NLO properties of the chiral conjugated polybinaphthyls as represented by (*R*)-**1** have been investigated.[11,12] Significant $\chi^2$ was observed for the Langmuir–Blodgett films of this polymer.

Recently, organic molecules with two-photon absorption properties have attracted significant research attention because of their potential applications in areas such as two-photon fluorescence imaging, optical data storage, and microfabrication.[13–15] Efficient two-photon absorbing compounds have been obtained through molecular engineering. For example, molecules such as **2** and **3** with the symmetrical strong electron-donating amino substituents at both ends of the conjugated structure have shown large two-photon absorption cross sections.[15]

We envision that if this type of two-photon absorbing chromophores could be incorporated into the chiral conjugated polymers, materials with interesting chiral optical properties could be obtained and new applications could be developed. Herein, we report an efficient strategy to construct chiral polymers containing conjugated chromophores analogous to compounds **2** and **3**.
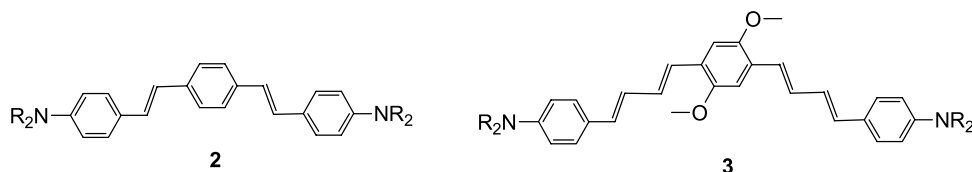
## 2. Results and discussion

### 2.1. Monomer synthesis

Starting from the optically pure (*R*)-1,1′-binaphthyl-2,2′-diamine, (*R*)-**4**, and using the procedures developed earlier in our laboratory,[16] we have synthesized compounds (*R*)-**5** and (*R*)-**6** as the optically active monomers. The linear alkyl chains on the nitrogen atoms of these compounds are introduced in order to enable the subsequent polymers soluble in organic solvents. In addition, the *N,N*-disubstituted aryl amines are also chemically more stable than the corresponding primary or secondary aryl amines. The halogen atoms at the 6,6′-positions of these binaphthyl compounds will allow cross-coupling polymerizations to take place specifically at these positions (Scheme 1).

