

Spiro-Bridged Ladder-Type Poly(*p*-phenylene)s: Towards Structurally Perfect Light-Emitting Materials

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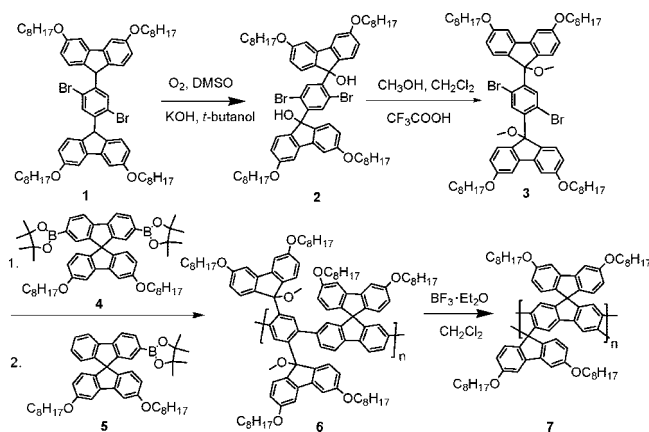
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Conjugated polymers have received remarkable scientific attention in recent years owing to their potential applications as light-emitting materials.¹ An important member of the conjugated polymer family, the conjugated ladder-type polymer possesses a rigid coplanar structure, which enhances the conjugation, carrier mobility, and luminescence intensity.² The synthesis and investigation of photophysical properties of ladder-type poly(*p*-phenylene)s (LPPP) were first reported by Scherf and Müllen in 1991.^{2d} Although more than 15 years have passed, no one has yet achieved the goal of synthesizing structurally perfect and stable LPPP free of ketonic defects.³ For the application of fluorene-based polymers as light-emitting materials, the structural perfection of the polymers is very crucial. The presence of a small amount of ketonic defects in the polymers, which even cannot be detected by IR and UV–visible spectroscopy, can completely change the film emission spectra of polymers, because in solid film the ketonic defects are low energy trap-sites to which the excited energy can be transferred very efficiently.³ Studies by Müllen et al. have shown that the aryl substituted polyfluorenes exhibit much better thermal stability than the corresponding alkyl substituted ones.⁴ Recent studies by Holmes et al. indicate that the structural perfection of the fluorene-based light emitting materials depends on the synthetic route of the monomers.⁵ The structural perfection also plays a very important role in determining the film electro-optic properties of the ladder type poly(*p*-phenylene)s. Ma et al. have modified the synthetic route of ladder-type poly(*p*-phenylene)s developed by Scherf and Müllen by using 9,9-dihexylfluorene-2,7-bis(boronic acid pinacol ester) instead of benzene-diboronic acid.⁶ The modified route gives LPPP ladder-type poly(*p*-phenylene)s with much better structural perfection.⁶ Very recently, we have developed a new synthetic approach to synthesize spiro-bridged ladder-type oligo(*p*-phenylene)s.⁷

The established classical synthetic strategies of ladder type poly(*p*-phenylene)s are described as follows: (1) A keto-functionalized precursor polymer was prepared using a palladium-catalyzed Suzuki polycondensation (SPC). (2) The ladder polymer was then generated in two steps: (i) the keto groups were reduced with lithium aluminum hydride or, alternatively, the carbonyl groups alkylated with alkyllithium or an alkylmagnesium halide followed by (ii) ring closure in a Friedel–Crafts alkylation.⁶ After carefully studying the known synthetic route of LPPP, we suppose that the incomplete keto reduction on the precursor polymer chain is the key source of ketonic defects in the final product. To avoid the defects caused by the incomplete keto reduction, we combine the classical two-step route into a single-step one, in which only a Friedel–Crafts-type cyclization is required to afford a LPPP after obtaining a PPP precursor. Furthermore, to avoid the irresistibility to oxidation of alkyl-substituted methylene bridges,⁸ we introduce all aromatic spirobifluorene linkages into the polymer structure. Our previous results have demonstrated that spirobifluorene structure can effectively suppress the formation of ketonic defects and thereby

Scheme 1. Synthetic Route to Spiro-Bridged Ladder-Type Poly(*p*-phenylene)s



endow the polymer with excellent color stability.⁷ Also, the three-dimensional bulky structure of spirobifluorene units can effectively reduce the aggregation of the molecular chains ensuring a high luminescent efficiency.⁹ Here we report a novel route to spiro-bridged ladder-type polymers that exhibit excellent thermal and color stability and are free of low energy ketonic defects.

The synthetic route leading to the LPPP is shown in scheme 1. Compound **1** was oxidized by oxygen in a mixture of KOH, DMSO, and *t*-butanol to yield the diol **2** in a 93% yield. Monomer **4** was synthesized according to literature procedures.¹⁰ The polymerization of monomers **2** and **4** was not successful under standard Suzuki–Miyaura polycondensation conditions; the hydroxyl groups on monomer **2** had a harmful effect on the polymerization. Therefore, monomer **2** was converted to monomer **3**, in which the two hydroxyl groups were capped by methyl groups, in a 96% yield by the treatment with CH₃OH and CF₃COOH in CH₂Cl₂. The polymerization of monomer **4** and **3** was carried out in a biphasic mixture of aqueous NaHCO₃ and THF with freshly prepared Pd(PPh₃)₄ as the catalyst precursor. Polymer **6** was obtained in a 94% yield after the capping of bromo endgroups with compound **5**. Polymer **6** was converted to the spiro-bridged LPPP **7** in a 90% yield by the treatment with a catalytic amount of BF₃·etherate. The efficient ring closure reaction was confirmed by the complete disappearance of the characteristic signal of the methoxy group at $\delta = 2.41$ ppm in the ¹H NMR spectrum of the spiro-bridged LPPP (see Supporting Information). Both the polymer precursor **6** and the spiro-bridged LPPP **7** are readily soluble in common organic solvents such as dichloromethane and chloroform, which make the structural characterization very convenient.

