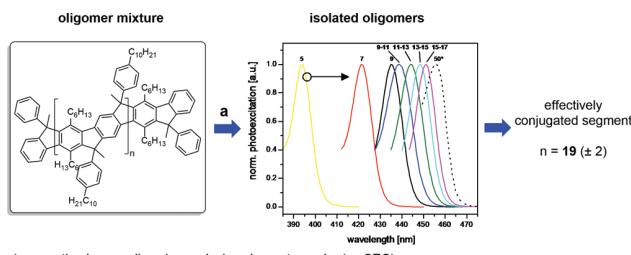


Reliably Estimating the Length of the Effectively Conjugated Segment in Ladder Poly(*para*-phenylene)s

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a) separation by recycling size exclusion chromatography (recSEC)

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Abstract In 1995 we extrapolated the so-called “effective conjugation length” in (*para*-phenylene) ladder polymers by relating the optical absorption energy to the reciprocal chain length of ladder-type oligo(*para*-phenylene)s, but only based on three short-chain oligomers (a trimer, a pentamer, and a heptamer). The resulting value of 11–12 benzene rings was distinctly lower than the numbers reported for corresponding single-stranded, soluble poly(*para*-phenylene)s. Here, we report a series of elongated (*para*-phenylene)-type ladder oligomers that were isolated via repeated recycling size exclusion chromatography steps from an oligomer mixture. Now we are able to extrapolate the length of the “effectively conjugated segment” with much more precision to be 19 ± 2 benzene rings.

Key words ladder, poly(*para*-phenylene)s, effectively conjugated segment, SEC

Introduction

In 1995 we reported an extrapolation of the optical absorption energy versus the reciprocal chain length of ladder-type oligo(*para*-phenylene)s for an estimation of the so-called “effective conjugation length” in the corresponding (*para*-phenylene) ladder polymers (**LPPP**).¹ At this time the extrapolation was based on only three data points, namely the data for a trimer (an indenofluorene derivative), a pentamer, and a heptamer.² The length of the “effectively conjugated segment” of the corresponding **LPPP** polymer was estimated to be ca. 11–12 benzene rings.^{1,3} This value was distinctly different from the numbers reported for the corresponding single-stranded, soluble poly(*para*-phenylene)s such as

poly(2,7-fluorene)s (ca. 20–24 benzene rings)^{4,5} or poly(2,7-tetrahydropyrene)s (ca. 19–20 benzene rings).¹ At this time, we speculated on the reason for the distinctly decreased length of the “effectively conjugated segment” in the case of our double-stranded ladder **LPPPs**.

Results and Discussion

In this study, we isolated a series of elongated (*para*-phenylene)-type ladder oligomers via a three-step synthesis of an oligomeric mixture by co-reacting bi- and monofunctional monomers, followed by a subsequent oligomer separation procedure including repeated recycling size exclusion chromatography (recSEC) steps. Hereby, we could isolate pentamer (5-mer), heptamer (7-mer), and 9-mer as well as 9–11-mer, 11–13-mer, 13–15-mer, and 15–17-mer mixtures; the first three with two monofunctional endcaps, the last four as mixtures with 0, 1, or 2 monofunctional endcaps and 2, 1, or 0 deborylated terminals. Based on this extended oligomer series, we are now able to extrapolate the length of the “effectively conjugated segment” with much more precision. By correlating the 0–0 optical transition peaks with the reciprocal chain length, a linear dependency can be assumed for longer chain oligomers. An extrapolation towards the polymer value gives the approximated length of the “effectively conjugated segment” [Figure 1, left: absorption energies, derived from the photoluminescence (PL) excitation (PE) spectra; right: PL energies of the respective 0–0 optical transition peaks; the dashed lines are the corresponding values for the peak absorption and PL energies of the polymer **MeLPPP**]. Please note that the first two data points on the right-hand side plot correspond to the pentamer and heptamer model compounds that have been used in our initial extrapolation in the 1995 study. It is obvious that these two data points do not fit to the linear E_n versus $1/n$ dependency observed for the longer oligomers, most probably due to fringe-group effects. The extended data set now results in a distinctly increased length of the “effectively conjugated segment” for **LPPP**-type ladder polymers of ca.