Conjugated linker monomers **10** and **12** are synthesized according to Scheme 2. Following the literature procedure,[17] 2,2′-ethynediyl-bis-thiophene (**8**) was prepared from the reaction of 2-iodothiophene (**7**) with trimethylsilylacetylene. Treatment of **8** with *n*BuLi followed by the addition of 2-isopropoxyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**9**) gave the diboronic ester monomer **10**.[18] Compound **8** was also converted to the 5,5′-diiodo compound **11** by reaction with *n*BuLi and then I₂.[19] Cross-coupling of **11** with tributylvinyltin gave the conjugated linker monomer **12**.[20] Since compound **12** was not very stable in air over time, it was freshly prepared each time
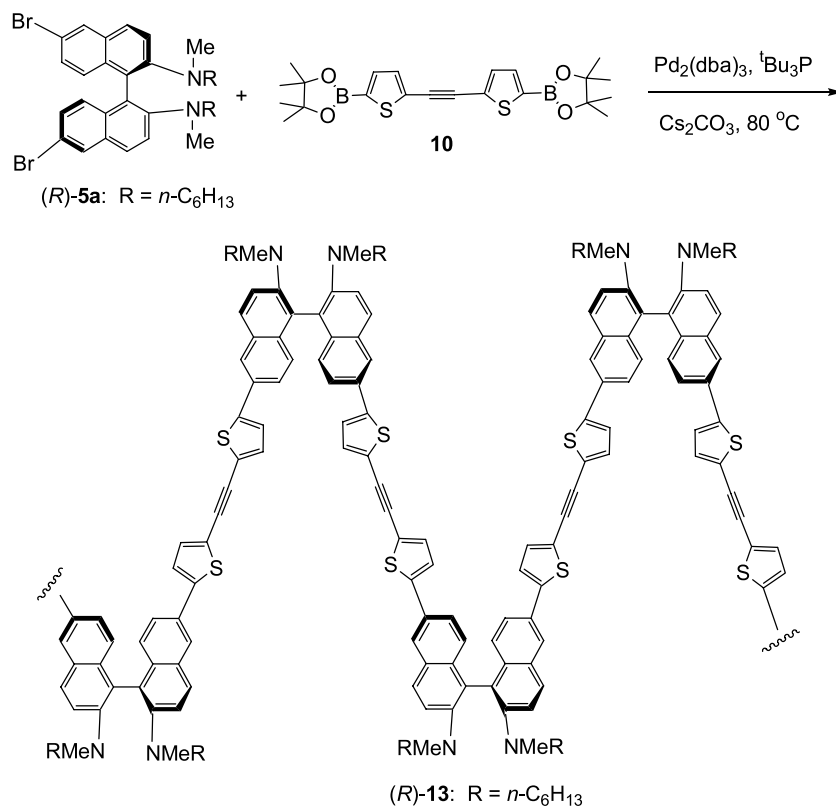
**Scheme 3.** Synthesis of the chiral conjugated polymer (*R*)-**13**.
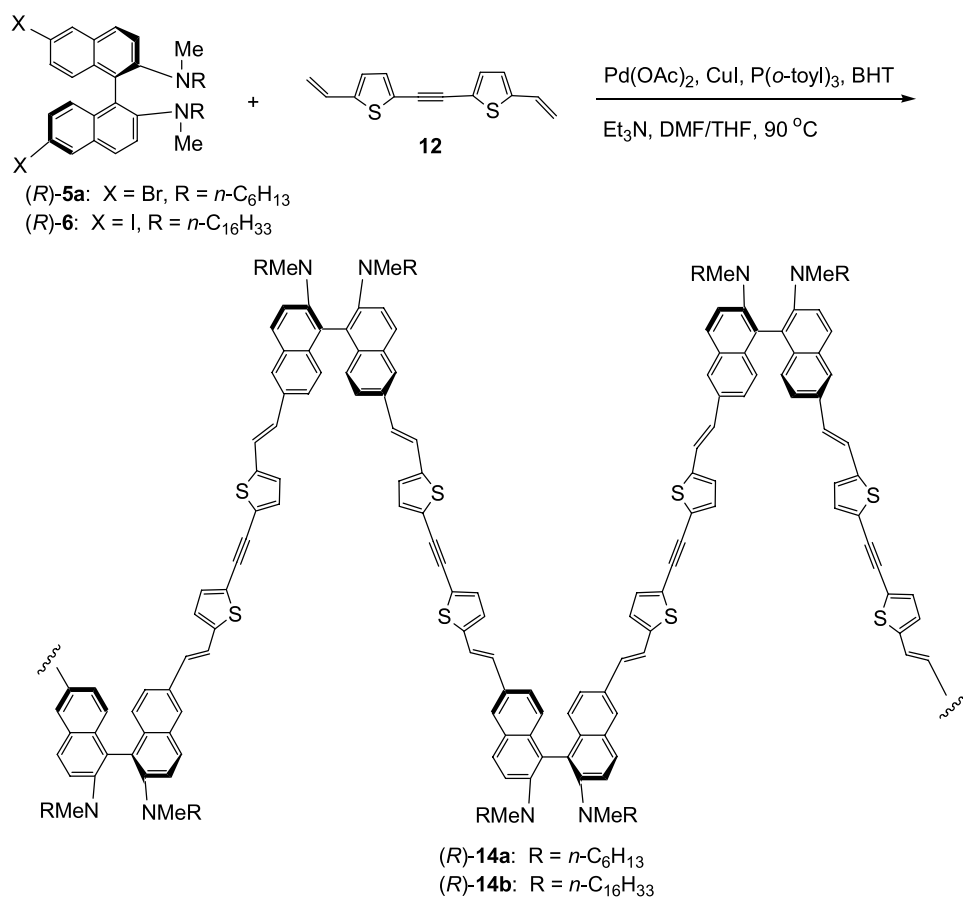


**Scheme 4.** Synthesis of the chiral conjugated polymers (*R*)-**14a**,**b**.

**Table 1**. Optical spectral data of the chiral conjugated polymers

| Polymers | (*R*)-**13** | (*R*)-**14a** | (*R*)-**14b** |
|---|---|---|---|
| UV−vis $\lambda_{max}$, nm ($\varepsilon$), CHCl$_3$ | 376 (2.88×10$^4$) | 397 (2.83×10$^4$) | 401 (5.25×10$^4$) |
| | 263 (4.73×10$^4$) | 263 (4.25×10$^4$) | 260 (6.34×10$^4$) |
| CD ($\theta$) (nm), CHCl$_3$ | −6.78×10$^4$ (275) | −1.48×10$^5$ (275) | −1.28×10$^5$ (277) |
| FT-IR cm$^{-1}$ KBr | 2956 | 2934 | 2924 |
| | 1594 | 1595 | 2847 |
| | 1498 | 1500 | 1589 |
| | 1365 | 1378 | 1465 |
| | | | 1367 |

immediately before its polymerization with the chiral binaphthyl monomers.