The molecular weights of polymers were measured by gel permeation chromatography (GPC) against polystyrene standards with chloroform as an eluent. The M_n and M_w of polymer **6** are

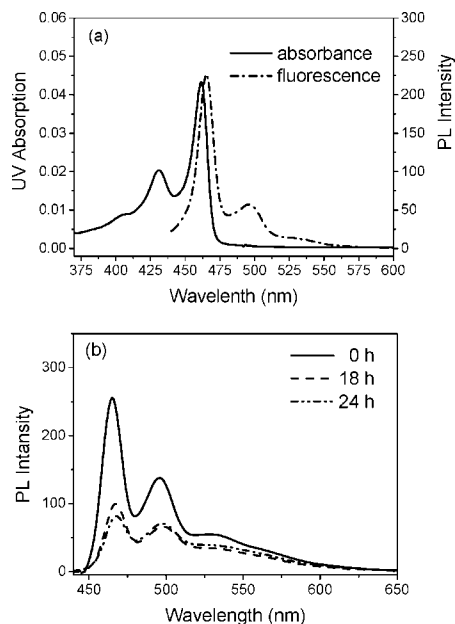


Figure 1. (a) The UV–vis absorption and photoluminescence spectra of LPPP **7** in chloroform solutions 1×10^{-6} M (concentration of repeat unit); (b) the unnormalized film PL spectra of spiro-bridged LPPP **7** before and after annealing at $110\text{ }^{\circ}\text{C}$ in air.

12.6 and 23.7 kDa, respectively; whereas after ring closure the M_n and M_w of the ladder polymer **7** increased to 21.2 and 62.0 kDa, respectively. The molecular weights determined by GPC are only a relative measurement of the hydrodynamic volume of polymers. The differences in the elution curve may be due to increased backbone rigidity and to a different interaction with the column material. The thermal properties of polymer **7** were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Polymer **7** exhibits very good thermal stability, undergoing less than 5% weight loss up to $435\text{ }^{\circ}\text{C}$, and loss of about 50% of its weight at about $700\text{ }^{\circ}\text{C}$. No distinct glass transition was observed from 25 to $350\text{ }^{\circ}\text{C}$ in its DSC curves of the second heating and cooling runs ($10\text{ }^{\circ}\text{C}/\text{min}$).

Polymer **6** exhibited a strong absorption band in the ultraviolet region with a maximum at 332 nm and a broad featureless emission band with a maximum at 414 nm, and its Stokes shift was 81 nm (see Supporting Information). The normalized UV–visible absorption and photoluminescence (PL) spectra of polymer **7** in dilute chloroform solution are shown in Figure 1a. Polymer **7** displayed well-resolved spectra with the absorption and emission maxima at 462 and 464 nm, respectively. A very small Stokes shift of 2 nm reflects that such spiro-bridged LPPP is extremely rigid. It is worth noting that the three-dimensional spirobifluorene structure can effectively suppress the aggregation of the polymer chains, and there is essentially no shift of the UV and the PL spectra on going from solution to film (see Supporting Information). The backbone structure of polymer **7** is identical to the ladder polymer prepared by Ma et al. Their solution absorption and emission spectra are quite similar. Solid films of polymer **7** on quartz plates used for UV–vis and fluorescence were prepared by spin-coating from a 1% chloroform solution at 1500 rpm. Figure 1b shows the emission spectra of as-prepared film and the subsequently annealed ones at $110\text{ }^{\circ}\text{C}$ in air. Unlike the published results of Me-LPF,⁶ the annealing of the film of LPPP **7** at $110\text{ }^{\circ}\text{C}$ in air did not result in the origin of the low energy band at 2.2–2.3 eV. This result indicated that the spiro-bridged LPPP is free of low energy defects and that it exhibited very good thermal and color stability.

The electrochemical behavior of polymer **7** was investigated by using cyclic voltammetry (see Supporting Information). The cathodic wave was not observed for polymer **7** within the solvent limit. The onset of oxidation wave determined with ferrocene as the internal reference standard is 1.03 V. The energy levels of the HOMO and the band gap (E_{gap}) were thus estimated to be -5.66 and 2.64 eV from the cyclic voltammogram and the onset of the absorption spectra. The LUMO level of polymer **7** was calculated to be -3.02 eV according to the equation: $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{gap}}$.

A single-layer light-emitting diode (LED) of the type ITO/PEDOT/ladder-polymer/LiF/Al was fabricated to investigate the electroluminescence (EL) property of the ladder-type polymer. The EL spectrum (see Supporting Information) is almost identical to the PL one, indicating that there is no ketonic defect on polymer chains.

In conclusion, a novel type of blue light-emitting spiro-bridged ladder-type poly(*p*-phenylene)s was synthesized. The newly developed synthetic method allows the preparation of LPPP with good structural perfection. No low energy green emission was observed after the film was annealed at $110\text{ }^{\circ}\text{C}$ for 24 h in air. Spiro-bridged ladder-type polymer **7** is the first LPPP that exhibits excellent thermal and optical stability.

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Supporting Information Available: Detailed experimental procedures, characterization of all compounds, and their spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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