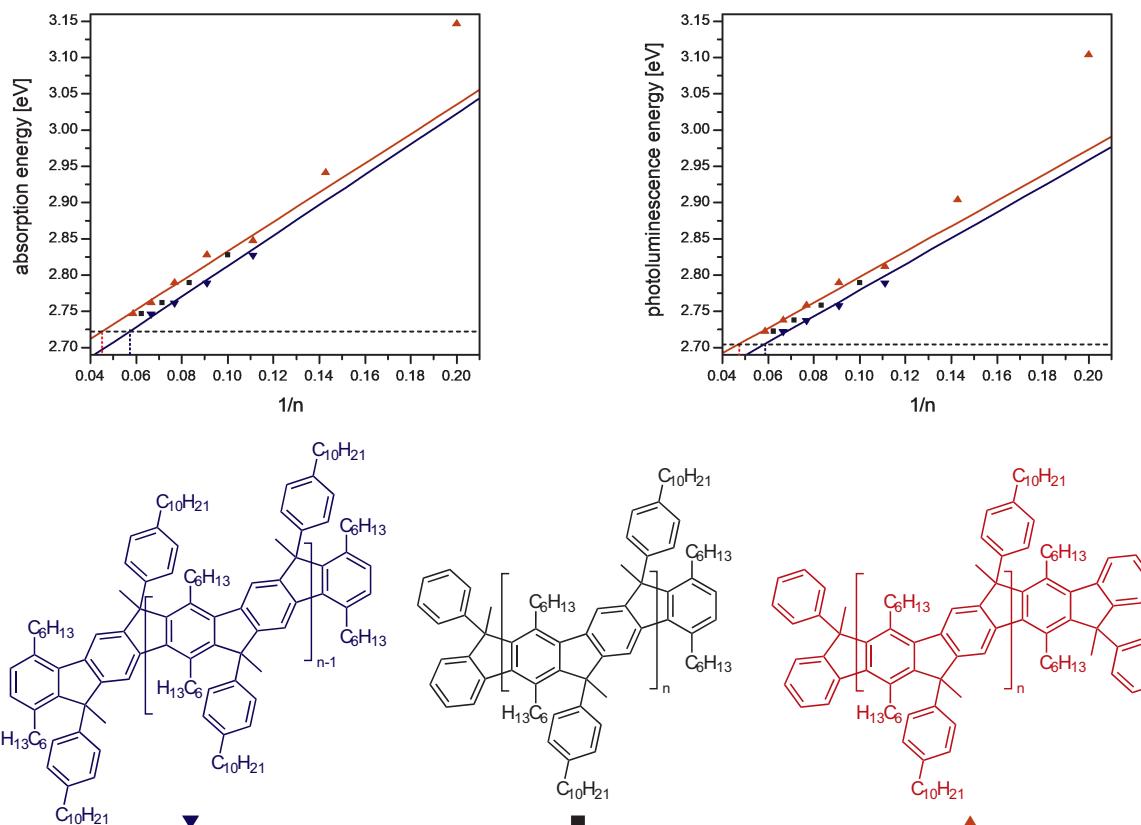


Figure 1 Plot of absorption and photoluminescence (PL) peak energies E_n vs. the reciprocal chain length for ladder-type oligo(*para*-phenylene)s [n : number of benzene rings; left: absorption energies derived from the PL excitation (PE) spectra; right: PL energies of the respective 0–0 transitions; the dashed lines are the values for the 0–0 peak energies of absorption and PL of the corresponding ladder polymer **MeLPPP**], the chemical structures of the di- (up-pointing triangles), mono- (squares) and not-endcapped oligomers (down-pointing triangles).

19 ± 2 benzene rings, in full agreement with the numbers reported for related single-stranded (*para*-phenylene)-type polymers such as poly(2,7-fluorene)s and poly(2,7-tetrahydropyrene).^{1,4}

There is no or only a negligible influence of the fixation of the poly(*para*-phenylene) backbone into the ladderized framework on the length of the “effectively conjugated segment,” which is estimated consistently to be 19–24 benzene rings for the examples discussed here of single- or double-stranded, soluble poly(*para*-phenylene)s as an important class of π -conjugated polymers.

