# Synthesis and Ionochromic Effect of Hyperbranched and Linear Poly(thienylene−phenylene)s

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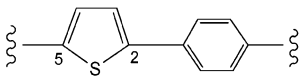
ABSTRACT: A novel hyperbranched poly(thienylene−phenylene) is synthesized, which is compared with a poly(2,3-thienylene−phenylene) and a poly(2,5-thienylene−phenylene). The hyperbranched polymer has much greater solubility in organic solvents than its isomeric linear polymers. A pronounced ionochromic effect is observed for the poly(2,5-thienylene−phenylene) in the presence of $LiBF_4$. This polymer shows a large red shift in its UV−vis spectrum when treated with the metal salt solution. The ionochromic effect is also ion selective. However, both the hyperbranched polymer and the poly(2,3-thienylene−phenylene) show almost no such ionochromic effect probably because of the ortho-substituted thiophene units in their structure. The hyperbranched polymer and the poly(2,5-thienylene−phenylene) are found to be green light emitters and the poly(2,3-thienylene−phenylene) a blue light emitter. These materials are potentially useful for electroluminescence and photovoltaics.

## Introduction

Conjugated polymers such as polyacetylenes, polyphenylenes, poly(phenylene−vinylene)s, and polythiophenes have been extensively studied, and many important electrical and optical properties have been discovered.[1,2] Thienylene−phenylene copolymers with 2,5-thienylene and *p*-phenylene linkages as represented by **1** have also been synthesized, and recent studies have shown their potentials as electroluminescent materials for the preparation of light-emitting diodes (LED).[3−6]

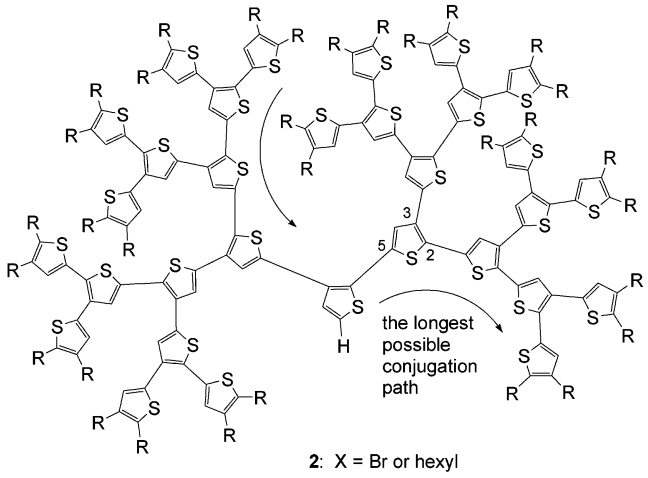



**1**

In our laboratory, we are interested in building unsymmetrically hyperbranched light-harvesting materials. For example, we have synthesized the hyperbranched polythiophene **2** by polymerization at the 2,3,5-positions of the thiophene monomer.[7] Because only the 2,3- and 2,5-linked units are conjugated but not the 3,5-linked units, this polymer contains an inherently built-in conjugation gradient with the longest possible conjugation path indicated by the arrows in the structure. Materials with conjugation gradient have been demonstrated to have efficient light-harvesting properties.[8,9] They are potentially useful for electroluminescence and photovoltaics. We have also studied the use of 2,3,5-tribromothiophene to construct a hyperbranched thienylene−phenylene copolymer that is structurally similar to **2**. We have compared the properties of this hyperbranched material with those of the 2,3-thienylene−phenylene and 2,5-thienylene−phenylene copolymers. The ionochromic effects of these materials in the presence of alkaline metal cations have been investigated. Herein, these results are reported.

