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Synthesis of Extremely Stable Blue Light Emitting Poly(spirobifluorene)s with Suzuki Polycondensation

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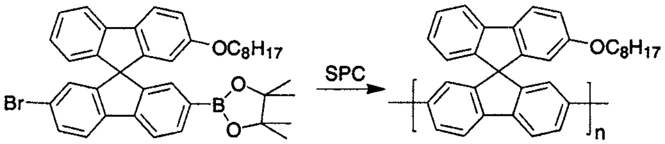
ABSTRACT



Full spirobifluorene-based blue light emitting polymers, which exhibited extraordinary thermal and color stability, were prepared with SPC through an AB-type monomer route.

Polymer light emitting materials have received considerable scientific and industrial attention due to their potential application in large area flat-panel displays.[1] For full-color displays, three primary color emitting materials, i.e., blue, green, and red, are required. High brightness and efficiency and lifetimes of greater than 10 000 h have already been achieved for green and red light emitting polymers. However, as yet, no example of blue light emitting polymers fully meets requirements for commercially feasible light emitting diodes.[2] A challenging goal is to produce blue light emitting materials with long-term stability and high efficiency and that are free of blue-green emission. Highly soluble poly-2,7-(9,9-dialkyl)-fluorenes (PFs) and their copolymers are considered as very promising blue light emitting materials because of their exceptionally high solid-state quantum yields not reached with other conjugated polymers.[3] Problems encountered with these rodlike PFs and their copolymers are their color stability. A low energy green band emission is generated during operation or annealing in air.[4] In the literature, two popular points of view ("aggregation or excimer formation" and "on-chain defects") on the origin of green band emission have been proposed.[4] Many studies have been done to understand the origin of this green band emission and to search for effective ways to suppress it.[5]

Compared with the huge amounts of publications on fluorene polymers and copolymers, less attention was paid to spirobifluorene polymers. Spirobifluorene building blocks had been used by Salbeck et al. to construct blue light emitting oligomers, dendrimers, and star-shaped molecules.[6] Yu et al. showed that spirobifluorene-fluorene copolymers exhibited better color stability than polyfluorenes.[7] A mono-

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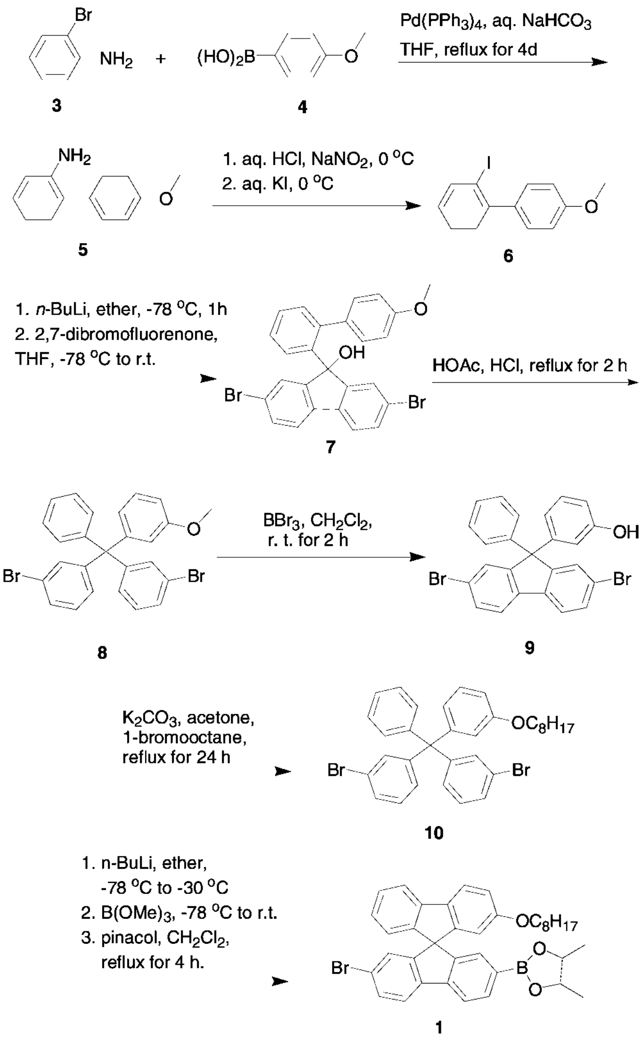
disperse spirobifluorene trimer has been synthesized and used as a blue light emitting material.[8] Spirobifluorene-linked bisanthracene exhibited pronounced thermal stability.[9] Lee et al. have recently prepared spirobifluorene polymers using Yamamoto coupling reactions, however, their color stability upon annealing in air was not investigated.[10] For most fluorene-based blue light emitting polymers, annealing in inert atmosphere does not change their PL properties.[4]