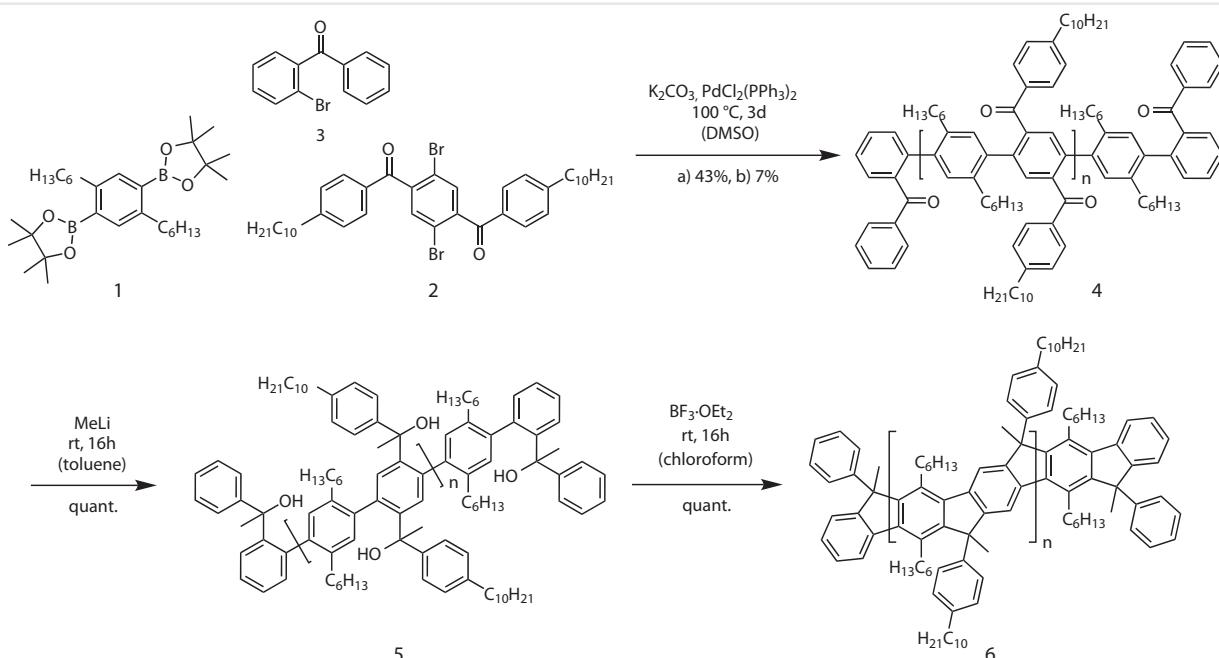
The linear absorption or emission energy E_n versus $1/n$ relation that is used here for fitting the experimental data is, of course, a simplification of a more complex mathematical and physical context.^{6–10} However, since the saturation point of the fit is known (the absorption or emission energy values $E_{\infty, \text{PE}}$ and $E_{\infty, \text{PL}}$ of the corresponding, well-characterized polymer **MeLPPP**), the main difference in certain equations under use concerns the transition region between virtually linear E_n versus $1/n$ behavior and saturation (which means the

asymptotic region of the fit).^{6–10} In our report we use the crossing point between the linear E_n versus $1/n$ branch of the oligomer data and the polymer energies $E_{\infty, \text{PE}}$ and $E_{\infty, \text{PL}}$ for determining the value of the effectively conjugated segment, hereby, of course, not considering the asymptotic convergence of the energy values in the transition region.

Oligomer Separation

In this study, a postsynthetic separation process of an oligomer mixture by recSEC was used to isolate oligomer mixtures of different chain lengths. Compared to a regular SEC, recSEC can achieve a far better resolution by accomplishing a cycling of the solution through a set of SEC columns via increasing the peak separation distance.

