Conjugated Ladder Polymers Containing Thienylene Units

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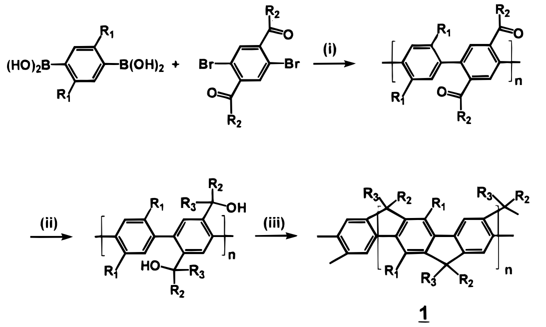
Introduction. The first synthesis of a soluble, fully conjugated ladder-type polymer, a poly(*para*-phenylene)-type ribbon, a Ladder-PPP (LPPP) **1**, in 1991[1] marks an important step of polyarylene chemistry. The general synthetic procedure of LPPP involves (i) the generation of a suitably functionalized, single-stranded poly(*para*-phenylene) (PPP) precursor and (ii) its polymer-analogous cyclization including a Friedel−Crafts-type alkylation reaction as key step. For the first time, fully soluble and processable PPPs which are characterized by a maximum degree of conjugative interaction were accessible on a gram scale (see Scheme 1).

1 exhibits an excellent solubility and processabilty into thin films and layers. Its electronic properties were extensively investigated during the last years. **1** displays a steep, vibronically structured absorption band ($\lambda_{\text{max abs.}}$ = ca. 446 nm at 2.78 eV), a mirror-symmetrical blue photoluminescence (PL) and a very small Stokes loss ($\geq$150 cm^{-1}) (see Figure 1). The PL quantum efficiency in solution reaches values of >90%, in the solid state of up to 50%. It was possible to design efficient multicolor (blue-green, yellow, and red), polymer-based light-emitting diodes (LEDs) based on LPPP-type materials.[2,3] These LEDs show high electroluminescence (EL) quantum efficiencies of up to 4% (applied voltages: 4−9 V). LPPPs were also applied in optically pumped, blue solid-state lasers in open cavity and distributed feedback (DFB) configuration.[4,5] LPPP is also characterized by large charge carrier mobilities (up to 10^{-3} cm^2/Vs for holes at room temperature).[6] The unique performance of **1** is unquestionable related to an extraordinary low concentration of electronically active traps (topological defects or impurities) in **1**.[7] This set of attractive properties has established LPPP as a widely used material for organic polymer-based LEDs and optically pumped solid-state lasers.[2−5]

The chemical structure of **1** has been varied by introducing *meta*-phenylene subunits,[8] as well as by replacing the aryl−aryl linkages with aryl−S−aryl bridges.[9] Both strategies lead to a reduction of the conjugative interaction, and therefore, to a distinct hypsochromic shift of the long wavelength absorption band. However, we are also very much interested in shifting the absorption toward lower excitation energies. A well-established way to realize this goal is the replacement of *para*-phenylene by electron-rich heteroarylene moieties, e.g., 2,5-thienylene units.

Scheme 1. Synthesis of Ladder Poly(*para*-phenylene) LPPP 1[a]



[a] Key: (i) Pd(PPh$_3$)$_4$, toluene/H$_2$O/Na$_2$CO$_3$; (ii) LAH/toluene/THF or Me−Li/toluene/diethyl ether; (iii) BF$_3$·Et$_2$O/methylene chloride (R$_1$ = -*n*-C$_6$H$_{13}$; R$_2$ = −1,4-C$_6$H$_4$-*n*-C$_{10}$H$_{21}$; and R$_3$ = −H or −CH$_3$).