## Results and Discussion

**Synthesis of the Isomeric Thienylene−Phenylene Copolymers.** We have conducted the Suzuki coupling[10] polymerization of 2,5-dihexyloxy-1,4-phenylenediboronic acid (**3**)[11] and 2,3,5-tribromothiophene (**4**) (Scheme 1). In the presence of 5 mol % of $Pd(PPh_3)_4$, reaction of **3** with **4** gave the hyperbranched polymer **6** over 3 days.[12] Because of the less steric hindrance, we propose that the 5-bromine of **4** should be more reactive than the 2,3-dibromine atoms in the coupling with **3**. This would generate the $AB_2$ monomer **5**, leading to the hyperbranched polymer **6**. However, because of the competitive coupling of the 2,3,5-tribromine atoms with **3**, the resulting polymer **6** is expected to have an imperfect branching structure as indicated in Scheme 1. This polymer was obtained as a yellow solid. It was very soluble in common organic solvents such as chloroform, methylene chloride, and THF, which ruled out a cross-linked structure. Polymer **6** was purified by dissolving in methylene chloride and precipitating with methanol. During the purification, two portions of the polymer, **6a** and **6b**, were obtained. Polymer **6a** was insoluble in methanol, and its molecular weight was $M_w$ = 28 400 and $M_n$ = 8500 (PDI = 3.3) as determined by gel permeation chromatography (GPC) relative to polystyrene standards. Polymer **6b** was partially soluble in methanol with a lower molecular weight of $M_w$ = 16 600 and $M_n$ = 4300 (PDI = 3.9).




**2**: X = Br or hexyl

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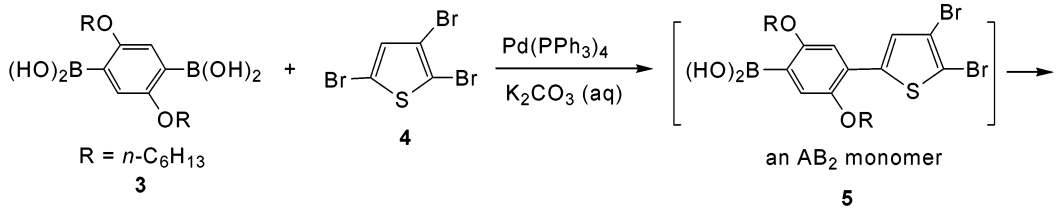
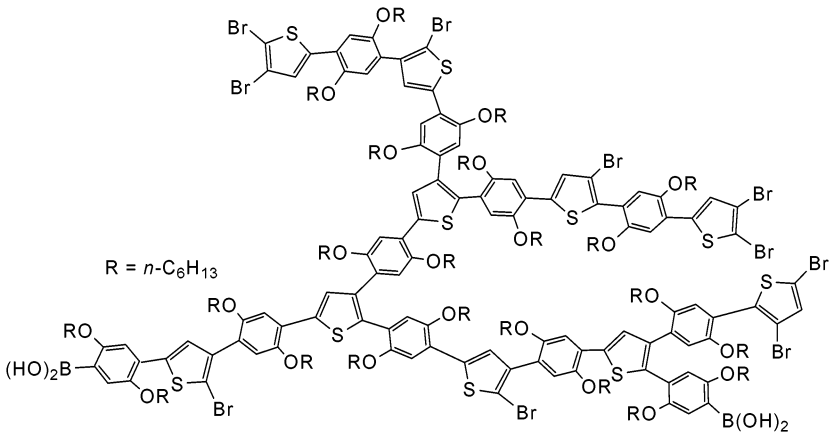
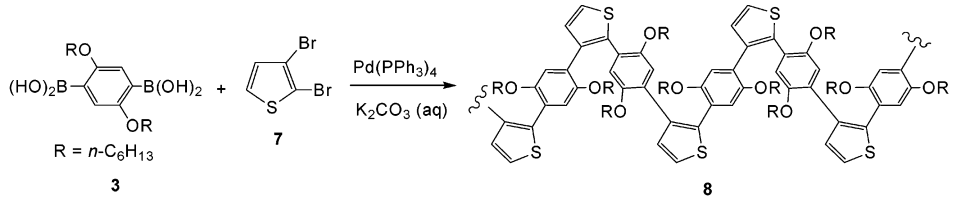
**Scheme 1. Synthesis of the Hyperbranched Poly(thienylene−phenylene) 6**