First, bi- and monofunctional monomers were co-reacted in a three-step synthetic sequence (Scheme 1) for the generation of an oligomeric product mixture. **4**, **5**, and **6** were prepared as described in the literature with slight



Scheme 1 Synthetic pathway to (para-phenylene) ladder oligomers [quant. = nearly quantitative yield, (a) chloroform fraction and (b) acetone fraction].

improvements.^{11,12} Detailed synthetic procedures for the monomers **1** and **2** are given in the Supporting Information. The stoichiometric composition of the monomer mixture is given by **Equation 1**. The reactivities of the monofunctional endcapper **3** and the difunctional diketone monomer **2** are assumed to be similar. A decreasing amount of endcapper ($a \rightarrow 0$) causes an increase of the average molar mass of the product (also for the acetone and chloroform fractions investigated here).

$$B + (1 - a)K + 2aE$$

Equation 1: Stoichiometric composition of the monomer mixture, with B = equivalent of difunctional borylated monomer **1**, K = equivalent of difunctional diketone monomer **2**, E = equivalent of monofunctional endcapper **3**, $0 < a < 1$.

In the Suzuki-type coupling reaction, the use of DMSO as a solvent and 5 equivalents of base at 100 °C appeared best suited for obtaining high oligomer yields compared to THF/water (4/1) as the solvent and 10 equivalents of base at 75 °C. The most efficient conditions are described in the Experimental Section.

After postpolymerization modification of the oligomer mixture **4** into the ladder-type oligomer targets **6**, the product mixture was separated by repeated recSEC steps. The use of THF as an eluent (flow rate: 5 mL/min) at 25 °C and an application of 150 mg oligomer mixture per run (injection volume: 1.5 mL; sample concentration: 100 mg/mL) seemed best suited as efficient compromise

between separation time and resolution. The separation process of the acetone fraction is shown in Figure 2a and uses seven separation cycles of the recSEC procedure. A separation cycle consists of passing all (3) SEC columns and re-application on the first column. According to this method, the monodisperse pentamer (5-mer), heptamer (7-mer), and nonamer (9-mer) could be isolated. Due to absence of a complete baseline separation, only material near the peak maxima was collected. Longer elution times increased the resolution only in a minor way. Because of smaller differences in the elution time for longer oligomers due to the decreasing mass difference, their separation was accomplished in two steps (Figure 2b–d). First, two “crude fractions” were isolated from the chloroform fraction according to a “short” procedure involving only two separation cycles. In a subsequent separation step with 16–18 cycles the 9–11-mer, 11–13-mer, 13–15-mer, and 15–17-mer oligomer mixtures could be isolated.

All oligomers were purified in a final SEC-separation step (to remove residues of other oligomers) and precipitated into cold methanol. The longer oligomers (9–11-mer, 11–13-mer, 13–15-mer, and 15–17-mer) were isolated as three-compound mixtures containing oligomers with 0, 1, and 2 endcaps due to an ongoing deborylation during the Suzuki-type coupling. However, a very low polydispersity of ≤ 1.01 could be achieved. As the molar ratio of the three respective compounds is ca. 1:1:1, the average numbers of

