Coplanarity in the Backbones of Ladder-type Oligo(p-phenylene) Homologues and Derivatives

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ABSTRACT

p-Tolyl-substituted ladder-type oligo(p-phenylene)s containing three, four, and five phenylene rings were readily synthesized. The uniform aryl substitution of these systems allowed us to determine the coplanarity of the π-conjugated backbones crystallographically. The intramolecular annulations eliminate almost all of the conformational disorder and enhance the degree of π-conjugation of the backbones, resulting in significant red shifts in the absorption and emission maxima and lower oxidation potentials in the higher homologues.

In recent years, advances in organic optoelectronics—for example, organic light-emitting diodes (OLEDs), organic solar cells, and organic thin-film transistors (OTFTs)—have imposed substantial demands on the required electroactive oligomeric and polymeric materials. For example, ladder-type poly(p-phenylene)s (LPPPs) that possess coplanar π-conjugated backbones, obtained through intramolecular annulation, have received a considerable amount of research interest; they have been exploited successfully as active materials in electronic devices because of their favorable properties, such as enhanced π-conjugation,2 high photoluminescent efficiency, and remarkable hole mobility.3 Unfortunately, the intrinsic polydispersity of polymers normally impedes their detailed structural characterization and further understanding of their structure—property relationships. Monodisperse oligomers, with their well-defined molecular sizes and structures, often can serve as model systems for their polymeric counterparts. This approach has provided a substantial amount of information relating to the electrical and optical phenomena displayed by polymers.4 Although, ladder-type p-phenylene oligomers [e.g., terphenylene (indenofluorene),5 pentaphenylene,6 and undecaphenylene7] have been synthesized and characterized as discrete chromophoric systems with which to probe the structure—property relationships of LPPP. However, the coplanarity of ladder-type oligo(p-phenylene) backbones usually attached with different pendent alkyl and/or aryl groups to improve their solubility remains speculative at higher numbers of repeating units because of the lack of direct evidence for

the molecular configuration; this information is accessible only through computer simulation.\textsuperscript{8} In this Letter, we report the synthesis of a homologous series of \textit{p}-tolyl-substituted ladder-type oligo(p-phenylene)s containing three, four, or five phenylene units and exhibiting extensive $\pi$-conjugation. The introduction of the \textit{p}-tolyl groups as peripheral substituents was beneficial not only to provide high thermal and morphological stability but also to allow us to obtain solid-state structures, making detailed analyses of the backbone structures feasible. We have found that the photophysical and electrochemical properties, as well as the thermal stabilities, correlated well with the degree of $\pi$-conjugation.

Scheme 1 depicts the synthesis of the \textit{p}-tolyl-substituted coplanar ter-\textit{p}-phenylene 3Ph.

### Scheme 1. Syntheses of the Coplanar Ter-\textit{p}-phenylene 3Ph and Penta-\textit{p}-phenylene 5Ph

Taking advantage of commonly used synthetic strategy for the syntheses of ladder-type oligomers and polymers,\textsuperscript{3-8} Pd-catalyzed Suzuki coupling of diethyl 2,5-dibromoterephthalate (1) and phenylboronic acid afforded the diester 2 in an isolated yield of 98%. The reaction of the diester 2 with an excess amount of 4-methylphenyllithium, generated in situ by reacting 4-bromotoluene with $n$-BuLi at $-78^\circ$C, afforded a diol, which subsequently underwent ring closure through Friedel–Crafts alkylation under acidic conditions to give the coplanar ter-\textit{p}-phenylene 3Ph in 87% yield. Its longer homologue, the coplanar penta-\textit{p}-phenylene 5Ph, was synthesized through a similar synthetic pathway (Scheme 1). The Suzuki coupling of 1 with 9,9-ditolyfluorene-2-diboronic ester (3)\textsuperscript{9} gave the diester 4 in 92% yield. Subsequent double addition of 4-methylphenyllithium onto the ester groups of 4, followed by acid-catalyzed intramolecular cyclization, gave the desired product 5Ph in 90% yield.