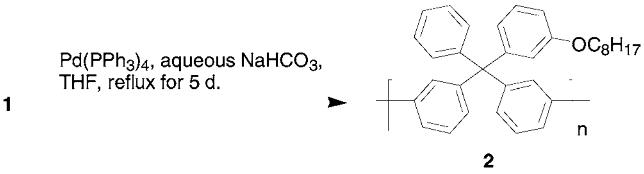
Suzuki polycondensation (SPC) has become a very effective and widely used method for preparing conjugated polyarenes.[11] To obtain blue light emitting materials with long-term stability, we designed a kind of novel spirobifluorene polymer. The polymers were synthesized through an AB-type monomer route via palladium-catalyzed Suzuki polycondensation (SPC). The synthetic route, which leads to the fully spirobifluorene polymer **2**, is shown in Scheme 2. The synthesis of AB-type monomer **1** is rather straightforward (Scheme 1). Starting from commercially available compounds **3** and **4**, cross-coupling of **3** and **4** under Suzuki cross-coupling reaction conditions gave biphenylamine **5** in a yield of 96%. Compound **5** was converted to its corresponding iodide **6** in a 80% yield through iododediazonium salt reaction. Lithium−halo exchange of **6** with *n*-butyllithium in ether at −78 °C followed by quenching with 2,7-dibromofluorenone afforded the tertiary alcohol **7** in a 75% yield. Treatment of **7** with HOAc/HCl under refluxing for 2 h afforded the spirobifluorene **8** in a 90% yield. Cleaving of the methoxy group of **8** with BBr_3 in CH_2Cl_2 afforded the spirobifluorene phenol **9** in a 95% yield. Reaction of **9** with 1-bromooctane under standard Williamson etherification conditions (K_2CO_3/acetone) gave **10** in a yield of 97%. The introduction of flexible alkyl chains helps to increase the solubility of the aimed polymers. Monobromo/lithium exchange on **10** with *n*-BuLi at −78 °C in diethyl ether and subsequent reaction of the anion with $B(OMe)_3$ gave the spirobifluorene boronic acid whose esterification with pinacol furnished the desired boronic ester **1** in a total 30% yield. High purity (>98%) was confirmed by ^1H and ^{13}C NMR spectroscopy and combustion analysis.

Scheme 1



Suzuki polycondensations (SPC) of AB-type monomer **1** were performed in a biphasic system (THF/aqueous $NaHCO_3$) with freshly prepared $Pd(PPh_3)_4$ as a catalyst precursor (Scheme 2).[12] The reactions were stirred at reflux for 5 days. During the reaction, the spirobifluorene polymer **2** precipitated from the reaction mixture in about 2 days.

Scheme 2



All the precipitated polymers could be fully redissolved in common organic solvents, such as methylene chloride, chloroform, and THF, but were only partially soluble in toluene. Standard workup afforded the spirobifluorene polymer **2** as an amorphous, slightly yellow solid. The crude polymers were redissolved in a small amount of methylene chloride and filtered through a short pad of silica gel to remove the catalyst residues, taken into benzene, and freeze-dried in a high vacuum line. The yield is 96%. The GPC elution curve of **2** shows a bimodal distribution. This is probably due to its limited solubilty in a mixture solvent of THF and water. The molecular weights were determined by

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GPC against polystyrene standard. The weight average molecular weights (M_w) was found up to 32 kg/mol. GPC is known not to be a good method to determine the actual molecular weight of rodlike polymers; the number presented here should be treated with carefulness. The polymers were unambiguously characterized with ^{1}H and ^{13}C NMR spectroscopy as well as elemental analysis.

The thermal properties of the spirobifluorene polymer **2** were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Polymer **2** exhibits good thermal stability. It shows less than 5% decomposition up to 400 °C under nitrogen but lost about 50% weight at about 450−480 °C. In the DSC trace of second heating (10 °C/min), polymer **2** exhibited only a glass transition at about 121 °C; no crystallization or melting peak was observed.

