

Notes

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

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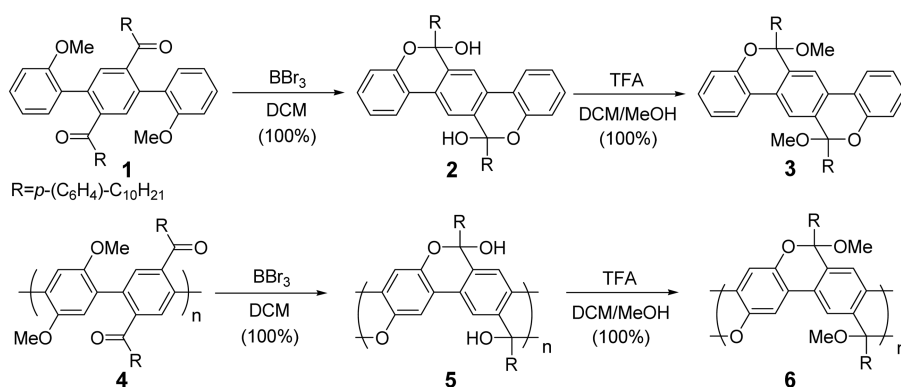
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Ladder π -conjugated polymers are promising materials for broad applications in organic-based devices,¹ including light-emitting diodes,² thin film transistors,³ and solar cells.⁴ Their rigid coplanar structures promise resistance to deformation and enhanced π -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.

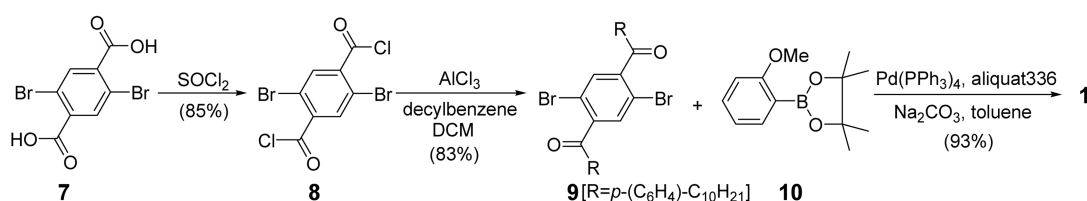
We have recently developed a BBr₃-promoted cyclization to produce an ether and ester-bridged ladder-type poly(*p*-phenylenes).⁸ This method constitutes significant improve-

ments 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.

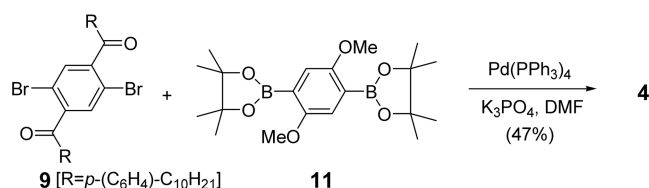
As a new entry into this class of polymers, we introduce herein a novel ladder poly(*p*-phenylene) with an acetal-bridge. The strategy to construct an acetal-bridged ladder system is based on our chemical cyclization method. Thus, phenoxide, generated by BBr₃-promoted demethylation, acts as a nucleophile 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 ladder structure **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** and **3**) and their extended polymeric structures (**5** and **6**) with heteroatom-bridges.



Scheme 2. Synthesis of the precursor compound **1**.



Scheme 3. Synthesis of the precursor polymer **4** using Pd-catalyzed cross-coupling reaction.

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)methanone] **9** was prepared by first conversion of the acid **7** to acid chloride **8**, followed by AlCl_3 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 BBr_3 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**¹⁰ 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 ^{13}C NMR spectroscopic analyses, and was compared with its precursor counterpart **4**. It showed disappearance of the signal corresponding to the carbonyl carbon ($\delta_{\text{C}} = 195$) of the precursor **4**, whilst shifting the methoxy signal ($\delta_{\text{H}} = 3.3$ for **4** and 2.4

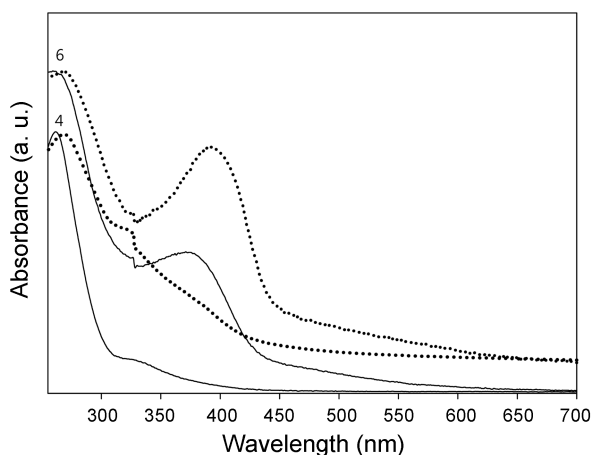


Figure 1. UV-vis spectra of precursor polymer **4** and its cyclized form **6** in THF solution (solid line) and on film (dotted line).

Table 1. Optical and electrochemical properties of polymer **6**

Polymer	Uv-Vis absorption spectra		CV		
	Solution ^a λ_{max} (nm)	Film λ_{max} (nm)	$E_{\text{g}}^{\text{opt b}}$ (eV)	Homo (eV)	Lumo (eV)
6	261, 371	280, 398	2.80	-4.95	-2.17

^aSolution: in tetrahydrofuran (THF); ^b $E_{\text{g}}^{\text{opt}}$: optical bandgap estimated from the band edge (λ_{onset}) of the absorption spectra

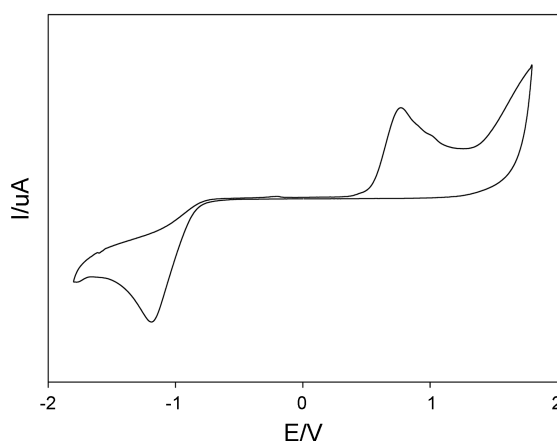


Figure 2. Cyclic voltammograms of the polymer film **6** coated on ITO electrodes measured in acetonitrile containing 0.1 M tetrabutylammonium phosphate solution at a scan rate of 100 mV/s at room temperature.

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 $E_{\text{HOMO}} = (E_{\text{ox}} - \text{onset (vs Ag/AgCl)} - E_{\text{ox}}(\text{Fc/Fc}^+ \text{ vs Ag/AgCl}))$.¹² The LUMO level (electron affinity) was estimated by subtraction of the band gap energy E_{g} from the HOMO level following $E_{\text{LUMO}} = E_{\text{HOMO}} - E_{\text{g}}$. 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-

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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- See Supporting Information for details.
- 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.
- For polymer **6**, pronounced absorption tails are revealed between 430 and 700 nm, and are ascribed to aggregates of the planar polymers.
- Ferrocenium/ferrocene (Fc^+/Fc) redox couple with a potential of 4.80 eV relative to vacuum as the reference potential was used.