9,9-Ditolyfluorene-2,7-diboronic ester (5)\textsuperscript{10} was reacted with ethyl 2-iodobenzoate under Suzuki coupling conditions to give the diester 6 in 90% yield (Scheme 2). Following the usual reaction sequence—double alkylation of the ester groups followed by acid-catalyzed intramolecular cyclization—we obtained the target product, the coplanar tetra-\textit{p}-phenylene 4Ph in an isolated yield of 95%.

We characterized the morphological and thermal properties of the homologues 3Ph–5Ph using differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA), respectively. Table 1 summarizes the data. These homologues exhibit distinct glass transition temperatures ($T_g$) that are higher than 159 $^\circ$C. As a consequence, these novel homologues can form homogeneous and stable amorphous films, an essential property for any potential device application, such as organic light-emitting diodes (OLEDs), upon thermal treatment.

### Table 1. Properties of the \textit{p}-Tolyl-Substituted Ladder-type Oligo(p-phenylene)s 3Ph–5Ph

<table>
<thead>
<tr>
<th>compound</th>
<th>$\lambda_{\text{abs}}$ (nm)</th>
<th>$\lambda_{\text{PL}}$ (nm)</th>
<th>$T_g$ (°C)</th>
<th>$T_w$ (°C)</th>
<th>$T_d$ (°C)</th>
<th>$E_{1/2}\text{ox/d}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3Ph</td>
<td>347</td>
<td>355, 369</td>
<td>159</td>
<td>234, 353</td>
<td>353</td>
<td>1.44</td>
</tr>
<tr>
<td>4Ph</td>
<td>375</td>
<td>382, 403</td>
<td>225</td>
<td>301, 404</td>
<td>438</td>
<td>1.27</td>
</tr>
<tr>
<td>5Ph</td>
<td>397</td>
<td>403, 427</td>
<td>293</td>
<td>n.d.</td>
<td>506</td>
<td>1.16, 1.59</td>
</tr>
</tbody>
</table>

* In CHCl$_3$. \textsuperscript{b} In CHCl$_3$, upon excitation at the absorption maximum. \textsuperscript{c} Analyzed using DCS. \textsuperscript{d} Analyzed using TGA (5% weight loss). \textsuperscript{e} In CH$_2$Cl$_2$ containing 0.1 M nBu$_4$NPF$_6$ as a supporting electrolyte; potentials were recorded vs Ag/AgCl.


evaporation. We ascribe the amorphous behavior and high values of \( T_g \) to the rigidity of the conjugated backbones and the presence of the \( p \)-tolyl substituents, which effectively suppress intermolecular interactions. The aryl substituents impart the oligomers with a high tolerance to heat, as indicated by their high decomposition temperatures. DSC analyses also revealed that these homologues exhibit crystallization temperatures \( (T_c) \) and melting points \( (T_m) \), which suggested the feasibility of obtaining single crystals for X-ray crystallographic analysis.

Gratifyingly, we obtained single crystals of each of \( 3\text{Ph} \), \( 4\text{Ph} \), and \( 5\text{Ph} \) that were suitable for X-ray diffraction analyses.11 As an example, in Figure 1, we present the structure of the highest homologue, \( 5\text{Ph} \), which we crystallized from a tetrachloroethane solution.

To the best of our knowledge, \( 5\text{Ph} \) is the longest ladder-type \( p \)-phenylene oligomer that has been characterized using X-ray crystallography. The conjugated backbone of \( 5\text{Ph} \) adopts a nearly coplanar configuration with plane-to-plane twisting between phenylene rings of \(-2.3\) (rings 1 and 2) and \(2.5^\circ\) (rings 2 and 3). All of the phenylene rings are slightly distorted from hexagonal because of the presence of the annulated rigid and strained five-membered rings. The molecular length of \( 5\text{Ph} \) was ca. 2.1 nm. As indicated in Figure 2, the \( p \)-tolyl substituents occupied the top and bottom faces of the conjugated molecular plane to effectively suppress any interchromophore interactions. Although we observe no evidence for effective chromophore aggregation, interdigitation of the peripheral \( p \)-tolyl groups of neighboring molecules appears to play an important role in crystal packing.12

These homologues are readily soluble in chlorinated solvents, rendering the study of structure–property correlate-

![Figure 1](image1.png)

**Figure 1.** (a) Solid-state structure of \( 5\text{Ph} \). (b) Top and (c) side views of the structure with the \( p \)-tolyl substituents omitted for clarity.

