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Synthesis of Monodisperse Spiro-Bridged Ladder-Type Oligo-*p*-phenylenes

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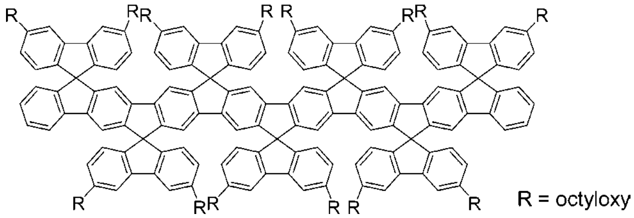
ABSTRACT



Monodisperse spiro-bridged ladder-type oligo-*p*-phenylenes, which have very rigid backbones, exhibited intensive emissions with very small Stocks shifts, displayed very good color stability upon thermo-oxidation, and were synthesized by Suzuki cross-coupling, oxidation, and BF_3·ether-catalyzed cyclization reactions.

Both conjugated ladder structures[1−13] and spiro-bifluorene-based compounds[14,15] have attracted tremendous attention in recent years for their applications in light-emitting diodes, photovoltaic cells, plastic lasers, and field-effect transistors. The ladder-type oligomers and polymers possess a rigid coplanar structure, which enhances the conjugation, carrier mobility, and luminescence intensity.[1−13] The synthesis of ladder-type oligo-*p*-phenylenes and the investigation of their photophysical properties have been reported by Scherf and Müllen et al.[4−12] These ladder-type poly-*p*-phenylenes exhibited blue emission with high fluorescence quantum efficiency. However, similar to polyfluorenes, the ketonic defects also impeded the practical application of ladder-type poly-*p*-phenylenes.[16−18] In our earlier work, we have demonstrated that spirobifluorene structure could significantly suppress the formation of ketonic defect and endowed the polymer with good color stability.[19] The unusual rigid three-dimensional structure makes spirobifluorene an ideal building block in construction of stable blue-light emitting and plastic laser materials.[14,15] The spiro-concept can overcome the photo/thermal oxidation of the 9-position of the fluorene unit to the undesired ketonic defect.[14,15,19] To the best of our

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knowledge, there is no report on the synthesis of ladder-type oligomers based on spiro bridges. The synthesis of well-defined conjugated ladder oligomers and polymers is considered challenging in the material-related chemistry area. Stimulated by the work of Scherf's and Müllen's groups, we report here the synthesis of ladder-type oligomers based on spirobifluorene units.

The chemical structures of ladder-type oligomers **1**−**4** with 2, 3, 4, and 7 spiro bridges, respectively, are shown in Figure 1. These oligomers are of unique three-dimensional conformation, which prevents planar ladder backbones from aggregation in solid films. Figure 2 shows a computer-generated three-dimensional model of oligomer **4** as an example. The octyloxy chains have been removed for clarity. By evaluating the literature synthetic strategies[4−12,20] for the synthesis of ladder-type poly-*p*-phenylenes and dispirofluorne-indenofluorene, we could design two routes for the synthesis of ladder-type oligomers as shown in Scheme 1. In route A, the addition of biphenyldilithiums to the four ester groups on the oligomer chain is complicated; in route B, the synthesis of the tetraketone precursor would be sophisticated. Considering the above-mentioned bottlenecks in the synthesis, we did not think the existing approaches were suitable for the synthesis of the aimed ladder oligomers. As shown in Scheme 2, a new route was designed for the synthesis of monodisperse ladder-type oligomers.

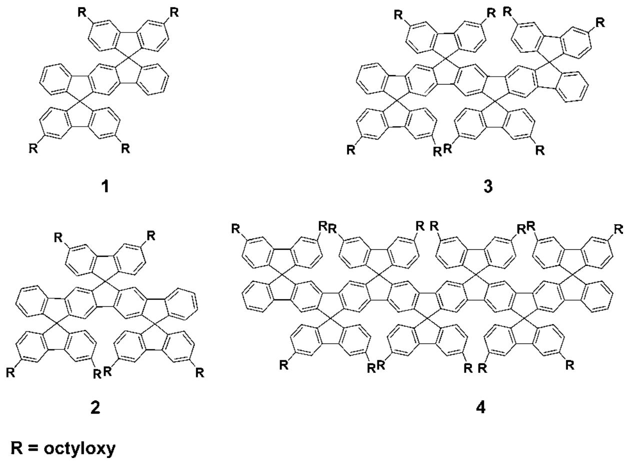


Figure 1. Structures of monodisperse spiro-bridged ladder oligo-*p*-phenylenes.