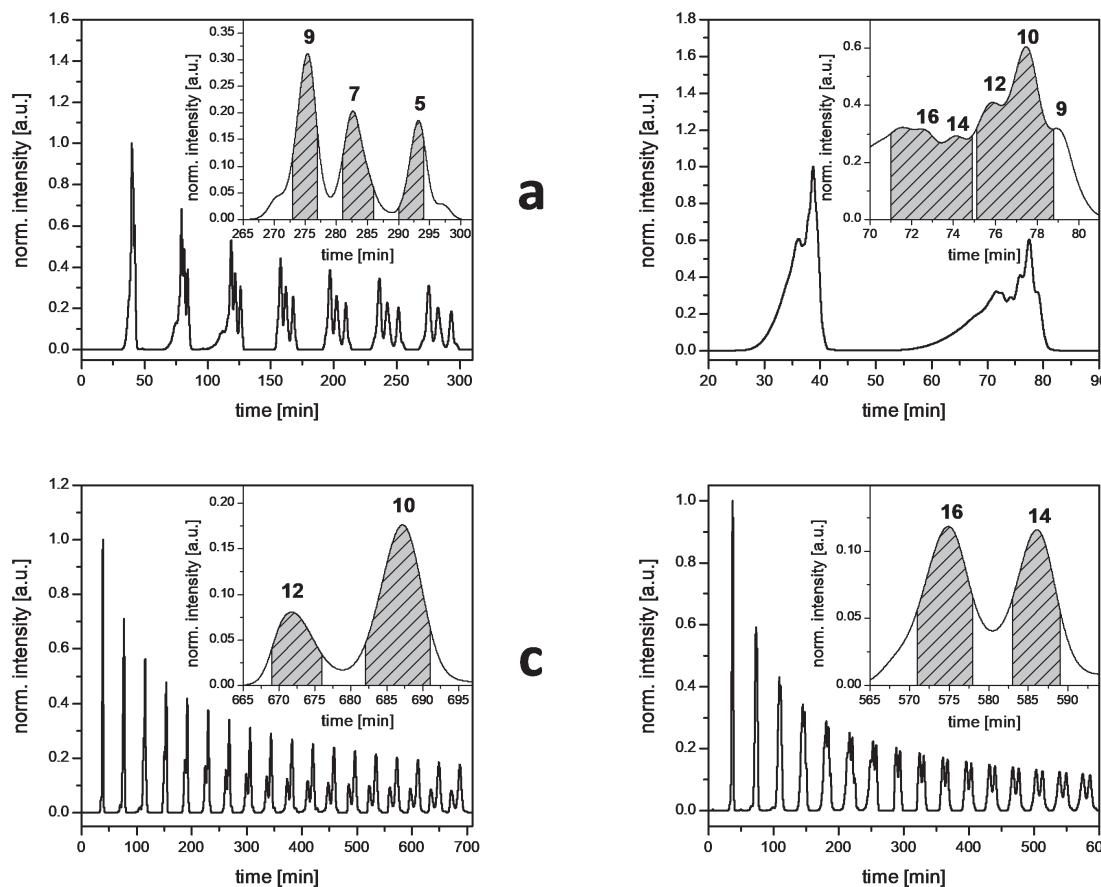


Figure 2 SEC elograms of the oligomer separations for (a) the acetone fraction, (b) the crude chloroform fraction, and (c and d) the isolated fractions of the chloroform fraction after the first separation step. The insets show the collected areas highlighted in grey in the last separation cycle and the (average) number of benzene rings.

Table 1 Peak maxima of 0–0 transition in relation to the number of benzene rings in the oligomer backbone

n	UV/vis [nm]	PE ^c [nm]	PL ^d [nm]
5	395	394	400
7	423	422	427
9	437	436	441
9–11 ^a	439	438	444
11–13 ^a	445	444	450
13–15 ^a	449	448	453
15–17 ^a	452	451	456
50 ^b	456	456	458

^aThree-component mixture (PDI < 1.01).

^bAverage value for several polymer fractions ($M_n \approx 19000$ g/mol, PDI < 1.3).

^cPhotoluminescence excitation (PE).

^dPhotoluminescence.

benzene rings are assumed to correspond to the respective oligomers with one endcap.

The 0–0 optical transition peak energies of the obtained oligomers are listed in Table 1. For increased precision, the PE spectra, which were recorded on the same instrument as the PL spectra, were used for extracting the absorption data instead of the UV/vis absorption spectra.

As shown in Figure 3 (top: PE, bottom: PL), a bathochromic shift with an increasing number of benzene rings can be observed with the peak energies converging to a limit (the polymer value).

Conclusions

Our results for an extended series of elongated (*para*-phenylene) ladder oligomers precisely define the length of the so-called effectively conjugated segment (19 ± 2

