Ladder Polymers

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Incorporating an Alternating Donor–Acceptor Structure into a Ladder Polymer Backbone

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Dedicated to Professor Klaus Müllen

Abstract: *Incorporation of the donor–acceptor structure of an alternating conjugated copolymer into a rigid ladder polymer backbone is reported. The resulting ladder polymers show optical features typical of rigid ladder polymers, but present an increased Stokes shift if compared to their non-polar counterparts. This behavior reflects the occurrence of charge transfer processes during excitation and leads to a positive solvatochromism.*

Fully conjugated ladder polymers are still a very attractive and challenging target of fundamental or application-driven polymer science.[1] They are characterized by a well-defined, rigid backbone, with very little reorganization during transition into the excited state, and they show promising application potential as active materials in optoelectronic devices.[2] However, the synthesis of structurally defined conjugated ladder polymers is challenging. If made in post-polymerization transformations of suitably substituted single-stranded precursors, the applied ring-closure reactions must fulfill two requirements: 1) a nearly quantitative turnover of functional groups, and 2) side reactions leading to crosslinking, or imperfect ladder formation should not occur.

Multiple powerful strategies have been developed for the generation of conjugated ladder polymers.[3–6] One of the most promising strategies is the polymer-analogous ring closure accomplished by a Friedel–Crafts-type intramolecular alkylation.[3,4] This method has been employed for the synthesis of polyphenylene, poly(thienylene-*alt*-phenylene), or poly(carbazole-*alt*-phenylene) ladder polymers, for example.[7,8] Currently, conjugated low band gap copolymers that are composed of alternating electron-rich and electron-poor building blocks, so-called donor–acceptor (D–A) copolymers, are extensively investigated as the donor component of bulk heterojunction-type organic solar cells.[9,10] In particular, D–A copolymers containing at least one multi-fused ladder-type arene segment are favored for use as an active material in organic solar cells.[10,11] Combination of the donor–acceptor concept and the already mentioned ladder polymer approach is now a very promising and challenging target, particularly when it comes to incorporation of an alternating donor–acceptor structure into a ladder-type polymer backbone.

Herein, we report the first synthesis of a high molecular weight ladder copolymer composed of alternating donor and acceptor units, which was achieved by modifying the general synthetic method developed by us 25 years ago.[3] The optical and electronic properties of the polymeric products confirm the rigid ladder-type structure of the backbones.

The well-established synthetic method proceeds as follows. A single-stranded precursor substituted with two dibenzoyl substituents in each repeat unit is assembled into a ladder backbone using a post-polymerization sequence that involves reduction of the keto groups and subsequent alkylating ring closure after Friedel–Crafts. Two issues should be mentioned concerning the synthetic method: 1) the substitution pattern of the AA/BB-type monomer couple is inverted with respect to our initially published method[3] so as to obtain the best results (cross-coupling of the dibrominated acceptor monomer with a newly discovered diboronic ester-substituted terephthalophenone derivative); 2) the reaction conditions during addition of methyllithium or lithium aluminum hydride to the obtained single-stranded polyketone precursors were carefully adjusted to circumvent unidentified side/decomposition reactions, which most probably occur as a result of nucleophilic attack of the benzothiadiazole ring.

Scheme 1 shows the synthetic pathway towards the donor–acceptor-type ladder polymers containing *N*-dialkylated benzothiadiazolodithienopyrrole (**BTDTP**) units. Dibrominated BTDTP (**BTDTP-Br**) was synthesized according to the literature.[12] The diboronic ester-substituted terephthalophenone derivative **C(O)P-BPin** (BPin = pinacolato boron) was prepared from the corresponding dibrominated compound **C(O)P-Br**[3,6] in a Miyaura borylation.[13] The synthesis of **C(O)P-Br** follows a known procedure.[3,6] The ^{1}H NMR spectrum of **C(O)P-BPin** is shown in Figure S1 (Supporting Information) with the three expected aromatic hydrogen signals. The use of the AA/BB-monomer couple **BTDTP-Br** and **C(O)P-BPin** in a Suzuki-type polycondensation reaction was favored over a Stille-type coupling of distannylated **BTDTP** and the dibrominated terephthalophenone derivative **C(O)P-Br**. Stille-type coupling resulted in high molecular weight polyketone precursors with M_P up to 72 kDa, but because of their poor solubility they were not suitable for subsequent post-polymerization reactions. Peak molecular weight (M_P) is used as an indicator of best fit in the proceeding discussion, since aggregation occurs during GPC analysis and leads to tailing of the GPC curves. Stille-type coupling of **BTDTP-Br** and the distannylated terephthalophenone derivative **C(O)P-SnMe$_3$** only leads to the formation