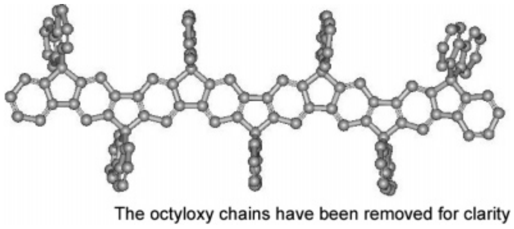
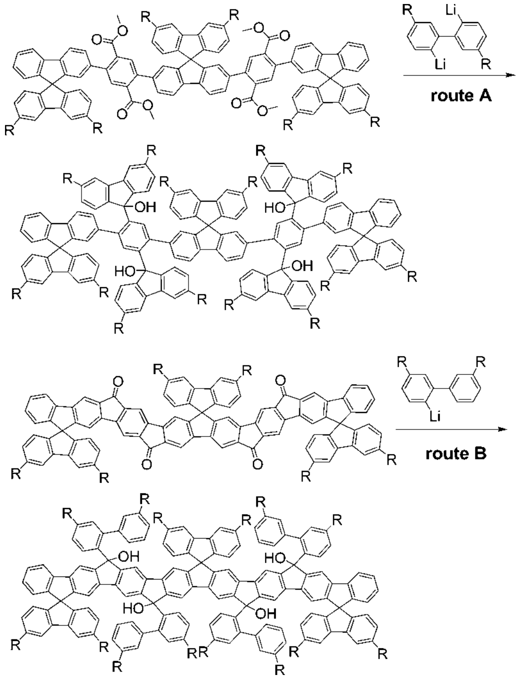


Figure 2. Computer-generated 3-D model of oligomer **4**.

Scheme 1. Possible Synthetic Routes to Monodisperse Ladder Oligomers with 7 Spiro Centers



Starting from the biphenyl bromide **5**, lithium−halo exchange by the treatment of **5** in diethyl ether with *n*-BuLi at −78 °C was followed by quenching with 2,5-dibromobenzene-1,4-dialdehyde to afford the intermediate **6** in a 49% yield. Ring closure of **6** in dry CH_2Cl_2 with BF_3·ether as the catalyst afforded the key intermediate **7** in an 83% yield. Suzuki cross-coupling of compound **7** and phenylboronic acid gave compound **8** in a 97% yield. The benzylic hydrogen could be readily oxidized under basic condition through the carbanion mechanism.[21] Compound **8** was oxidized by oxygen in a mixture of KOH, DMSO, and *tert*-butyl alcohol to afford the diol **9**, which was directly converted to the desired ladder oligomer **1** in a yield of 93%. It is worth noting that a similar compound with two spiro-centers has recently been reported by Horhant et al.[20] Suzuki cross-coupling of compound **7** with 0.4 equiv of spirobifluorene monoboronic ester **10** afforded compound **11** in a 43% yield. The cross-coupling of compound **11** and phenylboronic acid brought about the intermediate **12** in a 92% yield. The coupling of **7** with 2.4 equiv of spirobifluorene monoboronic ester **10** furnished compounds **13** in a 95% yield. The oxidation of **12** and **13** with oxygen under basic conditions furnished the corresponding diols, which converted ladder-type oligomers **2** and **3** in yields of 91% and

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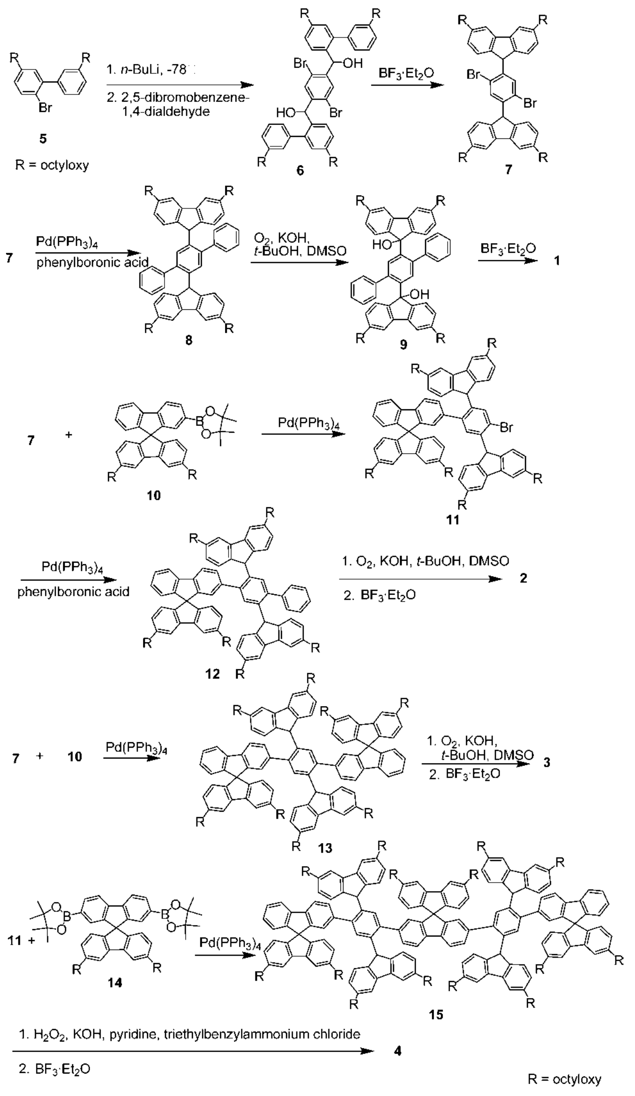
Scheme 2. Synthesis of the Key Building Block **7** and Monodisperse Ladder-Type Oligomers **1**−**4**