## 2.2. Polymer synthesis

The Suzuki coupling of the binaphthyl compound (*R*)-**5a** with the diboronic ester **10** was conducted (Scheme 3).[21,22] A 1:1 mixture of (*R*)-**5a** and **10** was heated in 1,2-dioxane under nitrogen at 80°C in the presence of Pd$_2$(dba)$_3$, tri-*tert*-butylphosphine and cesium carbonate. After 24 h, polymer (*R*)-**13** was isolated and purified by repeated precipitation from its methylene chloride solution with methanol. The yield of (*R*)-**13** was 85%. This polymer was a dark red solid and soluble in common organic solvents such as methylene chloride, THF and chloroform. Gel permeation chromatograph (GPC) analysis showed its molecular weight as $M_w$=7500 and $M_n$=3000 (PDI=2.5) relative to polystyrene standards.

We also studied the Heck coupling of the chiral binaphthyl compound (*R*)-**5a** or (*R*)-**6** with the divinyl compound **12** (Scheme 4).[23,24] Both reactions were carried out at 70–80°C in the presence of Pd(OAc)$_2$, CuI and tri-*o*-tolylphosphine in DMF and triethylamine. 2,6-Di-*tert*-butyl-4-methylphenol (BHT) was added to inhibit the possible radical polymerization of **12**. The resulting polymers (*R*)-**14a** and (*R*)-**14b** are dark red solids and soluble in THF, methylene chloride

and chloroform. Their molecular weights as measured by GPC relative to polystyrene standards were $M_w$=12000 (PDI=2.4) and $M_w$=11800 (PDI=2.5), respectively. This indicates that neither the halogen atoms nor the size of the alkyl groups in the binaphthyl monomers had pronounced influence on the molecular weight of the polymer.

## 2.3. Spectroscopic analysis of the polymers

The repeating units of both chiral polymers (*R*)-**13** and (*R*)-**14** are made of conjugated structures with strongly electron-donating amino groups at both ends. Table 1 summarizes the UV, CD and IR spectral data of these polymers. Polymers (*R*)-**14** containing repeating units with longer conjugation length displays longer wavelength absorptions than (*R*)-**13**. This is consistent with our previous observation that the conjugation of the binaphthyl-based polymers is determined by their repeating units and there is no extended conjugation along the polymer chain. Both polymers (*R*)-**13** and (*R*)-**14** exhibit strong Cotton effects as shown in their CD spectra (Fig. 1).

We have studied the absorption and emission properties of polymer (*R*)-**14b** in various solvents. The UV absorption and fluorescence spectra of polymer (*R*)-**14b** (2.5 mg/25 mL) in hexane, benzene and methylene chloride are shown in Figures 2 and 3. The absorption of the polymer in
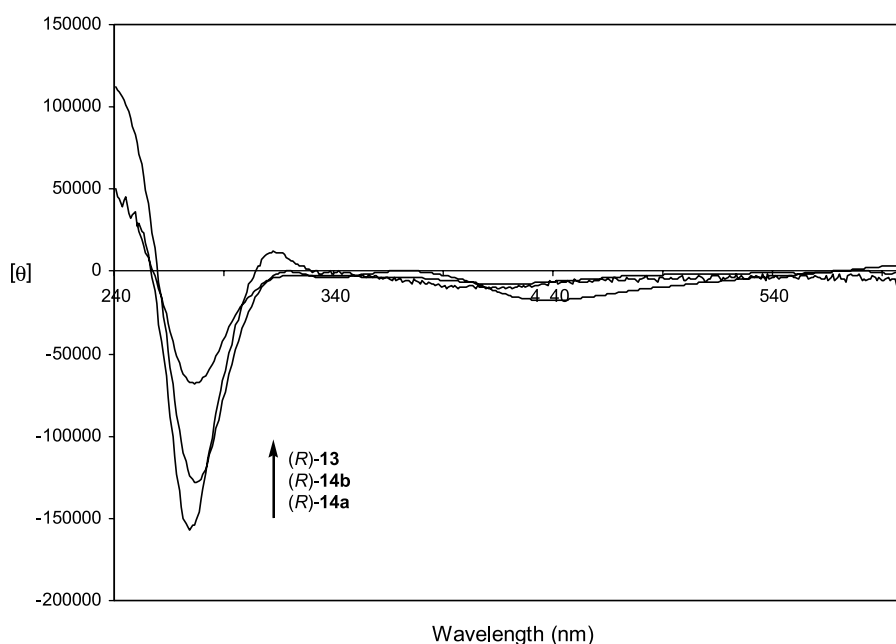