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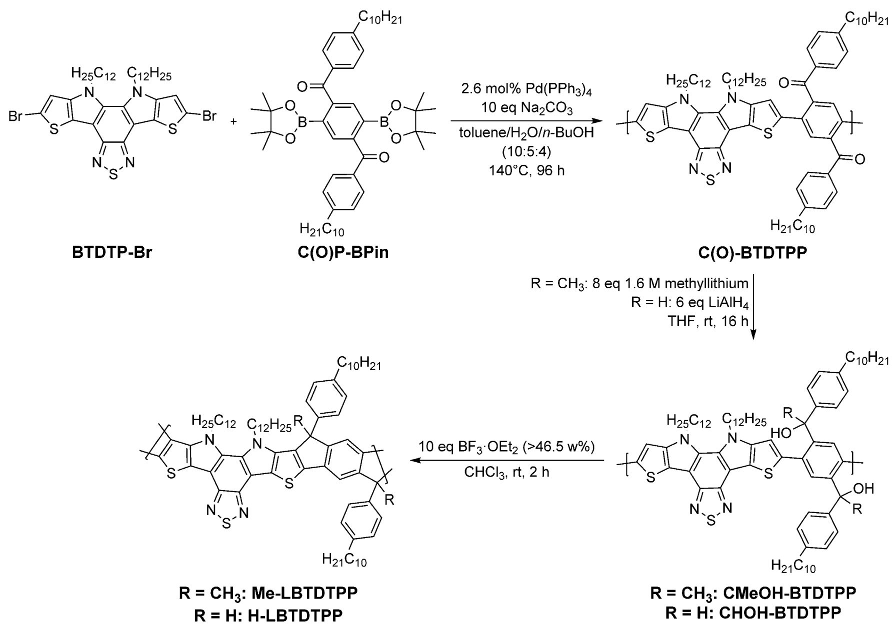

Scheme 1. Synthesis of the alternating donor–acceptor-type ladder polymers.

of low molecular weight oligomers. Suzuki-type coupling of **BTDTP-Br** and **C(O)P-BPin** was carried out under standard conditions that are typically applied for polyketone synthesis.[4,8] Tetrakis(triphenylphosphine)palladium(0) was used as catalyst together with an excess of sodium carbonate as base. The reaction produced red-colored, single-stranded polyketones **C(O)-BTDTPP**s (M_n, 18.3 kDa; M_P, 13.9 kDa). A complete list of the molecular weight data is provided in the Supporting Information; all polymers showed unimodal molecular weight distributions. The chloroform fraction of the precursor was isolated in 59% yield. The subsequent reduction was carried out in a fashion analogous with the synthesis of poly(*para*-phenylene) (**PPP**) ladder polymers (for **Me-LPPP** as an example see Figure 3b).[3,14] Methyllithium (MeLi in diethyl ether (DEE)) or lithium aluminum hydride ($LiAlH_4$) accomplished conversion into the orange-colored polyalcohols **CMeOH-BTDTPP** and **CHOH-BTDTPP** in 68% and 84% yield, respectively. For the synthesis of **LPPP** precursors, a large excess of the reducing agents can be used.[3,14] However, excess reductant is ineffectual for the D–A-system since side-reactions occur. Equivalent amounts, or only a slight 2.1 equiv excess, of MeLi and $LiAlH_4$ lead to incomplete conversion. However, eight and six equivalents of MeLi and $LiAlH_4$, respectively, achieved full conversion of the polyketones. The progress of the reaction can be tracked by IR spectroscopy (Supporting Information, Figures S19 and S20). After reduction, the -C=O stretching band around 1661 cm^{-1} vanished. The polyalcohols were directly converted into the corresponding double-stranded D–A-type ladder polymers **Me-LBTDTPP** and **H-LBTDTPP** by applying alkylating ring closure after Friedel–Crafts.[3,14] To achieve this, the polyalcohols were stirred with boron trifluoride in chloroform until reaction was complete. After aqueous workup, the red-purple-colored, “ladderized” polymers were precipitated in cold methanol. **Me-LBTDTPP** and **H-LBTDTPP** were obtained in greater than 98% and 95% yield, respectively. High temperature GPC measurements confirmed an M_P value of 19.8 kDa for **Me-LBTDTPP**. Unfortunately, **H-LBTDTPP** demonstrated low stability in the high temperature GPC analysis, whereas at room temperature GPC analysis of the polymer resulted in aggregation. Moreover, we could only record the $^{13}C\{H\}$ NMR spectrum of **H-LBTDTPP** at room temperature (Supporting Information, Figure S17). Therefore, the subsequent discussion is mainly focused on the stable **Me-LBTDTPP**.