93%, respectively, via the BF_3·ether-catalyzed cyclization reaction. The intermediate diols, which were all very susceptible to acid, formed rings partially during the workup. Therefore, all diols were used without characterization. Suzuki cross-coupling of **11** and spirobifluorene diboronic ester **14** furnished **15** in an 87% yield. The oxidation of **15** under the same conditions as the preparation of **1**−**3** did not afford the desired product **4**. Nevertheless, the oxidation of **15** with hydrogen peroxide and KOH in pyridine with benzyltriethylammonium chloride as the phase transfer catalyst was followed by the subsequent BF_3·ether catalyzed cyclization reaction to furnish **4** in an 8% yield. Except for the diols, all intermediates and final products were purified and characterized unambiguously with ^1H and ^{13}C NMR spectroscopy, combustion analysis, or matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy. Ladder-type oligomers **1**−**4** are readily soluble in common organic solvents such as THF, CH_2Cl_2, chloroform, and toluene. The gel permeation chromatography (GPC) elution peaks of **1**−**4** are symmetrical with the polydispersities within 1.02.

The normalized solution UV−vis absorption and photoluminescent spectra of ladder-type oligomers **1**−**4** are shown in Figure 3, panels a and b, respectively. All oligomers exhibited well-resolved absorption and emission spectra. With the increase of the chain length, all the absorption and emission peaks red-shifted. The Stokes shifts of oligomers **1**−**4** are only 4, 5, 3, and 6 nm, respectively, reflecting that such ladder-type oligomers are extremely rigid. With oligomer **3** as an example, the fluorescence quantum yield of **3** in toluene solution is very high (up to 100%), indicating that nonradiative decay pathways are significantly suppressed in such spiro-bridged ladder-type oligomers. The film absorption and PL spectra are shown in the Supporting Information. With oligomer **3** as an example, the spectral stability was investigated by heating the film at 200 °C in air. As shown in Figure 4, no evident PL spectral change was found after 2.5 h of heating.

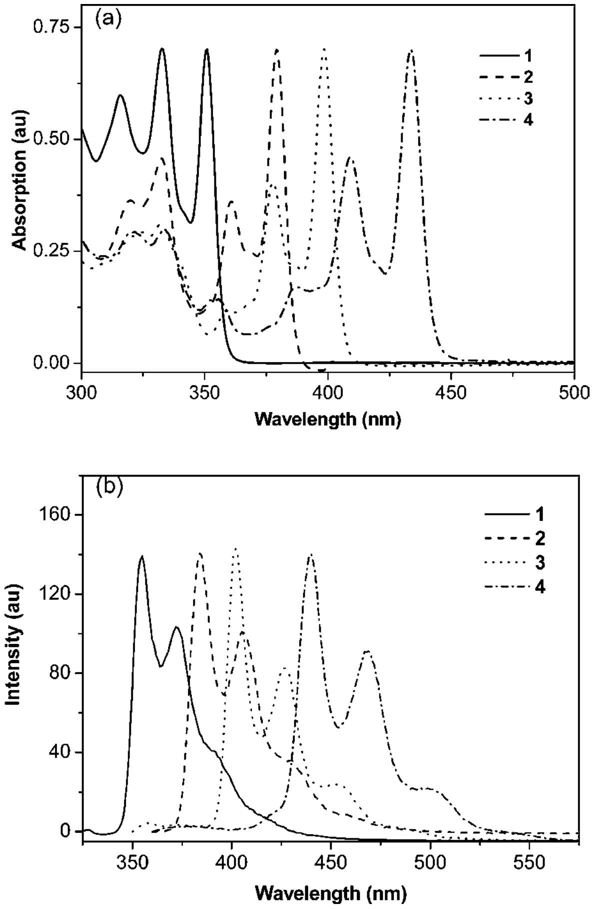


Figure 3. The normalized electronic absorption spectra of **1**−**4** in CH_2Cl_2 solutions (a) and the normalized photoluminescent spectra of **1**−**4** in toluene solutions (b).