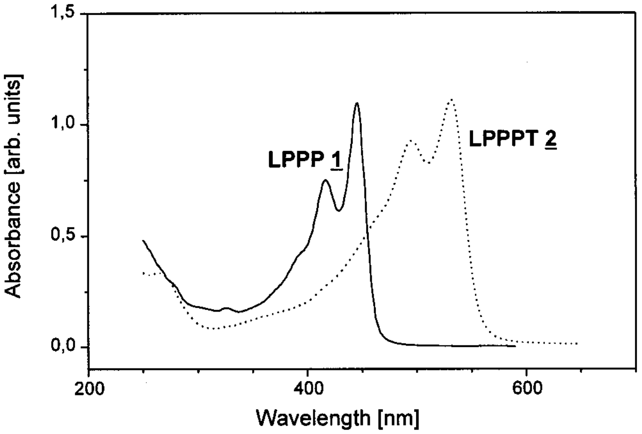


Figure 1. Absorption spectra of **1** (R$_1$ = -*n*-C$_6$H$_{13}$; R$_2$ = −1,4-C$_6$H$_4$-*n*-C$_{10}$H$_{21}$; and R$_3$ = −H) and **2** (R$_1$ = −1,4-C$_6$H$_4$-*n*-C$_{10}$H$_{21}$ and R$_2$ = −H) (solvent = methylene chloride).

In poly(arylene vinylene)s, PAVs, such a replacement of *para*-phenylene by 2,5-thienylene units [from poly(*para*-phenylene vinylene) PPV to poly(2,5-thienylene vinylene) PTV] leads to a reduction of the absorption energy by ca. 0.4−0.5 eV.[10,11] The reason for this effect is the lower aromatic resonance energy of the thiophene building block when compared to that of benzene. This results in a reduced $\pi-\pi^*$ transition energy between the benzoid ground state and the quinoid (singlet) excited state.

A first report on the synthesis of polyarylene ladder structures containing electron-rich 2,5-thienylene units was published recently by Tour and co-workers.[12] Their phenylene−thienylene- and thienylene-type ladder polymers contain imine bridging units and are characterized by a low solubility [only in trifluoroacetic acid (TFA)/halogenated hydrocarbons]. The alternating phenylene−thienylene ladder polymer displays an absorption spectrum with a pronounced tailing of the longest wavelength absorption band into the low energy visible region (occurrence of low-energy absorption shoulders). Tour et al. have related this absorption behavior to a (partial) protonation of the ⟩CH=N− bridges present in their ladder polymers by the strong acidic TFA. One of the ladder polymers, an all-thienylene-based ladder structure, is soluble in methylene chloride and exhibits an UV−vis spectrum with a steep absorption edge and well-resolved vibronic fine structure which is characteristic of planar and defect-free one-dimensional π-systems.

The aim of this work was now to apply our methodology toward phenylene-type aromatic ladder polymers (LPPPs) for the generation of related heteroarylene

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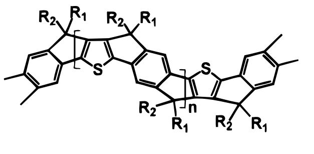
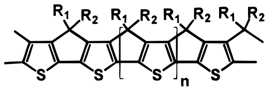
ladder polymers containing 2,5-thienylene units. Here, we were especially interested in the structure-type **2** [LPPPT, Ladder Poly(*para*-phenylene thienylene) which is composed of alternating 1,4-phenylene and 2,5-thienylene moieties] and **3** [LPT, Ladder Poly(thienylene) which is composed exclusively of 2,5-thienylene building blocks].