Figure 1 depicts the ^1H NMR spectra of **C(O)-BTDTPP**, **Me-LBTDTPP**, and **H-LBTDTPP** in tetrachloroethane. Assignment of signals was supported by the NMR spectra of the corresponding monomers **BTDTP-Br** and **(O)P-BPin**, as well as by DEPT and HSQC NMR spectra of the polymers (see the Supporting Information). For the polyketone precursor (black spectrum), the multiplet at 7.91–7.60 ppm corresponds to the aromatic protons in the β-position with respect to the electron withdrawing keto functional groups. Reduction and ring closure results in disappearance of this signal (solid rectangle). After formation of the ladder-type polymers, the remaining aromatic protons are identified as a broadened[15] multiplet (Supporting Information, Figures S11 and S16). An additional signal at 2.16 ppm is observed in **Me-LBTDTPP** (red spectrum) corresponding to the methyl group introduced during reduction with MeLi (dashed rectangle). In comparison to **Me-LPPP**, the methyl groups are detected at similar chemical shifts ($\delta = 1.93$ ppm).[14] For the methylene bridge of **Me-LBTDTPP**, a carbon signal at 51.3–53.1 ppm is observed

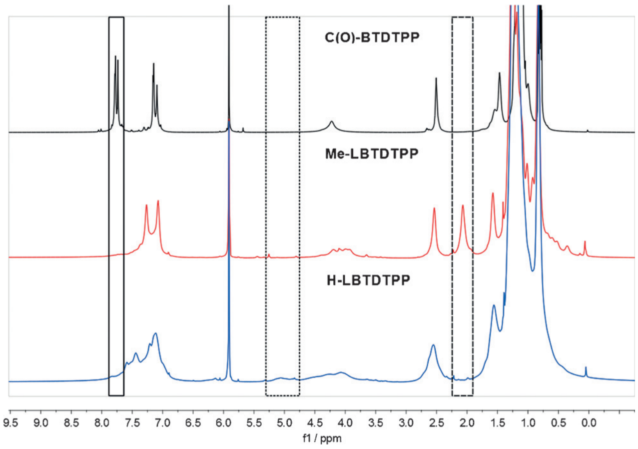

Figure 1. Comparison of ^1H NMR spectra in $C_2D_2Cl_4$: **C(O)-BTDTPP** (black), **Me-LBTDTPP** (red), and **H-LBTDTPP** (blue).

(Supporting Information, Figure S12). In comparison, for **Me-LPPP** this signal is found at 54.5 ppm.[14] An additional broad signal corresponding to the proton at the methylene bridge of **H-LBTDTPP** (blue spectrum) is observed around 5.0 ppm (dotted rectangle), which is in good agreement with **H-LPPP** ($\delta = 5.03$ ppm).[3] Additional small signals arise from end groups.

