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Novel unsymmetrically hyperbranched polythiophenes with conjugation gradient

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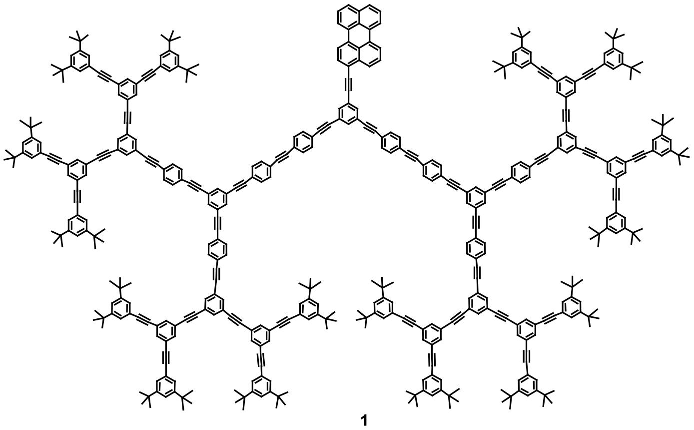
Abstract—Novel hyperbranched polythiophenes containing unsymmetrically substituted thiophene units have been synthesized. These materials are designed to have conjugation gradient in their structure and be capable of light harvesting. Study of their optical properties shows a broad-band absorption, strong fluorescence, and an effective intramolecular energy transfer. They are potentially useful for the preparation of efficient photovoltaic as well as light-emitting devices. © 2002 Elsevier Science Ltd. All rights reserved.

The study of conjugated polymers has become a highly prominent research subject for over two decades.[1] Among these materials, polythiophenes have received special attention because of their unique optical and electronic properties, environmental stability, and easily tunable structures.[1,2] They have shown promising applications in areas such as organic conductors and semiconductors, light-emitting diodes, photovoltaics, and sensors. For example, Granström et al. have used a polythiophene as a light-absorbing and electron-donor material to build a photovoltaic device of significant efficiency.[3] In our laboratory, we are interested in constructing light-harvesting dendritic polythiophenes to further improve their use in photovoltaics. A number of dendrimer-based light-harvesting materials have been synthesized and studied during recent years.[4] In 1994, Xu and Moore reported the synthesis of dendrimer **1** that contains increasing conjugation lengths from the periphery to the center.[5] Because the π–π* band-gap decreases going from the periphery to the core, the energy absorbed by the periphery units of **1** can be effectively funneled to the more conjugated core, leading to greatly enhanced fluorescence intensity. Peng and co-workers prepared dendrimer **2** using unsymmetrically substituted phenylene units.[6] This unsymmetric substitution on the aromatic ring produces a conjugation gradient as the dendritic generation increases without preparing individual units of different conjugation length as in the synthesis of **1**. Efficient energy migration has also been observed from the less conjugated units to that of the longest conjugation. We have applied a similar strategy to prepare light-harvesting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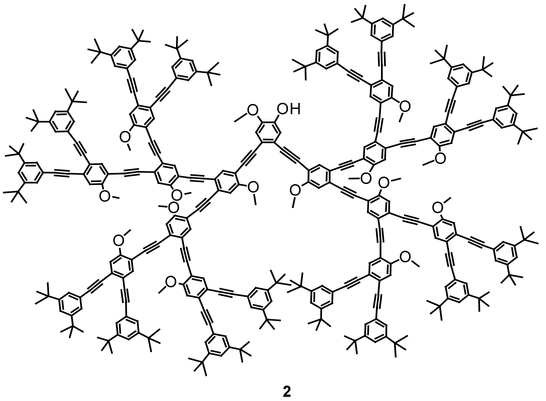