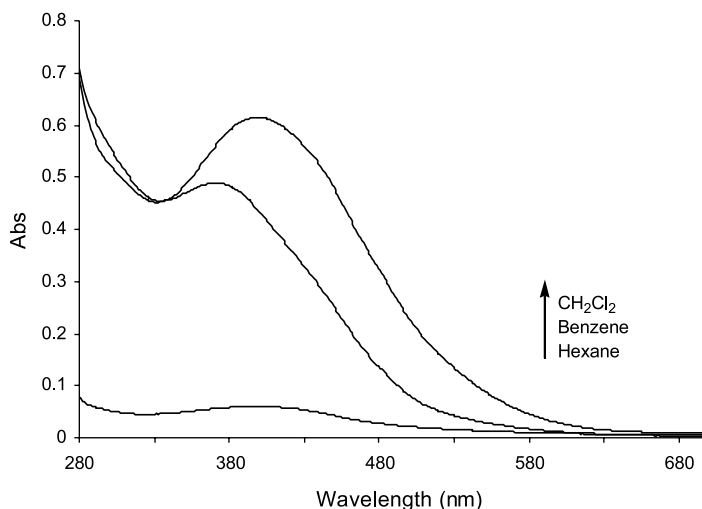**Figure 1.** CD spectra of the chiral conjugated polymers.

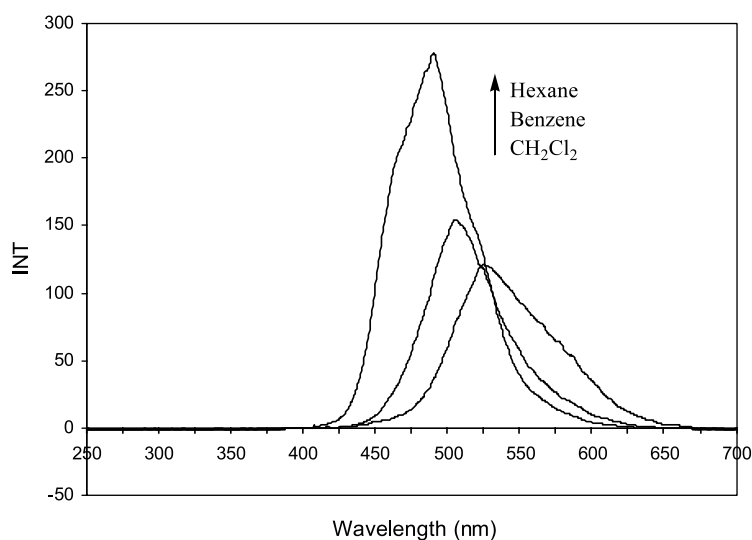**Figure 2.** UV spectra of polymer (*R*)-**14b** in various solvents.



**Figure 3.** Fluorescence spectra of polymer (*R*)-**14b** in various solvents ($\lambda_{exc}$=400 nm).

hexane is the weakest because of the lowest solubility. Polymer (*R*)-**14b** dissolved completely in $CH_2Cl_2$ but partially in benzene and poorly in hexane. The insoluble portions in the hexane and benzene solutions were filtered before the measurements. The fluorescence intensity of the polymer in hexane is much stronger than in the other two solvents.

### 2.4. Summary

In summary, we have developed an efficient strategy to incorporate new chromophores into chiral binaphthyl polymers. The repeating units of these polymers are made of conjugated structures with strongly electron-donating amino groups at both ends. These optically active materials contain the highest possible density of chromophores in a polymer chain since every repeating unit in these polymers is a chromophore. They are soluble in common organic solvents and can be easily processed. The spectroscopic properties of these polymers are studied. The structural similarity of the conjugated chromophores in these chiral polymers with those of two-photon absorbing molecules may lead to interesting optical properties.

### 3. Experimental

#### 3.1. General

Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) and diethyl ether ($Et_2O$) were distilled from sodium benzophenone ketyl immediately prior to use. Thin layer chromatography was performed on precoated silica gel plates. Silica gel (70–230 and 230–400 mesh) was used for column chromatography.