During post-polymerization reduction and ring closure, the expected changes in the optical spectra of the polymers are observed. For example, Figure 2a) depicts normalized absorption (filled symbols) and emission (blank symbols) spectra of **C(O)-BTDTPP**, **CMeOH-BTDTPP**, and **Me-LBTDTPP** in $CHCl_3$. After reduction with MeLi, the long wavelength absorption maximum blue shifts from 510 (——●——) to 372 nm (——▲——). The corresponding photoluminescence (PL) maximum is less blue-shifted, from 623 to 604 nm. After ring closure, the absorption maximum is distinctly red-shifted (——■——) with respect to both single-stranded precursors, with an absorption maximum peaking at 564 nm. This behavior is also observed in **LPPP**s and reflects the conversion of the twisted, single-stranded polyalcohol into the planar, double-stranded ladder polymer.[3,16] The absorption band of **Me-LBTDTPP** shows a well-resolved vibronic sideband at 538 nm. Such structured absorption bands are also observed for **LPPP**s.[17] The absorption feature around 380 nm is observed for all polymers and may be related to the heteroaromatic **BTDTP** building block. In the emission spectrum of **Me-LBTDTPP** in $CHCl_3$, the PL maximum is located at 665 nm (——□——) with an unexpectedly large Stokes shift of 101 nm. In comparison, **LPPP**s typically show very small Stokes shifts[17] (for **Me-LPPP** in $CHCl_3$, $\Delta\lambda_{Stokes} = 4$ nm; Supporting Information, Table S1). The color of the polymers (in $CHCl_3$) changes during conversion, from orange to yellow, and then to purple (Figure 2b). The corresponding optical spectra for **C(O)-BTDTPP**, **CHOH-BTDTPP**, and **H-LBTDTPP** are depicted in Figure S21 (Supporting Information).

As already mentioned, the Stokes shift between the absorption and emission maxima of **Me-LBTDTPP** in $CHCl_3$ seems very large compared to poly(*para*-phenylene) ladder polymers.[17,18] Additionally, the PL band is broad and does not show the mirror symmetry apparent in the optical spectra of **Me-LPPP**[17,18] (see Figure 3b). Since significant changes of the main chain geometry are impossible, it is expected that the large Stokes shift for **Me-LBTDTPP** in $CHCl_3$ results from the dipolar character of the ladder polymer main-chain. Therefore, we recorded absorption and emission spectra of **Me-LBTDTPP** in solvents of different polarity (Supporting Information, Table S1) and compared the results to **Me-LPPP**. Figure 3 depicts the optical spectra for four different solvents (toluene, tetrahydrofuran, chlorobenzene, and chloroform). In the case of **Me-LBTDTPP**, the absorption maxima are nearly identical for all solvents. In contrast, the PL maximum strongly red shifts with increasing solvent polarity. Additionally, the shape of the emission spectrum broadens and loses its vibrational structure. For low polarity

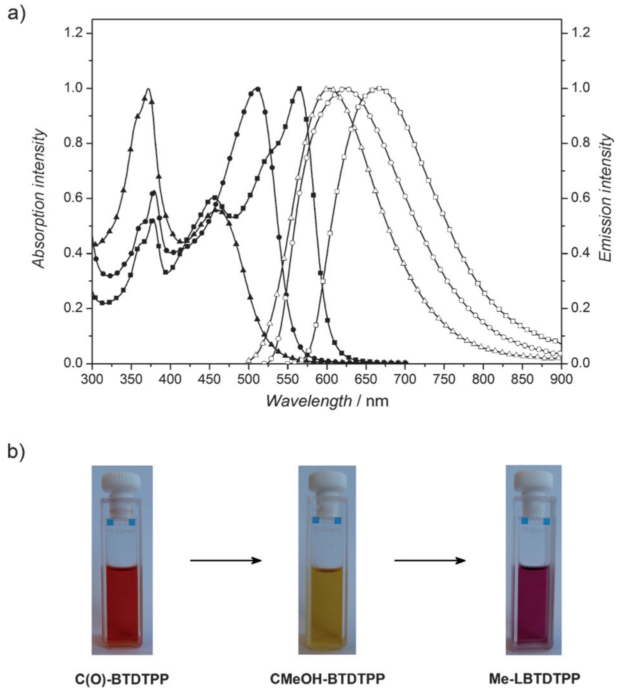

Figure 2. a) Normalized absorption (filled symbols) and emission (blank symbols) spectra of **C(O)-BTDTPP** (circles), **CMeOH-BTDTPP** (triangles) and **Me-LBTDTPP** (squares) in $CHCl_3$ ($\lambda_{exc.} = 500$ nm, 370 nm, and 540 nm, respectively); b) Color changes in $CHCl_3$.