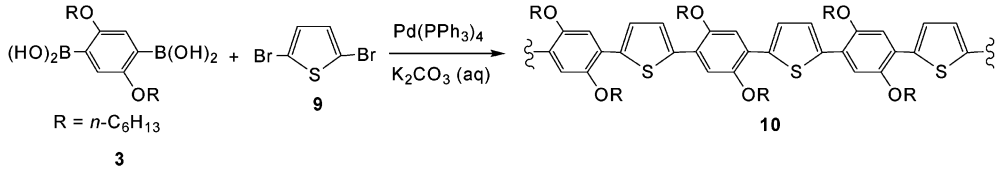



**Scheme 2. Synthesis of the Poly(2,3-thienylene−phenylene) 8**




**Scheme 3. Synthesis of the Poly(2,5-thienylene−phenylene) 10**




The Suzuki coupling of **3** with 2,3-dibromothiophene (**7**) was also carried out to generate the poly(2,3-thienylene−phenylene) **8** (Scheme 2). This polymer was obtained as a pale yellow solid and was soluble in common organic solvents. GPC gave its molecular weight as $M_w = 5800$ and $M_n = 3800$ (PDI = 1.5).

Previously, poly(2,5-thienylene−phenylene)s have been synthesized and studied by a number of research groups.[3−6] In many cases, these polymers were prepared by using the Stille coupling method initially developed by Yu.[3a] We have applied the Suzuki coupling to polymerize **3** with 2,5-dibromothiophene (**9**) to generate the poly(2,5-thienylene−phenylene) **10**.[3e−i] This polymer was obtained as a scarlet solid, a much deeper color than polymers **6** and **8**. Polymer **10** was only partially soluble in common organic solvents. GPC analysis of its soluble portion in THF gave its molecular weight as $M_w = 2600$ and $M_n = 1800$ (PDI = 1.4). As demonstrated by Yu and co-workers, only when the R groups are significantly longer alkyl chains in the poly(2,5-thienylene−phenylene) copolymers can high molecular weights and high solubility be achieved. In contrast, we found that polymer **6**, though with much higher molecular weight than **8** and **10**, had much greater solubility in organic solvents. This is consistent with the hyperbranched structure of **6**.

**Spectroscopic Analysis of the Polymers.** The $^1$H NMR signals for the hexyl groups of these polymers in chloroform-*d* are displayed in Figure 1. As shown in Figure 1, there are significant differences between the spectra of polymers **8** and **10**, especially for the $-OCH_2-$ signals. For polymer **10**, the signal of $-OCH_2-$ is observed at $\delta$ 4.12 (Figure 1c), but for polymer **8** at $\delta$ 3.45 (Figure 1b). In the $^{13}$C NMR spectra, the carbon signals for the $-OCH_2-$ groups of both polymers are almost the same ($\delta$ 69). These NMR data indicate that although the through-bond electronic effect of these groups are very similar, the methylene protons in **8** are less deshielded or even somewhat shielded by the aromatic chain of this ortho-substituted thiophene polymer because of the much more sterically crowded and probably coiled steric environment. Contrarily, polymer **10** has a more extended rigid rod and less sterically crowded chain structure which places its