![Figure 2](image2.png)

**Figure 2.** Crystal packing of \( 5\text{Ph} \) in its unit cell (hydrogen atoms and solvent molecules have been omitted for clarity).

![Figure 3](image3.png)

**Figure 3.** Normalized UV–vis absorption (dashed lines) and photoluminescence (solid lines) spectra of the \( p \)-tolyl-substituted ladder-type oligo(\( p \)-phenylene)s \( 3\text{Ph}–5\text{Ph} \) in CHCl\(_3\) at 25 °C.

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(11) Table S-1 in the Supporting Information provides a summary of the crystal data. Figure S-1 in the Supporting Information presents the crystal structures of \( 3\text{Ph} \) and \( 4\text{Ph} \).

(12) Crystal packing diagrams and the analyses of possible intermolecular interactions of \( 3\text{Ph} \), \( 4\text{Ph} \), and \( d\text{NpPh} \) are provided in the Supporting Information.

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backbone. The lower oxidation potentials observed upon increasing the molecular length is consistent with the effective extension of the degree of \( \pi \)-conjugation within the backbones of these coplanar oligo(p-phenylene)s; such higher HOMO energy levels are crucial for reducing the energy barrier for hole injection from the anode electrodes in active organic electronic devices. The lower oxidation potential (1.27 V) of 4Ph relative to that (1.42 V) of 9,9-di(p-tolyl)bifluorene (T2)\(^9\) is consistent with the coplanar structure having an greater degree of \( \pi \)-conjugation; this annulation approach appears to be a useful alternative method for modulating the energy levels in such systems.

The highly efficient and versatile synthetic strategy can be applied to the synthesis of other novel coplanar chromophores, for example, for introducing new arenes, such as naphthalene, as constituent units of the conjugated backbone (Scheme 3). Although, in principle, the ring closure of the diol intermediate 7 could occur at either the C2 or C8 positions of the naphthalene unit to generate five- or six-membered rings, respectively. The product obtained (dNpPh) underwent cyclization only at the C2 position, as confirmed through X-ray crystallography (Figure 4). The S-shaped molecular backbone of dNpPh is relatively coplanar, with the terminal naphthalene rings being twisted slightly (by ca. 6.8°, plane-to-plane) with respect to the central phenylene ring. In addition, we also synthesized the spiro-bridged coplanar ter-p-phenylene (indenofluorene) derivative (sInF). The orthogonal configuration of the two coplanar ter-p-phenylene branches in sInF further enhances its morphological and thermal stability while preserving the photophysical properties of the indenofluorene unit.\(^{13}\)

In summary, we have readily obtained p-tolyl-substituted ladder-type oligo(p-phenylene)s incorporating three, four, and five phenylene rings in high yields. The annulation of these oligomers eliminates their conformational disorder and enhances the degree of \( \pi \)-conjugation of their backbones; we confirmed these features through the observation of significant red shifts in the absorption and emission maxima, as well as lower oxidation potentials, in the longer homologues. We verified the limited twisting and resultant high coplanarity of the conjugated backbone of the longest homologue 5Ph through the use of X-ray crystallographic diffraction analysis. In addition, we used similar strategies to synthesize the novel coplanar chromophores dNpPh and sInF to demonstrate the versatility of this synthetic method. We are currently investigating the potential applications of 3Ph–5Ph and sInF as large band gap hosts and dNpPh as a blue emitter in OLEDs; the results will be reported in due course.

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**Supporting Information Available:** Detailed experimental procedures; spectroscopic characterization and NMR spectra of new compounds; comparison of the absorption and emission spectra of 4Ph and T2; cyclic voltammograms; crystal data; crystal packing; crystal CIF files. This material is available free of charge via the Internet at http://pubs.acs.org