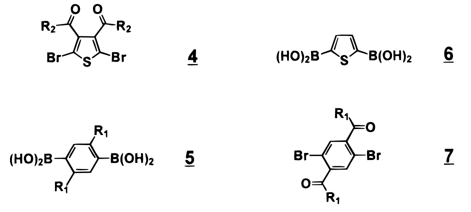
LPPPT 2



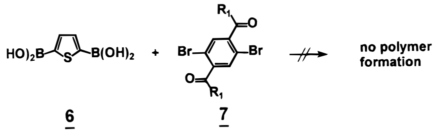
LPT 3

Results and Discussion. To realize this concept we have tried to adapt, as mentioned above, the synthetic methodology toward **1** for the synthesis of **2**. In principle, there exist two synthetic alternatives for the generation of the alternating copolymer **2** (see Scheme 2): (i) coupling of a 2,5-dibromo-3,4-dibenzoylthiophene derivative **4**[12] with a 2,5-dialkyl-1,4-phenylene diboronic acid **5**[13] in a aryl−heteroaryl cross coupling according to Suzuki or (ii) coupling of 2,5-thienylene diboronic acid **6**[14] with the corresponding dibenzoylbenzene derivative **7**[1] in a similar coupling reaction (see Scheme 3). All monomers are accessible as shown in literature procedures (see Experimental Section).

Scheme 2. Structures of Monomers 4−7



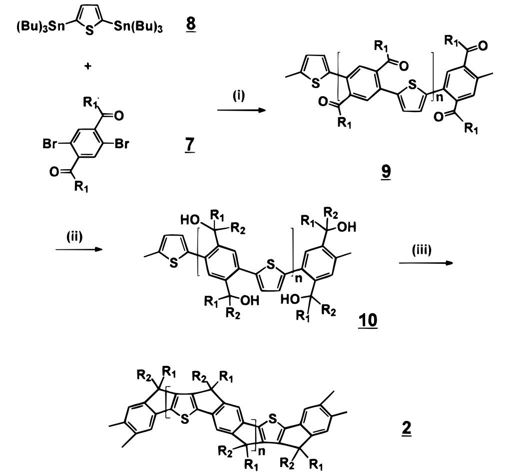
Scheme 3. Failure of Coupling 6 and 7



We have concentrated our experiments on the second alternative (**6** + **7**), because the proper synthesis of the diketone **4** is expensive. However, a coupling of **6** and **7** according to Suzuki was not successful. The 2,5-thienylene diboronic acid is not stable enough under the basic conditions of the Suzuki-type cross coupling, both in nonaqueous (DMF) and aqueous solvent systems (water/toluene), using $Pd(PPh_3)_4$ as coupling catalyst.

To circumvent these shortcomings, we have switched from the 2,5-thienylene *diboronic* acid to the corresponding *tin* organic compounds. Using 2,5-bis(tributylstannyl)thiophene (**8**)[15] instead of the diboronic acid **6**, we have carried out a Stille-type aryl−heteroaryl cross coupling using $Pd(PPh_3)_2Cl_2$ as catalyst (see Scheme 4). Coupling of **7** and **8** leads to a soluble LPPPT precursor polymer of structure **9**. Polymer **9** displays a number-average molecular weight of ca. 15 000, corresponding to a condensation of about 45 aromatic and heteroaromatic rings. The single-stranded polyketone **9** can then be further converted into the target ladder structure when our well-established polymer-analogous cyclization sequence is applied: (i) reduction with lithium aluminum hydride LAH under generation of the secondary polyalcohol **10** and (ii) polymer-analogous cyclization according to Friedel−Crafts under formation of the double-stranded ladder structure **2** with R_1 (−1,4-C_6H_4-*n*-$C_{10}H_{21}$) and R_2 (−H).

Scheme 4. Synthesis of Ladder Poly(*para*-phenylene thienylene) 2[a]