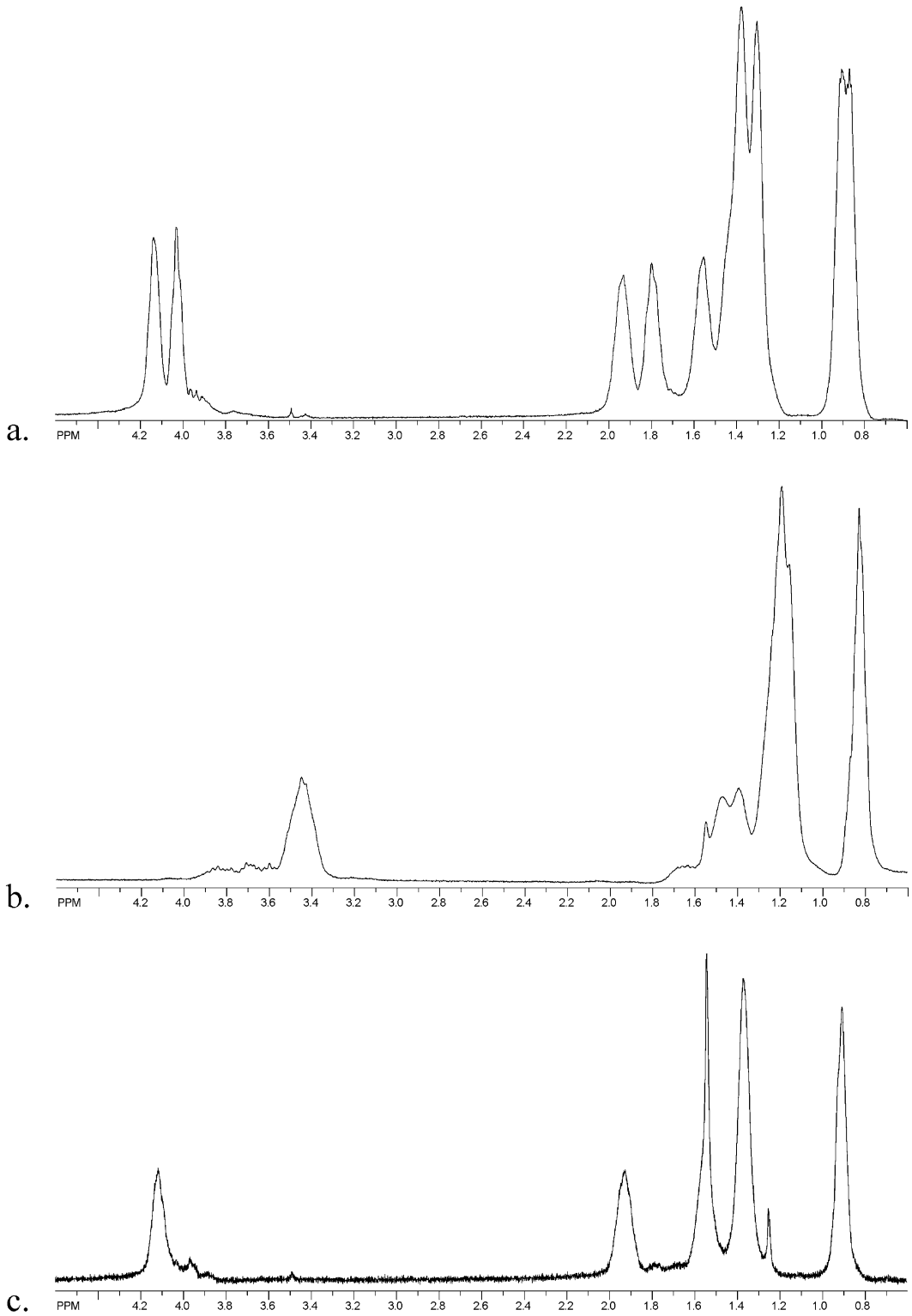



**Figure 1.** $^1$H NMR signals for the alkyl groups of polymers **6** (a), **8** (b), and **10** (c).

$-OCH_2-$ groups in the deshielded region of the conjugated aromatic polymer backbone. The hyperbranched polymer **6** contains the $^1$H NMR signal features of both polymers **8** and **10**, but more closely resembles **10**, indicating less steric interaction in **6** than in **8**. The $^1$H NMR and $^{13}$C NMR spectra of these materials allow us to clearly distinguish the structures of these three regioisomeric polymers.

The UV−vis absorptions of these polymers are studied. Figure 2 are the UV spectra of the hyperbranched polymers **6a** and **6b** in THF solution. Although polymer **6b** has only half of the average molecular weight of **6a**, there is almost no difference in their absorptions. This demonstrates that the conjugation length in the lower molecular weight polymer **6b** has almost reached saturation. The absorption maximum of **6a** ($\lambda_{max}$) is 408 nm, and that of **6b** is 405 nm.

Figure 3 compares the UV spectra of the hyperbranched polymer **6a** ($C = 0.016$ mg/mL) with the linear polymers **8** ($C = 0.03$ mg/mL) and **10** ($C < 0.016$ mg/mL). Polymer **8** has the shortest absorption wavelength with $\lambda_{max}$ at 259 and 345 nm. Polymer **10** shows the