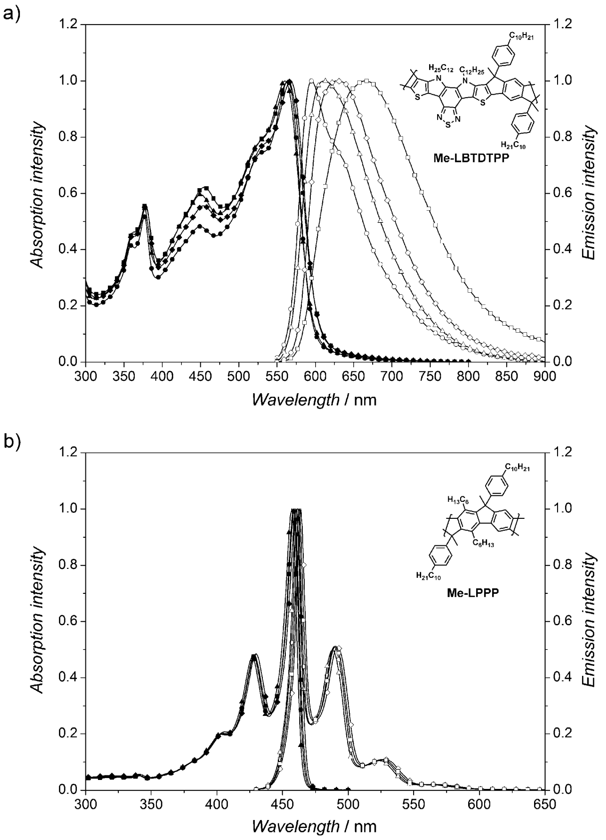

Figure 3. Normalized absorption (filled symbols) and emission spectra (blank symbols) of a) **Me-LBTDTPP** ($\lambda_{exc.} = 540$ nm) and b) **Me-LPPP** ($\lambda_{exc.} = 420$ nm) in different solvents: toluene (circles), tetrahydrofuran (triangles), chlorobenzene (rhombs), and chloroform (squares).

toluene, the PL maximum is observed at 595 nm, corresponding to a reduced Stokes shift of 31 nm if compared to chloroform ($\Delta\lambda_{\mathrm{Stokes}} = 101$ nm). Furthermore, the shapes of absorption and emission bands are nearly mirror-images. The feature, in toluene, compares well with the results for **Me-LPPP**, where the very small Stokes shift is related to the rigid geometry of the planar, non-polar polymer backbone.[3,16] However, the increased Stokes shift for **Me-LBTDTPP** (also in toluene) confirms the presence of a pronounced charge-transfer contribution in the excited state, as discussed for single-stranded donor–acceptor copolymers.[19] In contrast, **Me-LPPP** shows a negligible dependence of PL shape and position in response to solvent polarity (Figure 3b).

Figure 4 depicts the Stokes shift $\Delta\nu$ (in wavenumbers) of **Me-LBTDTPP** and **Me-LPPP** as a function of Reichard's solvent polarity parameters $E_T(30)$[20] for all solvents investigated. Following Pearson's correlation method,[21] a linear fit gives a good correlation for **Me-LBTDTPP** with r = 0.9522, in contrast to **Me-LPPP** with a correlation coefficient near zero. Bathochromic shifts of the PL maxima with increasing solvent polarity are termed positive solvatochromism.[20,22] The effect reflects an increase of the dipole moment during excitation of the molecule/polymer (π–π* transition). This indicates that the excited state is more polar than the ground state, and is thus better stabilized by increasing solvent polarity. Another way to describe solvent induced spectral shifts is the Lippert–Mataga formalism.[23] This theory describes the Stokes shift in terms of dipole moment changes during excitation as a function of dielectric constant and refractive index of the solvent (see the Supporting Information). The Lippert–Mataga plot depicts the Stokes shift as a function of the orientation polarizability of the solvent. Figure S22 (Supporting Information) shows the plots for **Me-LBTDTPP** and **Me-LPPP** with similar trends, as described for the solvent polarity parameters $E_T(30)$.