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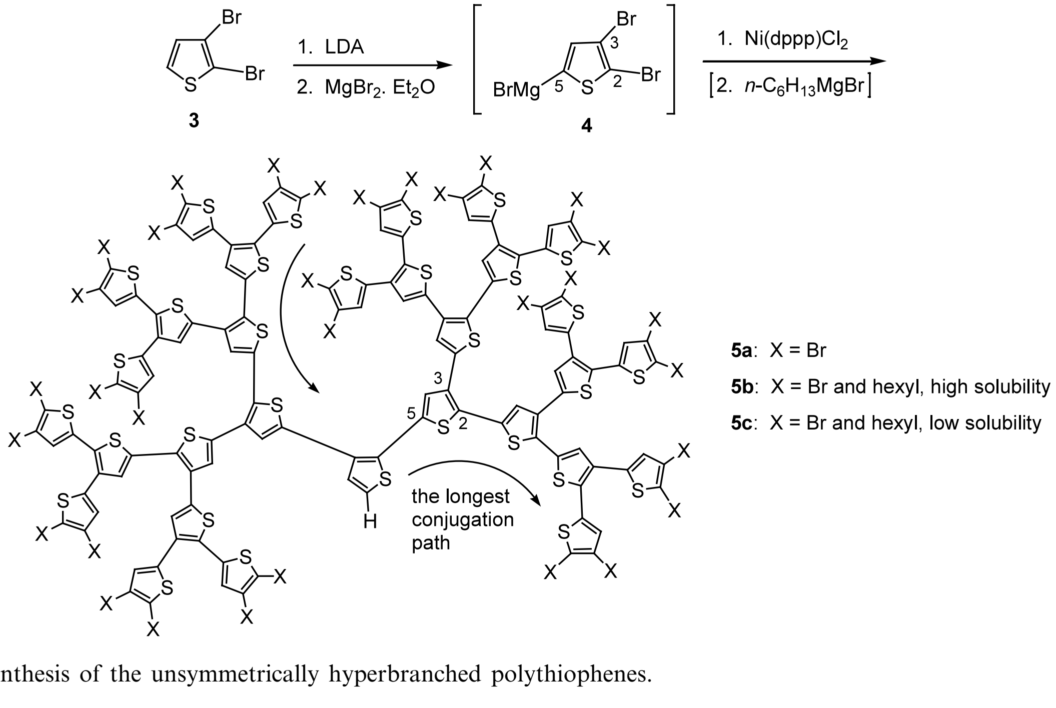
polythiophenes by polymerization of unsymmetrically substituted thiophenes. Herein, our preliminary results on the synthesis and study of the novel unsymmetrically hyperbranched polythiophenes are reported.

Using the method developed by McCullough and coworkers,[7] we conducted the polymerization of 2,3-dibromothiophene (**3**). As shown in Scheme 1, treatment of **3** with lithium diisopropylamide (LDA) followed by $MgBr_2$ should generate the Grignard reagent **4**. Compound **4** contains AB_2 type functional groups whose cross-coupling reaction should generate a hyperbranched material.[8–10] Because of the different electronic environment of the two bromine atoms at the 2,3-positions in **4**, their coupling reaction rates might be different. Polymerization of **4** in the presence of $Ni(dppp)Cl_2$ [dppp = bis(diphenylphosphino)propane] produced the hyperbranched polymer **5a**.[11] Although the solubility of **5a** was low, the molecular weight of its soluble portion relative to polystyrene standard could still be determined by gel permeation chromatography (GPC) using THF as the eluent, which showed $M_w = 4400$ and $M_n = 3400$ (PDI = 1.3). In order to improve the solubility of the polythiophene, we added a hexyl Grignard reagent at the end of the polymerization as an attempt to introduce alkyl groups to the periphery of the polythiophene. Indeed, materials with improved solubility were obtained. This process gave a highly soluble polymer (**5b**) as well as a portion of lower solubility (**5c**). It indicates a partial coupling of hexylmagnesium bromide with the periphery bromine atoms of the hyperbranched polythiophene. GPC analysis gave $M_w = 4100$ and $M_n = 2500$ (PDI = 1.7) for polymer **5b** and $M_w = 6000$ and $M_n = 3900$ (PDI = 1.6) for polymer **5c**.

The experimental procedure for the preparation of **5b**,**c** is given below. Under nitrogen, a solution of **3** (2.0 g, 8.1 mmol) in dry THF (40 mL) was syringed into a 100 mL two-neck flask fitted with an addition funnel. After it was cooled to −78°C, a solution of LDA (2.0 M in heptane/THF/ethylbenzene, 4.1 mL, 8.1 mmol) in combination with THF (10 mL) was added dropwise via the addition funnel. After 1.5 h, magnesium bromide etherate (2.1 g, 8.1 mmol) was added. The reaction mixture was stirred at −78°C for 5 h which presumably generated the intermediate **4**. It was then cannulated into a 100 mL dry Schlenk flask charged with $Ni(dppp)Cl_2$ (36 mg, 0.066 mmol) at −78°C. After 10 min, the reaction mixture was allowed to warm to room temperature and stirred for 40 h. The color of the mixture turned dark-red. A solution of hexylmagnisum bromide (2.0 M in Et_2O, 8.1 mL, 16.2 mmol) was added via syringe, which was followed by an additional amount of $Ni(dppp)Cl_2$ (15 mg, 0.028 mmol). The mixture was stirred at room temperature for 72 h, and then quenched with 1N HCl. The solvent was removed under vacuum, and the mixture was diluted with CH_2Cl_2. The precipitate was collected by filtration and washed with CH_2Cl_2. After drying under vacuum, **5c** (209 mg) was obtained as a dark-red solid. The CH_2Cl_2 solution was washed with 1N HCl and water. It was then dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was redissolved in CH_2Cl_2 and precipitated with hexane and MeOH. The dissolution and precipitation procedures were repeated two more times to give **5b** (85 mg) as a dark-red solid. The NMR data of **5b**: ^1H NMR (300 MHz, $CDCl_3$) δ 0.86 (br), 1.26 (br), 1.61 (br), 2.20–3.90 (br, weak signals), 6.60–7.70 (br); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 22.9, 29.9 (br, m), 31.9 (br), 123.0–132.5 (br, weak signals).