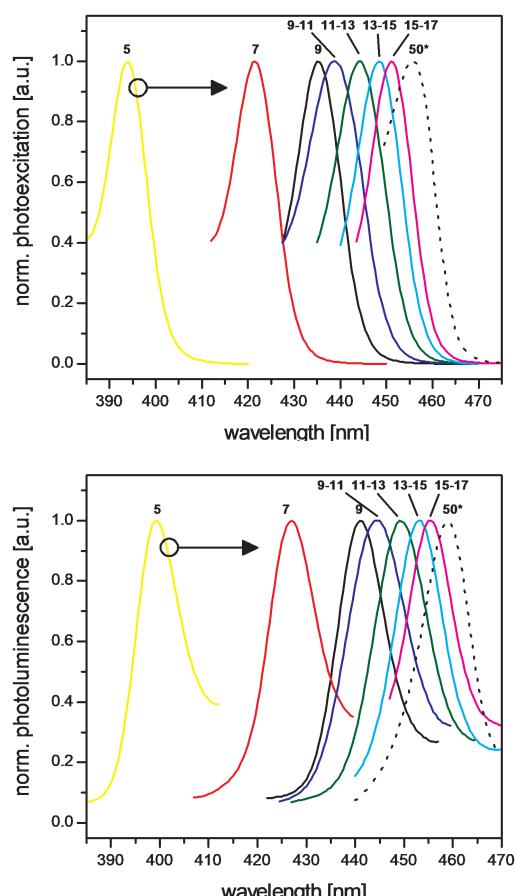


Figure 3 Maxima of 0–0 photoluminescence excitation (top) and photoluminescence (bottom) peaks related to the (average) number of benzene rings in the oligomer backbone. *Polymer value.

benzene rings) in corresponding poly(*para*-phenylene) ladder polymers, as an important, prototypical class of conjugated polymers. The new results allow extracting a conclusive picture on the convergence of the electronic properties in oligo-/polyphenylene-type materials when increasing the chain length.

Experimental Section

General Methods

All chemicals and solvents were purchased from commercial suppliers and used without further purification; 2-bromobenzophenone (CAS: 13047-06-8) was purchased from TCI Deutschland GmbH. Unless otherwise indicated, all reactions were carried out under an argon atmosphere in dry solvents. All oligomers and polymers were dried under

high vacuum. For the synthetic procedures, the listed concentrations are based on the molar mass of the repeat unit. Optical measurements as well as size exclusion chromatography were performed with HPLC grade solvents.

Instruments

For analytical size exclusion chromatography, an Agilent SECurity SEC system equipped with a diode array detector (ALS G1329A) and a refraction index detector (G1362A) was used. A pair of SEC columns (PSS Linear S SDV, 5 µm particle size, 8 × 300 mm), a guard column (PSS SDV guard column, 5 µm particle size, 8 × 50 mm), and THF as eluent (flow rate: 1 mL/min) at room temperature were used. A polystyrene calibration and BHT as an internal standard were used to determine the molecular-weight distribution. The recycling size exclusion chromatography was accomplished on a Shimadzu LC system equipped with a 20AD pump and an SPD-20AV UV detector (detection at 254 and 370 nm). A set of three SEC columns (PSS Linear S SDV, 5 µm particle size, 20 × 300 mm), a guard column (PSS SDV guard column, 5 µm particle size, 20 × 50 mm), and THF as an eluent (flow rate: 5 mL/min) at room temperature were used. IR spectra were recorded on a JASCO FT/IR-4200 spectrometer equipped with a Specac ATR unit. The relative peak intensities are described as s (strong), m (medium), w (weak), and br (broad). Mass spectrometry analysis was carried out on a JEOL AccuTOF-GCx in the case of field desorption ionization or on a Bruker-Reflex-TOF at the Max Planck Institute for Polymer Research in Mainz in the case of matrix-assisted laser desorption/ionization. NMR spectra were recorded either on a Bruker Avance III 600 or an Avance 400 spectrometer at 300 K using the indicated deuterated solvent as reference. Coupling constants are stated in Hz, and the multiplicity of the signals is described by s (singlet), d (doublet), t (triplet), and m (multiplet). For oligomers the stated integrals correspond to the average oligomer species. PL and PE measurements were realized on a Horiba FluoroMax-4 spectrometer. UV/vis spectra were measured on a JASCO V-670 spectrometer. All optical measurements were carried out in chloroform as the solvent at room temperature. The main (global) PL and PE maxima are given in italic letters.