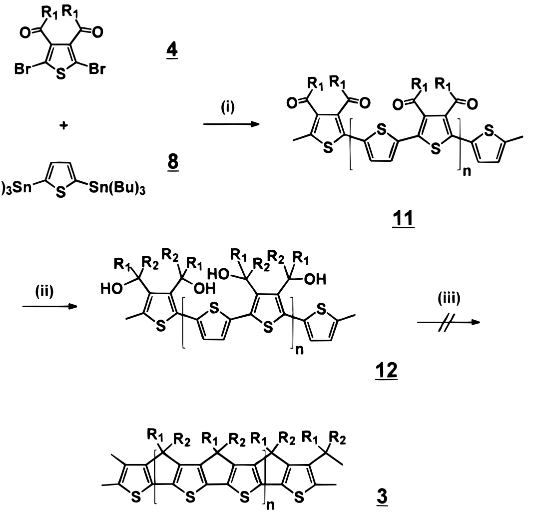
[a] Key: (i) $Pd(PPh_3)_2Cl_2$, THF; (ii) LAH/toluene/THF ($R_2 = -H$) or Me−Li/toluene/diethyl ether ($R_2 = -CH_3$); and (iii) $BF_3{\cdot}Et_2O$/methylene chloride ($R_2 = -H$) or $AlCl_3$/methylene chloride ($R_2 = -CH_3$) ($R_1 = -1,4\text{-}C_6H_4\text{-}n\text{-}C_{10}H_{21}$ and $R_2 = -H$ or $-CH_3$).

The ladder polymer **2** was fully characterized by ^1H and ^{13}C NMR spectroscopy. In the ^1H NMR spectrum, the signals of the $-CH(OH)R_1$ functions of **10** disappear completely, and **2** exhibits a new signal at $\delta = 5.6/6.0$ characteristic of the methylene bridge hydrogens. Remarkably, the hydrogen signal of the methylene bridges is split into a doublet which should be assigned to the formation of *cis*- or *trans*-configured diastereomeric 3,4-CHR_1-2,5-thienylene units. This splitting was not observed for the corresponding ladder poly(*para*-phenylene) **1**. The splitting in **2** is the result of the decreased distance of the methylene bridge substituents relative to the 2,5-thienylene units in **2**. A similar splitting was also observed in polyphenylene ladder polymers containing *meta*-phenylene building blocks.[8] The ^{13}C NMR spectrum of **2** displays the expected nine signals of nonequivalent carbons in the aromatic region ($\delta = 115.3$, 128.2, 128.6, 136.4, 140.6, 141.6, 144.9, 146.1, 150.3) and the signal of the methylene bridge carbon as a doublet at $\delta = 50.4/51.2$ due to the presence of *cis*- and *trans*-configured diastereomeric units, as mentioned above.

The cyclization of **10** to **2** is accomplished by a distinct change of the absorption properties. The only slightly yellow precursor **10** is converted into the deep red ladder polymer **2**, a consequence of the planarization of the whole π-electron system.

The absorption spectrum of **2** is characterized by a steep absorption edge of the delocalized long wavelength $\pi-\pi^*$-transition, which indicates a geometrically fixed, planar π-system. **2** displays a long wavelength absorption maximum $\lambda_{\text{max abs.}}$ of 532 nm (2.33 eV) escorted by one well-resolved vibrational sideband at 495 nm (2.51 eV). A comparison of the absorption properties of **2** to those of the parent **1** system leads to the following conclusions: (i) the spectral shape of the $\pi-\pi^*$-transitions of **1** and **2** is very similar, which indicates the occurrence of a planar, one-dimensional π-system for both LPPP and LPPPT, and (ii) the longest wavelength

Scheme 5. Synthetic Route to the Ladder Poly(2,5-thienylene) 3[a]



[a] Key: (i) $Pd(PPh_3)_2Cl_2$, THF; (ii) LAH/toluene/THF; and (iii) $BF_3 \cdot Et_2O$ or $AlCl_3$ or trifluoroacetic acid/methylene chloride ($R_1 = -1,4\text{-}C_6H_4\text{-}n\text{-}C_{10}H_{21}$ and $R_2 = -H$).

absorption maximum of **2** is red-shifted by ca. 85 nm (0.45 eV) when compared to **1**. These findings impressively illustrate the success of our synthetic strategy directed toward reduction of the optical excitation energy via replacement of aromatic *para*-phenylene by heteroaromatic 2,5-thienylene building blocks.

2 is characterized by an orange photoluminescence in solution (methylene chloride) centered at a $\lambda_{\text{max PL}}$ of 536 nm. The extraordinarily small Stokes loss between $\lambda_{\text{max abs.}}$ (532 nm) and $\lambda_{\text{max PL}}$ (536 nm) is, as already discussed for the *para*-phenylene analogue **1**,[16] a consequence of the geometrically fixed, planar ladder structure which allows only minimum changes of the polymer geometry during the transition from the ground to the excited state.

