Notes

**Synthesis and Properties of an Acetal-bridged Ladder Poly(p-phenylene)**

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Ladder \(\pi\)-conjugated polymers are promising materials for broad applications in organic-based devices,\(^1\) including light-emitting diodes,\(^2\) thin film transistors,\(^3\) and solar cells.\(^4\) Their rigid coplanar structures promise resistance to deformation and enhanced \(\pi\)-conjugation, which lead to a set of desirable properties, such as intense luminescence, high carrier mobility and environmental stability. Most of the studies in this field have been focused on poly(p-phenylene)-based polymers such as step ladder-type poly(phenylenes)\(^5\) and fully ladder-type poly(phenylenes).\(^1a,6\) There are, however, only limited reports of ladder poly(p-phenylenes) with heteroatom bridges.\(^7\) This is mainly due to a lack of useful synthetic routes in terms of efficacy as well as accessible structural diversity. The exploration of conceptually new methodology is thus a compelling subject in this chemistry.

We have recently developed a \(\text{BBr}_3\)-promoted cyclization to produce an ether and ester-bridged ladder-type poly(p-phenylenes).\(^8\) This method constitutes significant improvements over other routes to produce ladder polymers because the cyclization is fast and quantitative. Versatility of the reaction is another advantage of our method to prepare ladder polymers.

As a new entry into this class of polymers, we introduce herein a novel ladder poly(p-phenylene) with an acetal-bridge. The strategy to construct an acetal-bridged ladder system is based on our chemical cyclization method. Thus, phenoxide, generated by \(\text{BBr}_3\)-promoted demethylation, acts as a nucleophile for nucleophilic addition with the neighboring ketone, causing cyclization (Scheme 1).\(^9\) This constructs a hemiacetal-bridged triphenylene skeleton \(2\) in one spot. The subsequent methylation using methanol in TFA produces the desired acetal-bridged triphenylene skeleton \(3\),\(^9\) as a model for the corresponding poly(p-phenylene) \(6\), also in a quantitative yield. The photophysical and electrochemical properties of the acetal-bridged poly(p-phenylene) \(6\) are further described in this communication.

Scheme 1. Synthesis of the ladder-type compounds \((2\ \text{and}\ 3)\) and their extended polymeric structures \((5\ \text{and}\ 6)\) with heteroatom-bridges.

Scheme 2. Synthesis of the precursor compound \(1\).
The precursor of the cyclized compound, 1, was prepared as depicted in Scheme 2. Starting from 2,5-dibromoterephthalic acid 7, 2,5-dibromo bis[(dodecylphenyl)methaneone] 9 was prepared by first conversion of the acid 7 to acid chloride 8, followed by AlCl3 promoted Friedel-Crafts acylation with dodecyl benzene in 70% yield over two steps. Subsequent Suzuki coupling of dibromide 9 with o-methoxy phenyl boronic ester 10 gave the corresponding precursor molecule 1 in 93% yield (Scheme 2).

The BBr3 promoted cyclization was also applied to prepare the extended hemiacetal-bridged ladder poly(p-phenylene) 5 by the same procedure as described above (Scheme 1) using the precursor polymer 4. Further methylation gave the desired ladder poly(p-phenylene) with an acetal-bridge 6 in a same manner as that of 3. Both the cyclization and methylation were achieved in quantitative yields, rendering an efficacy to our methodology to prepare this type of system.

The hemiacetal and acetal-bridged ladder polymers (5 and 6) were both readily soluble in organic solvents like THF and dichloromethane, and any by-products formed during the cyclization can thus be easily removed by a Soxhlet method.

The precursor polymer 4 was obtained by Suzuki coupling reaction of the dibromide 9 with the corresponding dimethoxy diborate 11 (Scheme 3).

The structure determination of the acetal-bridged ladder poly(p-phenylene) 6 was carried out by the 1H and 13C NMR spectroscopic analyses, and was compared with its precursor counterpart 4. It showed disappearance of the signal corresponding to the carbonyl carbon (δ = 195) of the precursor 4, whilst shifting the methoxy signal (δ1 = 3.3 for 4 and 2.4 for 6). Similar results were obtained for the corresponding model compounds 1 and 3.9 The IR spectrum of 6 also showed disappearance of the ketone group at 1710 cm⁻¹.

The electronic properties of the acetal-bridged ladder poly(p-phenylene) 6 were investigated by UV-vis absorption spectroscopies both in solution and on film, and compared to its corresponding non-cyclized precursor 4 (Figure 1 and Table 1). The absorption spectra of the cyclized poly(p-phenylene) 6 showed new and strong peaks at 371 nm (for solution) and 398 nm (for film).11 This is a clear result of the acetal-bridge enforcing a planar conformation of the phenylene units.

The electrochemical redox behaviors of the acetal-bridged ladder poly(p-phenylene) 6 with its cast thin film were characterized by cyclic voltammetry (CV). The oxidation and reduction cyclic voltammograms of polymer 6 is shown in Figure 2 and summarized in Table 1.

The HOMO level (ionization potential) was calculated from the oxidation onset via \( E_{\text{HOMO}} = (E_{\text{ox onset (Ag/AgCl)}} - E_{\text{ox FC/e+ vs Ag/AgCl}}) \).12 The LUMO level (electron affinity) was estimated by subtraction of the band gap energy \( E_g \) from the HOMO level following \( E_{\text{LUMO}} = E_{\text{HOMO}} - E_g \). The estimated HOMO and LUMO energy levels of polymer 6 were −4.95 and −2.17 eV, respectively. The newly-prepared ladder poly(p-phenylene) with an acetal-bridge 6 revealed much smaller band gap (2.80 eV) than typical poly(p-phenylenes), confirming its planar ladder structure.

Finally, the possibility to prepare thin films of the ladder-type conjugated polymer associated with the above-men-

![Figure 1](image-url) **Figure 1.** UV-vis spectra of precursor polymer 4 and its cyclized form 6 in THF solution (solid line) and on film (dotted line).

![Figure 2](image-url) **Figure 2.** Cyclic voltammograms of the polymer film 6 coated on ITO electrodes measured in acetonitrile containing 0.1 M tetrabutylammonium phosphate solution at a scan rate of 100 mV/s at room temperature.

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<th>Table 1. Optical and electrochemical properties of polymer 6</th>
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<tr>
<td>Polymer</td>
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*Solution: in tetrahydrofuran (THF); \( E_g \): optical bandgap estimated from the band edge \( (\lambda_{\text{max}}) \) of the absorption spectra*
tioned electronic properties and its planar conformation of 6 incites us to realize field-effect transistors as an active semiconductor layer. We expect that this novel acetal-bridged ladder poly(p-phenylene), having a high electron density and planarity, would be an ideal p-type semiconductor. Possibilities of the prepared films for organic field effect transistors are currently under investigation.

In summary, a ladder-type poly(p-phenylene) with an acetal-bridge was introduced as a new entry into this class of π-conjugated ladder polymers by our chemical cyclization method.

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References and Notes


9. See Supporting Information for details.

10. The GPC analysis of the polymer 6 revealed molecular weights of $M_n = 4.4 \times 10^3$ and $M_w = 1.2 \times 10^4$, respectively.

11. For polymer 6, pronounced absorption tails are revealed between 430 and 700 nm, and are ascribed to aggregates of the planar polymers.

12. Ferrocenium/ferrocene (Fc+/Fc) redox couple with a potential of 4.80 eV relative to vacuum as the reference potential was used.