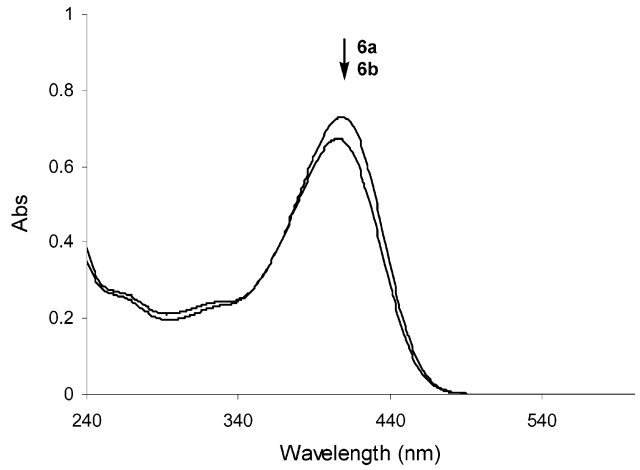



**Figure 2.** UV spectra of the hyperbranched polymers with two different molecular weights ($C$ = 0.016 mg/mL, THF).

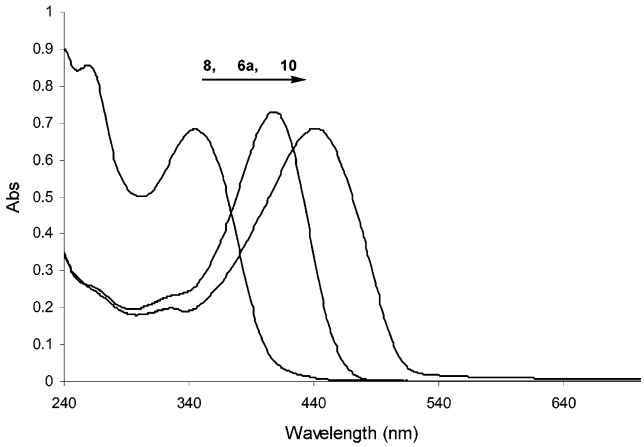



**Figure 3.** UV spectra of polymers **6a**, **8**, and **10** in THF.

longest wavelength absorption with $\lambda_{max}$ at 441 nm. These spectra demonstrate that polymer **8** has the shortest effective conjugation. This is attributed to the steric interaction of the two phenyl substituents at the ortho-positions of the thiophene unit in the polymer which twists the two phenyl rings out of planarity and disrupts the conjugation. The 2,5-thienylene-linked polymer **10** does not have such steric interaction and possesses the longest effective conjugation. The hyperbranched polymer **6** is in the middle because of its both 2,3- and 2,5-linkages. The 3,5-linkage in polymer **6** is not conjugated.

The fluorescence spectra of these polymers in THF are shown in Figure 4. Similar to what is observed in the absorption spectra, the emission wavelength increases going from the 2,3-thienylene−phenylene polymer **8** ($C$ = 1.6 × $10^{-3}$ mg/mL, $\lambda_{exc}$ = 341 nm), the hyperbranched polymer **6a** ($C$ = 4.0 × $10^{-4}$ mg/mL, $\lambda_{exc}$ = 405 nm), to the 2,5-thienylene−phenylene copolymer **10** ($C$ < 1 × $10^{-3}$ mg/mL, $\lambda_{exc}$ = 443 nm). The emission wavelengths ($\lambda_{emi}$) of these three polymers are at 454, 482, and 507 nm, respectively. Under a UV lamp, all the polymer solutions in THF exhibit strong fluorescence. Polymer **8** emits intense blue light, and both **6a** and **10** emit intense green light.

**Interaction of the Polymers with Alkaline Metal Cations.** In 1993, Swager and co-workers reported that polythiophenes anchored with crown ether macrocycles show significant ionochromic responses toward alkaline cations including $Li^+$, $Na^+$, and $K^+$.[13a] They found that