As described also for **1**, the hydrogen substituent (R_2) can be replaced by a methyl group if the first step of the polymer-analogous cyclization sequence is an addition of Me−Li in toluene/diethyl ether instead of a reduction of the keto groups with LAH.[17] Both LPPPT derivatives ($R_2 = -H$ or $-CH_3$) display very similar absorption properties. However, the polymer-analogous cyclization toward the methylated analogue ($R_2 = -CH_3$) requires aluminum trichloride as the Lewis acidic reagent of the cyclization step to guarantee a complete ring closure.

The logical continuation of our investigations was the extension of the synthetic concept to the generation of ladder polymers **3** which are merely composed of methylene-bridged 2,5-thienylene units, as planarized, ladder-type poly(2,5-thienylene)s (or polythiophenes). Roncali et al.[18] have predicted a "rigidification" strategy in order to maximize the π-conjugation in polythiophene derivatives via bridging of the thienylene subunits.

We also tried to synthesize **3** via a heteroaryl−heteroaryl cross coupling according to Stille, in this case starting with the two thienylene monomers **4** and **8**, followed by the well-established two-step polymer-analogous cyclization sequence (Scheme 5). However, all attempts to accomplish a quantitative ring closure during the final cyclization step from the polyalcohol intermediate **12** to the ladder polymer **3** were not successful. We obtained only partially cyclized products when applying Lewis acidic (aluminum trichloride, tin tetrachloride, titanium tetrachloride, and boron trifluoride) as well as protic (trifluoromethylsulfonic and trifluoroacetic acid) cyclization reagents.

We interpret this failure as related to the inherent steric strain of the LPT structure, which restricts the maximum degree of intramolecular cyclization and leads, therefore, to incompletely cyclized products.

Our results demonstrate the scope and limitations of our synthetic approach toward structurally well-defined ladder polymer architectures. With the choice of carefully selected monomers and synthetic procedures, the complex structure of **2** becomes accessible. The alternating phenylene−thienylene ladder polymer **2** shows the expected red-shift of the long wavelength absorption maximum $\lambda_{\text{max abs.}}$ when compared to the *all*-phenylene ladder structure **1**. Unfortunately, the *all*-thienylene ladder polymer **3** could not be generated following our general synthetic procedure. The target structure **3**, merely composed of annelated five-membered rings is sterically overstrained and is, therefore, not accessible via a polymer-analogous ring closure.

Experimental Section. General. All reactions were carried out in an argon atmosphere. The solvents were used as commercial quality (HPLC grade). The following compounds were synthesized according to the literature: 2,5-dibromo-3,4-bis(4′-decylbenzoyl)thiophene (**4**)[12] (using 4-decylbenzene instead of 4-butylbenzene), 2,5-dihexyl-1,4-phenylene diboronic acid (**5**),[13] 2,5-thienylene diboronic acid (**6**),[14] 2,5-dibromo-1,4-bis(4′-decylbenzoyl)benzene (**7**),[8] 2,5-bis(tributyl-stannyl)thiophene (**8**).[15] All other chemicals are commercially available.

^1H and ^{13}C NMR data were obtained on either a Bruker AMX 250 or a Bruker AMX 500 spectrometer. The UV−vis spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer (solutions in methylene chloride). Gel permeation chromatographic analysis (GPC) utilized PS-columns (three columns, 10 mm gel, pore widths 500, 10^4, and 10^5 Å) connected with UV−vis detection. All GPC analyses were performed on solutions of the polymers in 1,2-dichlorobenzene at 60 °C (concentration of the polymer = 2 g/L). The calibration was based on polystyrene standards with narrow molecular weight distributions.