As depicted in the structure of **5**, the unsymmetric substitution on the thiophene rings leads to oligothiophene fragments of a gradient of conjugation lengths in



Scheme 1. Synthesis of the unsymmetrically hyperbranched polythiophenes.

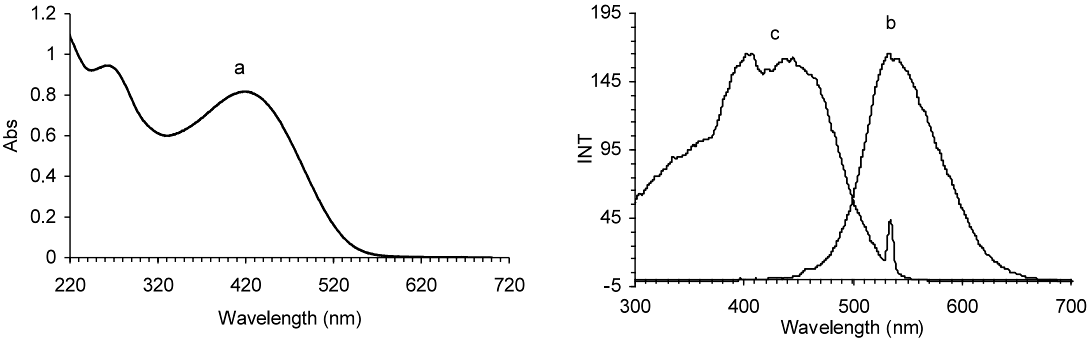


Figure 1. The UV (a), fluorescence (b), and excitation (c) spectra of **5b** in THF.

a single hyperbranched molecule. That is, only the 2,3 or 2,5-linked thiophene units in **5** are conjugated, but not the 3,5-linked thiophenes. The arrows in **5** point out the longest conjugation path in the hyperbranched structure. On the basis of this structure, it is expected that upon irradiation, light absorbed by the shorter conjugation units should be funneled to the most conjugated one, giving enhanced light emission or charge transfer. Fig. 1a shows the UV absorption spectrum of **5b** in THF. The broad absorption band in the range of 220–600 nm is consistent with the hyperbranched structure of assorted conjugation paths. The absorption maximums (λ_{max}) are at 419 and 264 nm. This hyperbranched polythiophene is strongly fluorescent upon irradiation. Fig. 1b and c are the fluorescence and excitation spectra of **5b** in THF. The emission maximum was observed at 533 nm while excited at 404 nm. When excited at other wavelengths such as 250, 300, 350, and 440 nm, no change in the shape and emission wavelength of the fluorescence spectrum was observed. The excitation spectrum was also very broad. These observations support an efficient intramolecular energy transfer in **5b** from the less conjugated units to the one with the longest conjugation. The UV spectrum of **5c**, which had a higher molecular weight than **5b**, showed a red-shift for the longest wavelength absorption (λ_{max} = 435 nm) over **5b**, but with the same broadness. The fluorescence spectrum of **5c** displayed an emission maximum at 548 nm, also red-shifted from that of **5b**. These results demonstrate that as the molecular weight increases, the conjugation length increases. The absorption maximums of **5b**,**c** at the longest wavelength and their emission maximums are close to those of the linear polythiophenes containing 3-alkyl groups at the thiophene units.[12] However, the relative absorption of the hyperbranched polythiophenes in the short wavelengths (220–400 nm) versus the longer wavelengths is much stronger than those of the linear polymers. Therefore, the hyperbranched polymers have a much broader distribution of conjugation lengths, which makes them potentially better light-absorbing materials for photovoltaics.

In summary, we have synthesized hyperbranched polythiophenes that contain unsymmetrically substituted thiophene units. These materials are designed to have conjugation gradient in their structure and be capable of light harvesting. This type of hyperbranched thiophene was never prepared before, although polythiophenes with a large variety of structures have been synthesized and investigated.[1,2,10] The study of the optical properties of the unsymmetrically hyperbranched polythiophenes shows a broad band absorption, strong fluorescence, and an effective intramolecular energy transfer. These polymers are potentially useful for the preparation of efficient photovoltaic as well as light emitting devices.

Acknowledgements

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