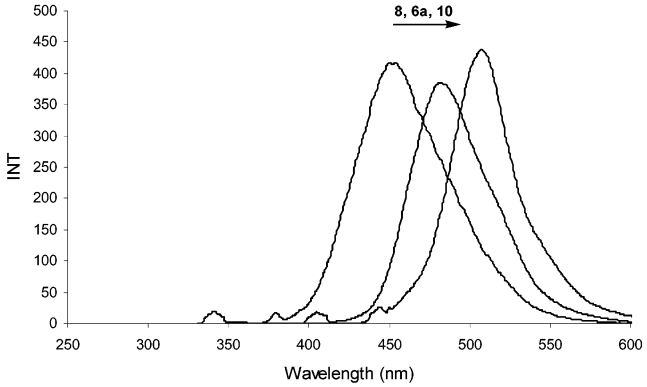



**Figure 4.** Fluorescence spectra of polymers **6a**, **8**, and **10** in THF.

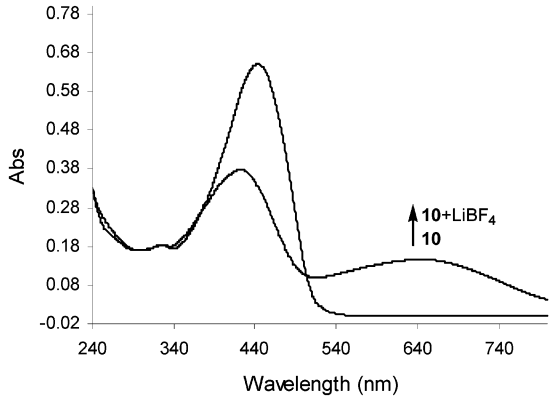



**Figure 5.** UV spectra of polymer **10** with and without $LiBF_4$.

this effect was ion selective. Different ions caused different blue shifts for the UV absorption maxima. These conjugated materials are potentially useful as ion sensors. Other researchers have also investigated the effect of metal cations on functionalized polythiophenes.[13b,c] Poly(2,5-thienylene−phenylene)s containing chelate binding units such as crown ethers and bipyridines have been synthesized, and their interactions with metal cations have been studied.[6a] However, the direct interaction of the poly(thienylene−phenylene)s with metal cations have not been reported. Since polymers **6**, **8**, and **10** are all rich in heteroatoms capable of cation binding, we have studied their interaction with alkaline metal salts.

When these polymers were treated with $LiBF_4$, we found that polymer **10** showed large change in the UV absorption. Figure 5 gives the UV spectra of polymer **10** (<0.03 mg/mL, <8.4 × $10^{-5}$ M) in a mixed solvent of $CH_2Cl_2/CH_3CN$ (7:3) with and without $LiBF_4$ (0.1 M). In the presence of $LiBF_4$, a new and broad absorption band appeared and reached equilibrium after 6 days. A similar long wavelength absorption band was also observed when **10** was treated with $LiPF_6$. In these measurements, addition of $CH_3CN$ was to help solubilize the metal salts. Under the same conditions as **10**, both the hyperbranched polymer **6** and polymer **8** showed almost no change in their UV spectra after treatment with $LiBF_4$ for 6 days.

Polymer **10** was also interacted with other alkaline metal salts including $NaBF_4$ and $KBF_4$. Figure 6 shows the UV spectra of **10** after treated with $LiBF_4$ (0.1 M), $NaBF_4$ (saturated solution, <0.1 M), and $KBF_4$ (saturated solution, <0.1 M) in $CH_2Cl_2/CH_3CN$ (7:3) for 6 days. Both $Li^+$ and $Na^+$ led to broad band absorptions

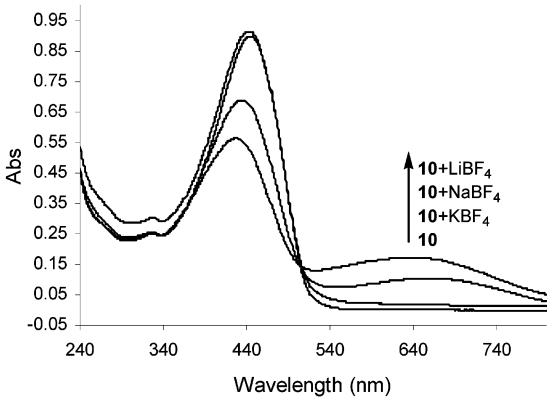
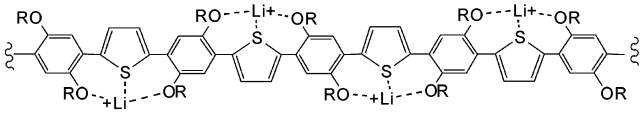



**Figure 6.** UV spectra of polymer **10** treated with $LiBF_4$, $NaBF_4$, and $KBF_4$.

at long wavelength with different maximum positions. The observed absorption maxima ($\lambda_{max}$) were 642 nm induced by $Li^+$ and 659 nm induced by $Na^+$. However, almost no change was observed for the polymer treated with $K^+$. This indicates that the cation-induced chromic effect is ion selective.