The absorption and photoluminescent (PL) spectra of polymer **2** in dilute toluene solution are fully superimposable with that of PFs. This indicates that in solution the spirobifluorene polymers exhibited similar electronic properties to PFs. The PL quantum yields (Φ_F) of polymer **2** in toluene were measured to be 0.91 with 9,10-diphenylanthracene as a reference standard (cyclohexane solution, $\Phi_F = 0.9$).[13]

The electrochemical behavior of the polymer **2** was investigated by using cyclic voltammetry (CHI 630A Electrochemical Analyzer) with a standard three-electrode electrochemical cell in a 0.1 M tetrabutylammonium tetrafluoroborate solution in PhCN at room temperature under nitrogen with a scanning rate of 30 mV/s. A glassy carbon working electrode, a Pt wire counter electrode, and an Ag/AgNO$_3$ (0.01M in PhCN) reference electrode were used. The experiments were calibrated with the standard ferrocene/ferrocenium (Fc) redox system and assumption that the energy level of Fc is 4.8 eV below vacuum.[14] The cathodic wave was not observed for polymer **2** within the solvent limit. The onset determined with ferrocene as internal reference standard is 1.03 V. The energy levels of the HOMO and the band gap (ΔE) were thus estimated from the cyclic voltammogram and the onset of the absorption spectra. The HOMO and the band gap were estimated to be −5.8 and 2.9 eV. Then the LUMO was estimated to be −2.9 eV.

Solid films of polymer **2** and PFs on quartz plates used for UV−vis and fluorescence characterization were spin coated with 1% toluene solution at 1500 rpm. After thermal treatment of the solid films of spirobifluorene polymer **2** at 200 °C for 3 h in air, no change was found for the absorption spectrum. In the control experiment, a long wavelength absorption tail appeared at 450 nm in the absorption spectrum of PFs film. The PL spectra of polymer **2** and PFs films before and after annealing at 200 °C in air for different times are shown in Figure 1. For the pristine film, the emission spectra of polymer **2** and PFs are almost superimposable. After thermal annealing at 200 °C for only 0.5 h, the PL spectrum of annealed PF film exhibits a new band at around 525 nm, which is typical for linear PFs films after annealing. In our point of view, this low energy long wavelength emission band in green-blue region might be due to the synergistic effect of keto defects and crystallization (in some case aggregation). The formation of crystallization or aggregation facilitates energy transfer from the high band-gap polyfluorene to the low band-gap fluorenone defects.[9] In case of polymer **2** film, the thermal treatment did not have any effect on the PL spectrum. No green-blue band emission was observed even after the film was annealed at 200 °C for 3 h in air.

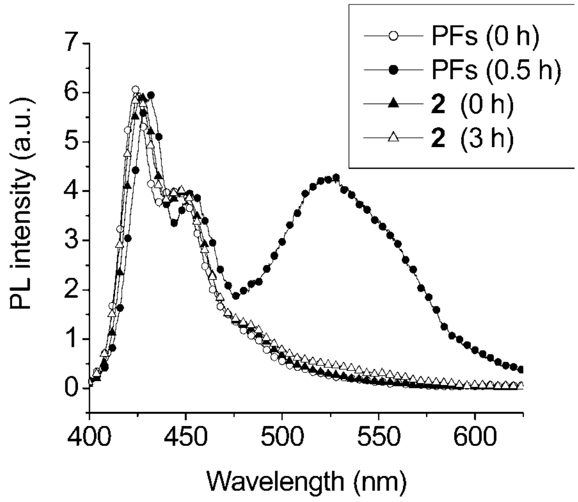

Figure 1. Photoluminescent spectra of polymer **2** and PFs in solid films before and after thermal annealing at 200 °C for different times (0.5 h for PFs and 3 h for polymer **2**).

In conclusion, full spirobifluorene polymers, which exhibited good solubility in THF, were synthesized using an AB-type monomer route via SPC. Polymer **2** exhibited extremely good luminescent stability; no green band emission was observed after the film was annealed at 200 °C for 3 h in air.

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Supporting Information Available: Detailed experimental procedures and characterization of the key compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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