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

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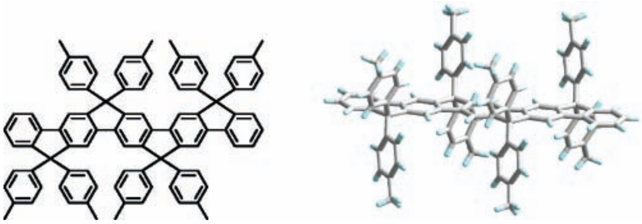
ABSTRACT



***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)[1] 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 undecaphenylene[7]] 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

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[1] (a) Scherf, U. *J. Mater. Chem.* **1999**, *9*, 1853. (b) Grimsdale, A. C.; Müllen, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 5592.

[2] (a) Setayesh, S.; Marsitzky, D.; Müllen, K. *Macromolecules* **2000**, *33*, 2016. (b) Jacob, J.; Zhang, J.; Grimsdale, A. C.; Müllen, K.; Gaal, M.; List, E. J. W. *Macromolecules* **2003**, *36*, 8240.

[3] Hertel, D.; Scherf, U.; Bässeler, H. *Adv. Mater.* **1998**, *10*, 1119.

[4] Mullen, K.; Wegner, G. *Electronic Materials: the Oligomer Approach*; Wiley-VCH: Weinheim, Germany, 1998.

[5] (a) Merlet, S.; Birau, M.; Wang, Z. Y. *Org. Lett.* **2002**, *4*, 2157. (b) Hadizad, T.; Zhang, J.; Wang, Z. Y.; Gorjanc, T. C.; Py, C. *Org. Lett.* **2005**, *7*, 795.

[6] (a) Jacob, J.; Sax, S.; Piok, T.; List, E. J. W.; Grimsdale, A. C.; Müllen, K. *J. Am. Chem. Soc.* **2004**, *126*, 6987. (b) Jacob, J.; Sax, S.; Gaal, M.; List, E. J. W.; Grimsdale, A. C.; Mullen, K. *Macromolecules* **2005**, *38*, 9933.

[7] Schindler, F.; Jacob, J.; Grimsdale, A. C.; Scherf, U.; Müllen, K.; Lupton, J. M.; Feldmann, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 1520.

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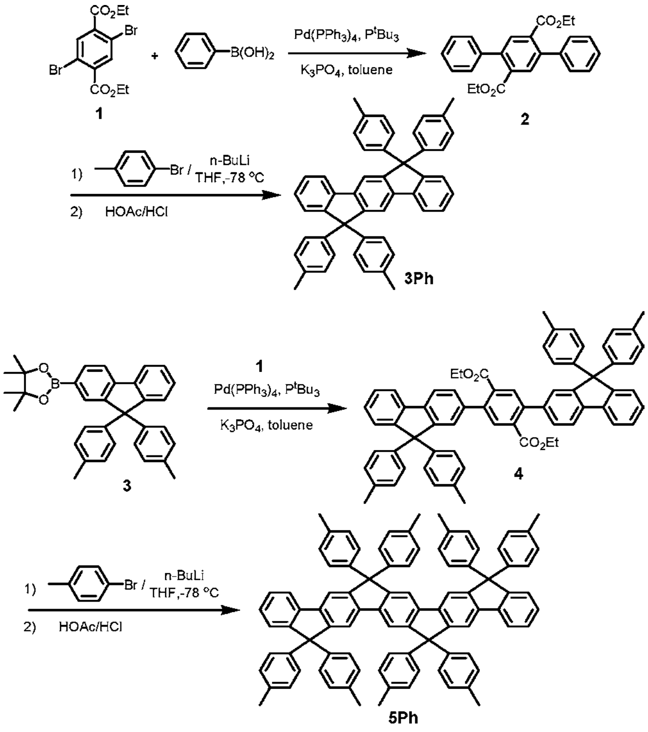
the molecular configuration; this information is accessible only through computer simulation.[8] In this Letter, we report the synthesis of a homologous series of *p*-tolyl-substituted ladder-type oligo(*p*-phenylene)s containing three, four, or five phenylene units and exhibiting extensive π-conjugation. The introduction of the *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 π-conjugation.

Scheme 1 depicts the synthesis of the *p*-tolyl-substituted coplanar ter-*p*-phenylene **3Ph**.