The NMR spectra were recorded on a Varian-300 MHz spectrometer. Mass spectra were recorded either at atmospheric pressure chemical ionization (APCI) or at electrospray ionization (ESI) mode. The high resolution mass data were obtained by the University of California Riverside

mass spectroscopy facility. Gel permeation chromatography (GPC) utilized a Waters 510 HPLC pump, A Waters 410 differential refractometer, and a Ultrastyragel Linear GPC column. THF was used as the eluting solvent in the GPC analysis, and polystyene standards were used. The UV–vis spectra were recorded with a Cary 5E UV–Vis-NIR Spectrophotometer. The CD was recorded with a JASCO J-720 Spectropolarimeter.

### 3.1.1. Preparation and characterization of 2,2′-bi-(5,5′-di-pinacoborate)thienylacetylene (10).

$^n$BuLi (1.6 M in hexane, 2.5 mL, 4.0 mmol) was added dropwise to a solution of **8** (190 mg, 1.0 mmol) in THF (20 mL) with stirring at $-78°C$ under nitrogen. The reaction mixture was then stirred for 1 h at the same temperature. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**9**) (0.82 mL, 4.0 mmol) was added dropwise to the mixture at $-78°C$ over 10 min under nitrogen. The resulting mixture was allowed to warm up to room temperature and stirred overnight. The reaction was quenched with saturated aqueous $NH_4Cl$ (20 mL). The organic layer was separated and the water phase was extracted with ether ($3\times30$ mL). The combined organic extracts were washed with brine, and dried over $Na_2SO_4$. After removal of the solvent, the residue was purified by recrystallization from ether/hexane to give compound **10** as a white solid in 90% yield (400 mg). $R_f=0.4$ (hexane). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.35 (s, 24H), 7.32 (d, $J=3.6$ Hz, 2H), 7.51 (d, $J=3.9$ Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 24.73, 84.32, 87.71, 129.17, 133.17, 136.97. MS (APCI): $m/z$ (relative intensity) 443 ($M^++1$, 28). HRMS (FAB) calcd for $C_{22}H_{28}B_2O_4S_2$: 442.1615; found: 442.1600.

### 3.1.2. Preparation and characterization of 2,2′-bi-(5,5′-diiodo)thienylacetylene (11).

$^n$BuLi (1.6 M in hexane, 4.7 mL, 7.5 mmol) was added dropwise to a solution of 2,2′-bithienylacetylene (**8**) (475 mg, 2.5 mmol) in dry diethyl ether (20 mL) with stirring at 0°C under nitrogen. The reaction mixture was then stirred for 1 h at room temperature. A solution of iodine (1.9 g, 7.5 mmol) in diethyl ether (40 mL) was added dropwise to the mixture at 0°C over 10 min under nitrogen. The reaction mixture was stirred for 1 h at room temperature before it was poured into ice water. After it was extracted with ether, the combined extracts were washed successively with saturated aqueous $NaHSO_3$ and brine, and dried over $Na_2SO_4$. The solvent was then removed, and the residue was purified by column chromatography on silica gel. Elution with hexane gave compound **11** as a white solid in 69% yield (750 mg). $R_f=0.35$ (hexane). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 6.92 (d, $J=3.9$ Hz, 2H), 7.15 (d, $J=3.6$ Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 75.67, 86.75, 128.55, 133.62, 137.16. MS (APCI): $m/z$ (relative intensity) 443 ($M^++1$, 100); 316 (36). HRMS (FAB) calcd for $C_{10}H_4S_2I_2$: 441.7844; found: 441.7857.

### 3.1.3. Preparation and characterization of 2,2′-bi-(5,5′-di-vinyl)thienylacetylene (12).

To a solution of **11** (117 mg, 0.26 mmol) in THF (5.0 mL) were added tri-butyl(vinyl)tin (0.17 mL, 0.55 mmol), $Pd_2(dba)_3$ (7.1 mg, 0.008 mmol), $^t$Bu$_3$P (6.3 mg, 0.03 mmol), CsF (174 mg, 1.14 mmol), and then 2,6-di-*tert*-butyl-4-methylphenol (3 mg) in drybox. The whole mixture was heated to reflux under nitrogen for 12 h and then cooled down to room

temperature. The undissolved solid was then filtered off through a pad of celite and washed with diethyl ether ($3\times10$ mL). After removal of the solvent from the filtrate, the residue was purified by column chromatography on silica gel. Elution with hexane gave compound **12** as a yellow crystal in 84% yield (53.6 mg). $R_f=0.33$ (hexane). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 5.19 (d, $J=10.8$ Hz, 2H), 5.58 (d, $J=17.4$ Hz, 2H), 6.75 (dd, $J=17.4$, 10.8 Hz, 2H), 6.86 (d, $J=3.6$ Hz, 2H), 7.12 (d, $J=3.6$ Hz, 2H).