There are three possible explanations for the observed ionochromic effect: (1) electrostatic interaction; (2) ion-induced polymer aggregation; (3) ion−polymer complexation to generate the planar conjugated ladder polymer structure **11**. The fact that no ionochromic effect was observed for polymers **6** and **8** in the presence of $LiBF_4$ suggests that the influence from the electrostatic interaction be small. In addition, the positive charge of the metal cation should cause a blue shift if any rather than a red shift for the UV absorption. We studied the relationship between the absorbance at the original $\lambda_{max}$ and that at the new long wavelength $\lambda_{max}$ after polymer **10** was treated with $LiBF_4$. The result indicates that at low concentrations of **10** (<0.03 mg/mL, $<8.4 \times 10^{-5}$ M) the two absorbances are close to a linear relationship which supports an intrapolymer chain conversion rather than an interchain aggregation. This could suggest the formation of **11**. In **11**, the free rotation around the phenyl−thiophene bond is restricted, which should be much better conjugated with a significantly red-shifted absorption. Both polymers **6** and **8** contain ortho-substituted thiophene units which make it impossible to generate a fully planar and conjugated structure like **11** by chelating coordination with $Li^+$. The measurement at higher concentrations of **10** shows a more complicated relation between the two absorbances, and its cause is under investigation.




**11**, a more planar and more conjugated ladder structure

## Summary

In summary, we have synthesized a novel hyperbranched poly(thienylene−phenylene) and have compared it with a poly(2,3-thienylene−phenylene) and a poly(2,5-thienylene−phenylene). The hyperbranched polymer shows much greater solubility in organic solvents than its isomeric linear polymers. We have discovered that the poly(2,5-thienylene−phenylene) exhibits a pronounced ionochromic effect in the presence of alkaline metal cations. A large red shift in the UV−vis spectrum is observed. This ionochromic effect is also ion selective. However, both the hyperbranched polymer and the poly(2,3-thienylene−phenylene) show almost no such ionochromic effect probably because of the ortho-substituted thiophene units in their structures. The hyperbranched polymer and the poly(2,5-thienylene−phenylene) are found to be green light emitters and the poly(2,3-thienylene−phenylene) a blue light emitter. These materials may be potentially useful in electroluminescence and photovoltaics.

## Experimental Section

**General Data.** NMR spectra were recorded on a Varian 300 MHz spectrometer. Chemical shifts are given in ppm relative to internal reference $CDCl_3$ ($^1H$, 7.23 ppm;$^{13}C$, 77.23 ppm). Fluorescence measurements were recorded using a Perkin-Elmer LS-50B luminescence spectrometer. UV−vis spectra were measured on a Varian Cary 5E UV−vis−NIR spectrophotometer. GPC data were collected using a Waters Corp. 515 pump, a 410 differential refractometer, and Ultrastyragel linear GPC columns. All reagents were purchased from Aldrich Chemical Co. and used as received unless otherwise noted. $Pd(PPh_3)_4$ was purchased from Strem Chemicals Inc.

**Synthesis and Characterization of the Hyperbranched Polymer 6.** Under nitrogen, to a 10 mL Schlenk flask containing 2,3,5-tribromothiophene (541 mg, 1.69 mmol), the diboronic acid **3** (617 mg, 1.69 mmol) and $Pd(PPh_3)_4$ (97 mg, 0.08 mmol) were syringed in aqueous $K_2CO_3$ (2 M, 3 mL, degassed with nitrogen) and THF (3 mL). The reaction mixture was degassed again by three freeze−pump−thaw cycles and was then heated at reflux under nitrogen. After 3 days, the reaction mixture was cooled to room temperature and diluted with $CH_2Cl_2$. The organic layer was washed with 1 N HCl, $H_2O$, and brine, dried over $Na_2SO_4$, and concentrated under vacuum. The residue was redissolved in $CH_2Cl_2$ and precipitated with MeOH. The precipitation procedure was repeated for three more times, which afforded polymer **6** as a yellow solid (800 mg). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 0.86−0.92 (m, br), 1.30−1.56 (m, br), 1.87 (d, br), 4.03 (br), 4.14 (br), 7.24−7.38 (m, br), 7.47−7.57 (m, br), 7.67−7.69 (m). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 14.25, 22.83, 25.94, 26.14, 29.53 (br), 31.76, 31.81, 69.98 (m), 109.83, 111.94, 112.52, 116.74, 117.02, 122.49 (m), 123.23, 128.04, 128.50, 128.62, 130.26, 131.11, 134.36, 134.57, 135.04 (m), 139.33, 139.49, 149.22, 149.70, 150.25, 150.77. Polymer **6** was redissolved in $CH_2Cl_2$, and the solution was added dropwise into MeOH slowly. The precipitation was collected and dried to give **6a** (690 mg). The solution part was concentrated under vacuum, which gave the lower molecular weight portion **6b** (110 mg).