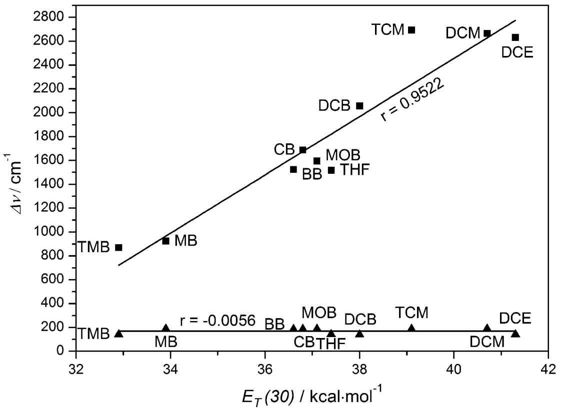

Figure 4. Stokes shift $\Delta\nu$ of **Me-LBTDTPP** (——■——) and **Me-LPPP** (——▲——) as a function of the solvent polarity parameter $E_T(30)$[20] for different solvents. The straight lines represent the linear fits (r = Pearson's correlation coefficient[21]). Solvent abbreviations: 1,2,3-trimethylbenzene (TMB), methylbenzene/toluene (MB), bromobenzene (BB), chlorobenzene (CB), methoxybenzene (MOB), tetrahydrofuran (THF), 1,2-dichlorobenzene (DCB), trichloromethane/chloroform (TCM), dichloromethane (DCM), 1,2-dichloroethane (DCE).

A comparison of absorption and emission spectra for **Me-LBTDTPP** in toluene, and in the solid state (Supporting Information, Figure S15), only shows a slight bathochromic shift of absorption and emission maxima (4 and 5 nm, respectively). In the solid state PL, the emission shoulder around 640 nm is more defined than that observed for the liquid phase, which is visible as a second emission band at 641 nm. The energies of the highest occupied molecular orbital (HOMO) of the polyketone precursor, as well as the D–A-type ladder polymers, were measured by atmospheric pressure photoelectron spectroscopy (AC2method). With the energy of the optical band gap determined from the onset of the UV/Vis absorption spectra in the solid state (see the Supporting Information), the corresponding energies of the lowest unoccupied molecular orbital (LUMO) were estimated. An optical band gap of 2.43 eV was determined for the polyketone precursor **C(O)-BTDTPP**, which is slightly larger than the band gaps for **Me-LBTDTPP** and **H-LBTDTPP** (both have a band gap of $E_g = 2.31$ eV). In comparison to the polyketone precursor (E_{HOMO} =-5.21 eV and E_{LUMO} =-2.78 eV), the HOMO and LUMO energies of the D–A-type ladder polymers are shifted to higher energies by 0.18 eV (HOMO) and 0.06 eV (LUMO).

In summary, the donor–acceptor-type backbone of an alternating copolymer was successfully embedded in a rigid ladder structure. The obtained ladder polymers, **Me-LBTDTPP** and **H-LBTDTPP**, show an increased Stokes shift when compared to related, non-polar phenylene-based ladder polymers (**Me-LPPP**), thus reflecting the occurrence of a charge-transfer-type electronic reorganization during excitation. The novel ladder polymers exhibit a positive solvatochromism with increasing solvent polarity. Future investigations will explore how these charge-transfer properties influence the charge transport behavior. This will be achieved by making direct comparisons with the well-known behavior of the non-polar counterpart **Me-LPPP** on a molecular and bulk level.

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Keywords: copolymerization · donor–acceptor systems · ladder polymers · solvatochromism · solvent effects

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