### 3.1.4. Preparation and characterization of polymer (R)-13.

In drybox, 1,2-dioxane (10 mL) was added to a mixture of **10** (66.3 mg, 0.15 mmol), (R)-**5a** (96 mg, 0.15 mmol), $Pd_2(dba)_3$ (4.1 mg, 0.0045 mmol), tri-*tert*-butylphosphine (2.2 mg, 0.011 mmol) and cesium carbonate (117 mg, 0.36 mmol). The mixture was heated at 80°C under nitrogen for 24 h which resulted in a black solution. It was then cooled down to room temperature. After removal of the solvent in vacuo, the residue was redissolved in methylene chloride. The undissolved solid was filtered off through a pad of celite and washed with methylene chloride ($3\times20$ mL). The solution was concentrated under vacuum, and methanol was added to precipitate out the polymer. It was redissolved in methylene chloride and reprecipitated with methanol for two more times to give polymer (R)-**13** as a dark red solid in 85% yield (85 mg) after drying under vacuum. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.6–1.1 (m, 22H), 2.6 (m, 10H), 7.1–8.0 (m, 14H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 14.0, 22.5, 26.3, 27.7, 31.5, 39.8, 56.6, 87.5, 86.5 (weak), 121.4–134.2 (many peaks), 146.7, 150.8.

### 3.1.5. Preparation and characterization of polymer (R)-14a.

In drybox, DMF (12 mL) and triethylamine (8 mL) were added to a mixture of **12** (94.2 mg, 0.39 mmol), (R)-**5a** (248 mg, 0.39 mmol), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol), CuI (3.8 mg, 0.02 mmol), tri-*o*-tolylphosphine (24 mg, 0.078 mmol) and 2,6-di-*tert*-butyl-4-methylphenol (3 mg). The whole mixture was heated at 80°C under nitrogen for 48 h which resulted in a dark red solution. After it was cooled down to room temperature, the insoluble solid was filtered away through a pad of celite and washed with methylene chloride ($3\times30$ mL). The solvent was then removed in vacuo, and the dark red residue was redissolved in a minimum amount of methylene chloride. Methanol was added to precipitate out the polymer, which was redissolved in methylene chloride and reprecipitated with methanol for two more times to give polymer (R)-**14a** as a dark red solid in 80% yield (222 mg) after drying under vacuum. $^1$H NMR (300 MHz, $CDCl_3$, contains residual solvents) $\delta$ 0.60–1.0 (m), 2.5 (m), 6.7–7.9 (m). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 13.9, 22.5, 26.3, 27.7, 31.5, 39.9, 56.5, 87.9 (weak), 117.1, 121.6–134.4 (many peaks), 145.4 (m), 150.6.

### 3.1.6. Preparation and characterization of polymer (R)-14b.

In dry box, THF (10 mL), DMF (8.0 mL) and triethylamine (8.0 mL) were added to a mixture of **12** (97 mg, 0.40 mmol), (R)-**6** (400 mg, 0.40 mmol), $Pd(OAc)_2$ (7.2 mg, 0.032 mmol), CuI (6.1 mg, 0.032 mmol), tri-*o*-tolylphosphine (39 mg, 0.13 mmol) and 2,6-di-*tert*-butyl-4-methylphenol (5.0 mg). The whole mixture was heated at 70°C under nitrogen for 48 h which resulted in a dark red solution. After it was cooled down to room temperature, the

insoluble solid was filtered away through a pad of celite and washed with methylene chloride (3×50 mL). The solvent was removed in vacuo, and the dark red residue was redissolved in a minimum amount of methylene chloride. Methanol was then added to precipitate out the polymer, which was redissolved in methylene chloride and reprecipitated with methanol for two more times to give polymer (*R*)-**14b** as a dark red solid in 96% yield (380 mg) after drying under vacuum. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 0.60–1.30 (m br, 62H), 2.5 (m br, 10H), 6.7–7.8 (many broad peaks). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 14.1, 22.7, 26.7, 27.9, 29.6 (overlapped peaks), 31.9, 39.9, 56.7, 87.9 (barely visible), 121.5–134.6 (many broad peaks), 145.6 (weak peaks), 150.6 (m).

## Acknowledgements

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