The electrochemical behaviors of oligomers **1**−**4** were investigated by cyclic voltammetry with a standard three-electrode electrochemical cell in acetonitrile solution contain-

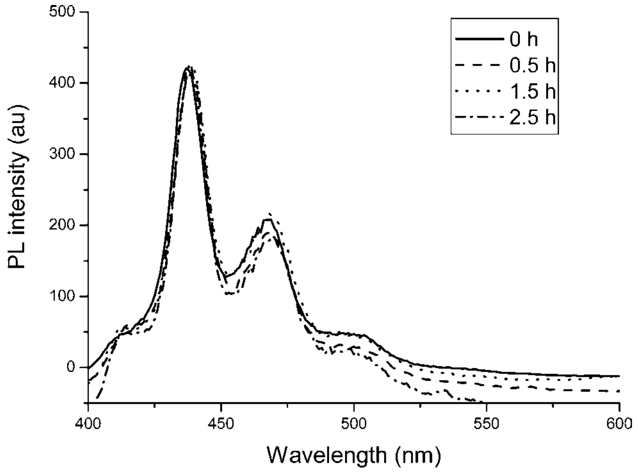


Figure 4. The normalized film PL spectra of spiro-bridged ladder-type oligomer **3** before and after annealing at 200 °C in air.

ing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) at room temperature. The oxidation potentials were measured versus Ag/AgNO$_3$ as the reference electrode and a standard ferrocene/ferrocenium redox system as the internal standard for estimating the HOMO of the oligomer films. Figure 5 shows the cyclic voltammograms of ladder-type oligomers **1**−**4** in films at a scan rate of 30 mV·s^{-1} in the range of 0−1.4 V. All the oligomer films showed irreversible p-doping processes in the first redox cycle. With decreasing conjugation length, the oxidation peaks of the oligomers moved to more positive values. The band gap (ΔE) of oligomers **1**−**4** was calculated from the UV−vis absorption onset of the films. The LUMO levels were calculated according to the following equation: $E_{\mathrm{LUMO}} = E_{\mathrm{HOMO}} + E_{\mathrm{gap}}$. The results are summarized in Table 1. With the increase in the conjugation length of the ladder oligomers, the band gap becomes narrower.

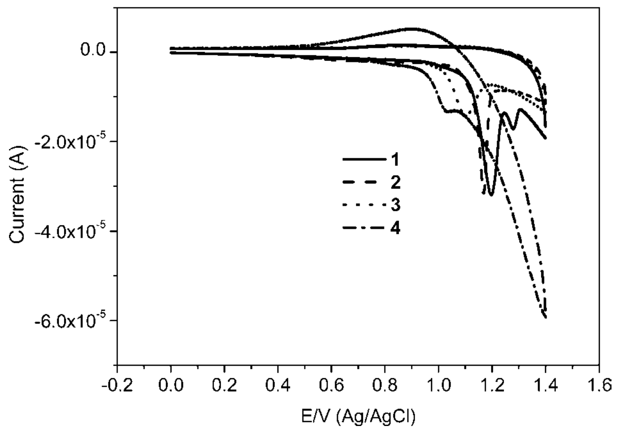


Figure 5. The cyclic voltammograms of ladder-type oligomers **1**−**4** in films at a scan rate of 30 mV·s^{-1}.

Table 1. HOMO and LUMO Energies and Band Gap Data of Monodisperse Spirobifluorene-Bridged Ladder Oligomers **1**−**4**

oligomer	**1**	**2**	**3**	**4**
HOMO	−5.86 eV	−5.80 eV	−5.74 eV	−5.68 eV
LUMO	−2.45 eV	−2.76 eV	−2.77 eV	−2.98 eV
band gap	3.41 eV	3.04 eV	2.97 eV	2.70 eV

The thermal properties of the ladder-type spiro-bridged oligomers **1**−**3** were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). In nitrogen atmosphere, oligomer **1** started to decompose at about 350 °C and lost 5% of its weight at 400 °C. Oligomers **2** and **3** displayed much better thermal stability; they started to decompose at about 400 °C and lost 5% of their weight at about 430 °C. DSC studies indicated that oligomers **1** and **2** had melting points at 197 and 203 °C, respectively, and no melting point or glass transition was observed for oligomer **3**.

In summary, we have developed the synthesis of ladder-type oligo-*p*-phenylenes based on spiro bridges. These oligomers exhibited very intensive fluorescence and very small Stokes shifts due to the rigidity of their backbones. The spiro-bridged ladder oligomers also showed very good color stability. The preparation of spiro-bridged ladder-type poly-*p*-phenylenes and the investigation of their photoluminescent properties are in progress.

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

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