**Synthesis and Characterization of the 2,3-Thienylene−Phenylene Copolymer 8.** The same procedure as the preparation of polymer **6** was applied. The reaction used 2,3-dibromothiophene (125 mg, 0.50 mmol), the diboronic acid **3** (183 mg, 0.50 mmol), $Pd(PPh_3)_4$ (29 mg, 0.03 mmol), THF (3 mL), and aqueous $K_2CO_3$ (2 M, 2.5 mL). The reaction mixture was heated at reflux under nitrogen for 3 days. Purification by multiple dissolution in $CH_2Cl_2$ and precipitation with MeOH gave polymer **8** as a pale yellow solid (152 mg). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 0.83 (s, br), 1.12−1.66 (m, br), 3.45 (m, br), 6.63−6.77 (m, br), 7.08−7.22 (m, br), 7.25−7.42 (m, br). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 14.23, 22.79, 25.87, 29.28, 31.76, 69.33 (m, br), 114.29 (m), 116.33−116.60 (m, br), 123.42−123.81 (m, br), 125.69 (m), 126.43 (m), 126.80 (m), 127.91 (m), 129.86−130.42 (m), 134.60 (m), 135.00 (m), 135.84−136.05 (m), 149.63, 149.90 (m), 150.22.

**Synthesis and Characterization of the 2,5-Thienylene−Phenylene Copolymer 10.** The same procedure as the preparation of polymer **6** was applied. The reaction used 2,5-dibromothiophene (153 mg, 0.60 mmol), the diboronic acid **3** (220 mg, 0.60 mmol), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol), THF (3 mL), and aqueous $K_2CO_3$ (2 M, 2.5 mL). The reaction mixture was heated at reflux under nitrogen for 16 h. Purification by

multiple dissolution in $CH_2Cl_2$ and precipitation with MeOH gave polymer **10** as a scarlet solid (205 mg). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 0.91 (s, br), 1.25−1.54 (m, br), 1.93 (s, br), 4.12 (m, br), 7.04 (m, br), 7.20−7.40 (m, br), 7.57 (s, br). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 14.27, 22.83, 26.13, 29.66, 31.84, 69.98 (br), 112.63, 113.03, 124.61, 126.01 (m), 128.16 (m), 129.48, 135.35 (m, br), 139.53 (m), 149.77.

**UV Study of Polymer 10 in the Presence of $LiBF_4$.** To a 10 mL volumetric flask was added polymer **10** (2.0 mg, 5.58 $\times$ $10^{-3}$ mmol) and 10 mL of a HPLC grade $CH_2Cl_2$. The resulting suspension was stored at room temperature for 2 h to achieve saturation. A clear yellow solution of this polymer was obtained by filtration using a Pall Gelman Acrodisc LC PVDF syringe filter (LC13, 0.45 $\mu$m). A 1.0 M stock solution of $LiBF_4$ was freshly prepared using a HPLC grade $CH_3CN$. For the UV study, a polymer solution was mixed with 1 mL of the lithium salt solution at room temperature in a 10 mL volumetric flask and diluted with $CH_2Cl_2$ and $CH_3CN$ to the desired concentration at a $CH_2Cl_2/CH_3CN$ ratio of 7:3. The resulting solution was allowed to stand at room temperature and measured at different time. A similar procedure was used for the UV study of other polymers in the presence of the metal salts.

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