Poly[2,5-bis(4′-decylbenzoyl)-1,4-phenylene-2,5-thienylene] (9). To a stirred solution of **8** (955 mg, 1.5 mmol) and **7** (1.088 g, 1.5 mmol) in 20 mL of potassium dried tetrahydrofuran (THF), 50 mg of bis(triphenylphosphino)palladium(II) dichloride in 5 mL of THF was added. The mixture was refluxed for 3 days. After cooling to room temperature, methylene chloride (50 mL) was added, and the organic layer was isolated and washed with water and 2 N HCl. The organic phase was dried over $MgSO_4$ and concentrated, and the polymer was precipitated into methanol (1:10). The crude polymer was then redissolved in 20 mL of methylene chloride and reprecipitated into methanol (1:10). Yield: 690 mg (73%). ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.50$ (4H), 7.28 (2H), 7.05 (4H), 6.62 (2H), 2.50 (4H), 1.45/1.19/0.85 (38H). ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 195.5$, 149.0, 140.7, 139.3, 133.5, 130.5, 129.5, 128.5, 127.8, 35.2, 31.2, 30.2, 28.8, 28,6, 27.1, 26.1, 21.9, 16.7, 12.6. $M_n = 15\,500$. $M_w = 28\,000$. $M_w/M_n = 1.8$ (GPC). $M_n = 12\,800$ (VPO, toluene). $(C_{44}H_{54}O_2S)_n$ $[(646.97)_n]$ Calcd: C, 81.69; H, 8.41; S, 4.96. Found: C, 81.06; H, 8.23; S, 4.55.

Poly[2,5-bis(4′-decyl-α-hydroxybenzyl)-1,4-phenylene-2,5-thienylene] (10). A solution of **9** (627 mg, 1.0 mmol) in 50 mL of toluene was treated with a suspension of lithium aluminum hydride (LAH) (450 mg, 11.8 mmol) in 50 mL of THF. The mixture was stirred for 30 min at room temperature and carefully quenched with ethanol, water, and dilute hydrochloric acid. The organic layer was isolated and washed twice with water. The organic solution was then dried over $MgSO_4$, filtered, and concentrated to dryness. The crude polymer was redissolved in 20 mL of methylene chloride and precipitated into methanol (1:10). Yield: 510 mg (81%). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.67$ (2H), 7.17 (8H), 6.94 (2H), 6.19 (2H), 2.54/2.31 (4H), 1.54/1.29/0.89 (38H). ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 142.6$, 141.0, 140.2, 136.9, 128.9, 127.5, 125.3, 78.6, 32.7, 30.4, 30.1, 23.4, 14.6.

Ladder-type Poly(*para*-phenylene thienylene) (LP-PPT, 2). A solution of **9** (510 mg, 0.811 mmol) in 50 mL of methylene chloride was treated with boron trifluoride etherate (1.8 g, 12.7 mmol). After being stirred for 15 min at room temperature, 20 mL of ethanol was added, followed by 50 mL of water. The organic layer was isolated and carefully washed with water. The resulting organic phase was dried over $MgSO_4$, filtered, and concentrated. Precipitation into methanol (1:10) gave **2** as a red polymer powder. Yield: 380 mg (76%). ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta = 8.49$ (2H), 8.33 (4H), 8.07 (2H), 7.88 (2H), 6.02/5.65 (2H), 3.82/3.67 (4H), 2.84/2.51/2.12 (38H). ^{13}C NMR (125 MHz, CD_2Cl_2): $\delta = 150.2$, 146.1, 144.9, 141.6, 140.6, 136.4, 128.6, 128.2, 115.3, 51.2/50.4, 35.7, 31.9, 31.4, 31.2, 29.6, 29.5, 29.3, 22.7, 14.1. $M_n = 17\,000$. $M_w = 35\,000$. $M_w/M_n = 2.0$. $(C_{44}H_{54}S)_n$ $[(614.97)_n]$ Calcd: C, 85.94; H, 8.85; S, 5.21. Found: C, 84.98; H, 8.89; S, 5.33.

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