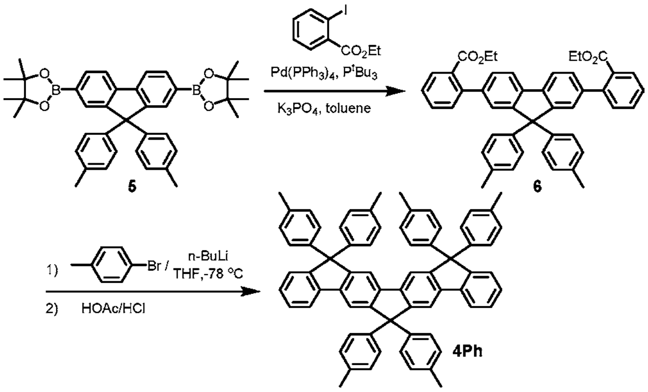
Scheme 1. Syntheses of the Coplanar Ter-*p*-phenylene **3Ph** and Penta-*p*-phenylene **5Ph**



Taking advantage of commonly used synthetic strategy for the syntheses of ladder-type oligomers and polymers,[5−8] 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 °C, afforded a diol, which subsequently underwent ring closure through Friedel−Crafts alkylation under acidic conditions to generate the coplanar ter-*p*-phenylene **3Ph** in 87% yield. Its longer homologue, the coplanar penta-*p*-phenylene **5Ph**, was synthesized through a similar synthetic pathway (Scheme 1). The Suzuki coupling of **1** with 9,9-ditolylfluorene-2-boronic ester (**3**)[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-Ditolylfluorene-2,7-diboronic ester (**5**)[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-*p*-phenylene **4Ph** in an isolated yield of 95%.

Scheme 2. Synthesis of the Coplanar Tetra-*p*-phenylene **4Ph**



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 °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

Table 1. Properties of the *p*-Tolyl-Substituted Ladder-type Oligo(*p*-phenylene)s **3Ph**−**5Ph**

compound	abs[a] λ_{max} (nm)	PL[b] λ_{max} (nm)	T_g[c] (°C)	T_c, T_m[c] (°C)	T_d[d] (°C)	$E_{1/2oxd}$[e] (V)
3Ph	347	353, 369	159	234, 353	353	1.44
4Ph	375	382, 403	225	301, 404	438	1.27
5Ph	397	403, 427	293	n.d., 470	506	1.16, 1.59

[a] In $CHCl_3$. [b] In $CHCl_3$, upon excitation at the absorption maximum. [c] Analyzed using DCS. [d] Analyzed using TGA (5% weight loss). [e] In CH_2Cl_2 containing 0.1 M $n$$Bu_4NPF_6$ as a supporting electrolyte; potentials were recorded vs Ag/AgCl.

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[8] Xia, C.; Advincula, R. C. *Macromolecules* **2001**, *34*, 6922.

[9] Chao, T.-C.; Lin, Y.-T.; Yang, C.-Y.; Hung, T. S.; Chou, H.-C.; Wu, C.-C.; Wong, K.-T. *Adv. Mater.* **2005**, *17*, 992.

[10] Wong, K.-T.; Chien, Y.-Y.; Chen, R.-T.; Wang, C.-F.; Lin, Y.-T.; Chiang, H.-H.; Hsieh, P.-Y.; Wu, C.-C.; Chou, C. H.; Su, Y. O.; Lee, G.-H.; Peng, S.-M. *J. Am. Chem. Soc.* **2002**, *124*, 11576.

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 **3Ph**, **4Ph**, and **5Ph** that were suitable for X-ray diffraction analyses.[11] As an example, in Figure 1, we present the structure of the highest homologue, **5Ph**, which we crystallized from a tetrachloroethane solution.

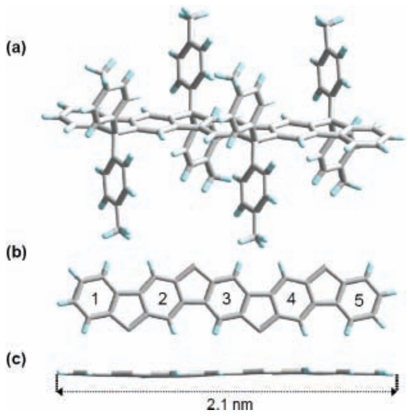

Figure 1. (a) Solid-state structure of **5Ph**. (b) Top and (c) side views of the structure with the *p*-tolyl substituents omitted for clarity.

To the best of our knowledge, **5Ph** is the longest ladder-type *p*-phenylene oligomer that has been characterized using X-ray crystallography. The conjugated backbone of **5Ph** adopts a nearly coplanar configuration with plane-to-plane twisting between phenylene rings of −2.3 (rings 1 and 2) and 2.5° (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 **5Ph** 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 correlation in solution feasible. Figure 3 illustrates the electronic absorption and photoluminescence (PL) spectra of the coplanar oligo(*p*-phenylene)s **3Ph**−**5Ph** in $CHCl_3$; Table 1 summarizes the data. Both the absorption and emission maxima were red-shifted significantly upon increasing the number of repeating phenylene units, indicating that the degree of π-conjugation was extended effectively in longer homologues. In addition, the small Stokes shifts and the mirror images of the absorption and emission spectra are consistent with the molecular coplanarity and rigidity observed in the solid-state structures. The absorption maximum of **4Ph** (centered at 375 nm) was red-shifted by 43 nm relative to that of 9,9-di(*p*-tolyl)bifluorene (**T2**)[9] (Figure S-5, Supporting Information), indicating the effectiveness of using this coplanar molecular configuration to enhance the degree of π-conjugation of the backbone.

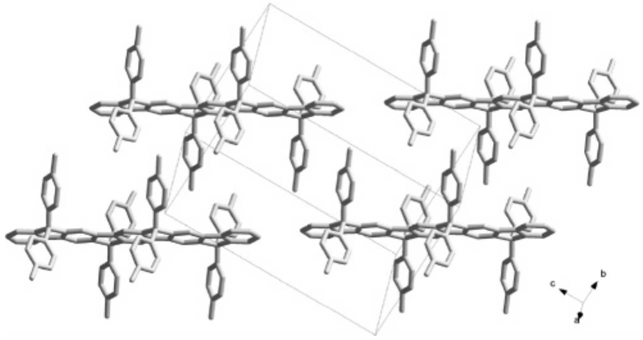

Figure 2. Crystal packing of **5Ph** in its unit cell (hydrogen atoms and solvent molecules have been omitted for clarity).

We used cyclic voltammetry (CV) to probe the electrochemical behavior of the homologues **3Ph**−**5Ph** (Figure S-6, Supporting Information); Table 1 summarizes the data. One reversible oxidation potential was detected for both **3Ph** and **4Ph**, at 1.44 and 1.27 V (vs Ag/AgCl), respectively. The homologue **5Ph** exhibited two reversible oxidation potentials, at 1.16 and 1.59 V, respectively. The large potential difference (0.43 V) between these signals is indicative of efficient radical cation delocalization within the conjugated

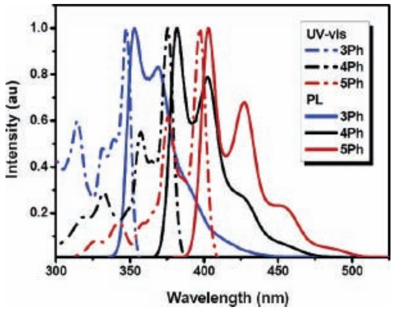

Figure 3. Normalized UV−vis absorption (dashed lines) and photoluminescence (solid lines) spectra of the *p*-tolyl-substituted ladder-type oligo(*p*-phenylene)s **3Ph**−**5Ph** in $CHCl_3$ at 25 °C.

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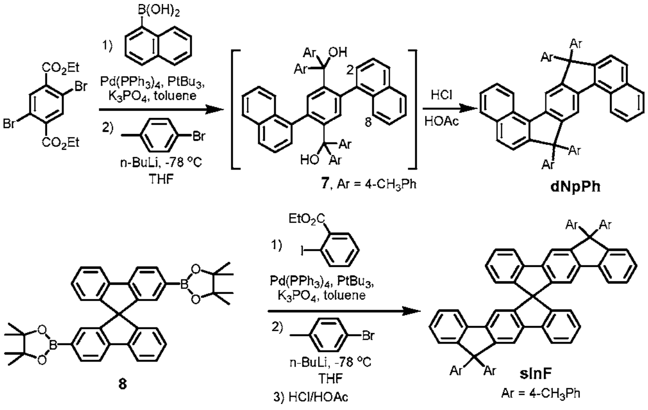
(11) Table S-1 in the Supporting Information provides a summary of the crystal data. Figure S-1 in the Supporting Information presents the crystal structures of **3Ph** and **4Ph**.

(12) Crystal packing diagrams and the analyses of possible intermolecular interactions of **3Ph**, **4Ph**, and **dNpPh** are provided in the Supporting Information.

backbone. The lower oxidation potentials observed upon increasing the molecular length is consistent with the effective extension of the degree of π-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 π-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]

Scheme 3. Syntheses of the Coplanar Chromophore **dNpPh** and the Spiro-Bridged Indenofluorene **sInF**



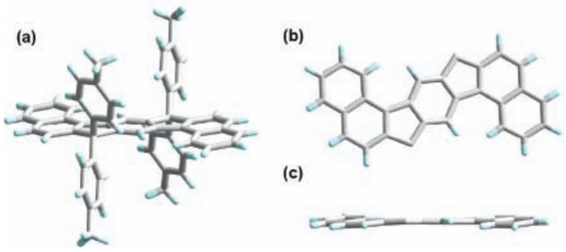


Figure 4. (a) Solid-state structure of **dNpPh**. (b) Top and (c) side views of the structure with the *p*-tolyl substituents omitted for clarity.

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 π-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

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[13] Wong, K.-T.; Liao, Y.-L.; Lin, Y.-T.; Su, H.-C.; Wu, C.-C. *Org. Lett.* **2005**, *7*, 5131.