General Procedure for the Synthesis of the Benzoyl-Substituted Oligo Phenylene Mixture 4

The monomers **1** (1.0 equiv.), **2** (0.9 equiv.), the endcapper 2-bromobenzophenone (0.2 equiv.) as well as potassium carbonate (5.0 equiv.) and bis(triphenylphosphine)palladium (II) chloride (5 mol%) were stirred at 100 °C in DMSO (80 mmol/L) for 3 days under light exclusion. After addition

of water the reaction mixture was extracted with chloroform and washed with water and saturated aqueous EDTA solution. The combined organic layers were dried over magnesium sulphate, and the solvent was removed in vacuo. After precipitation into cold methanol and purification by Soxhlet extraction (methanol, acetone, and chloroform), the polyketone **4** was obtained as colorless solid (yield: 43% chloroform fraction, 7% acetone fraction).

Chloroform fraction: IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 2953 (m), 2922 (s), 2852 (s), 1665 (s), 1605 (s), 1570 (w). ¹H NMR (600 MHz, C₂D₂Cl₄) δ [ppm] = 7.83–6.52 (m, 32H), 2.76–1.97 (m, 12H), 1.83–1.35 (m, 12H), 1.35–0.87 (m, 52H), 0.87–0.58 (m, 18H). ¹³C NMR (151 MHz, C₂D₂Cl₄) δ [ppm] = 197.3, 196.7, 149.4, 149.0, 146.9, 140.9, 140.7, 140.4, 139.2, 139.1, 139.0, 139.0, 138.9, 137.8, 137.6, 137.3, 135.5, 135.4, 131.0, 130.8, 130.7, 130.6, 130.5, 130.4, 129.9, 128.6, 128.4, 36.3, 36.2, 35.6, 33.3, 33.0, 32.2, 32.0, 31.3, 31.0, 29.9, 29.9, 29.7, 29.7, 29.6, 23.0, 22.9, 14.5, 14.5. UV/vis (CHCl₃): $\lambda_{\text{max.}}$ [nm] = 265. SEC (THF): M_n [g/mol] = 5100, M_w [g/mol] = 6300, M_p [g/mol] = 4100, polydispersity index (PDI) = 1.24.

Acetone fraction: UV/vis (CHCl₃): $\lambda_{\text{max.}}$ [nm] = 265. SEC (THF): M_n [g/mol] = 2500, M_w [g/mol] = 2900, M_p [g/mol] = 3200, PDI = 1.14.

General Procedure for the Conversion of the Oligomer Mixture **4** into the Oligomer Mixture **5**

4 was dissolved in toluene (4 mmol/L), and an excess of methyl lithium (20 equiv.) was added slowly at 0 °C under light exclusion. The reaction mixture was stirred overnight at room temperature and then ethanol, water, and 2 M hydrochloric acid were added. After the extraction with chloroform the combined organic layers were washed with water and brine, dried over magnesium sulphate, and the solvent was removed in vacuo. **5** was obtained as a colorless solid in nearly quantitative yield.

Chloroform fraction: IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 3548 (br, w), 2952 (m), 2921 (s), 2853 (s), 1507 (w). ¹H NMR (600 MHz, C₂D₂Cl₄) δ [ppm] = 7.79–6.65 (m, 32H), 2.73–2.32 (m, 12H), 2.32–1.90 (m, 12H), 1.90–1.44 (m, 12H), 1.44–0.94 (m, 52H), 0.94–0.67 (m, 18H). ¹³C NMR (151 MHz, C₂D₂Cl₄) δ [ppm] = 147.9, 145.4, 142.9, 141.1, 138.0, 131.0, 128.1, 126.6, 125.8, 125.3, 77.5, 35.9, 33.6, 32.9, 32.2, 32.1, 31.9, 31.8, 31.2, 30.0, 29.9, 29.64, 23.0, 14.5. UV/vis (CHCl₃): $\lambda_{\text{max.}}$ [nm] = 242.

PL(CHCl₃, $\lambda_{\text{exc.}}$ [nm] = 242): $\lambda_{\text{max.}}$ [nm] = 326. SEC (THF): M_n [g/mol] = 5200, M_w [g/mol] = 6700, M_p [g/mol] = 4000, PDI = 1.29.

Acetone fraction: UV/vis (CHCl₃): $\lambda_{\text{max.}}$ [nm] = 242. PL (CHCl₃, $\lambda_{\text{exc.}}$ [nm] = 242): $\lambda_{\text{max.}}$ [nm] = 321. SEC (THF): M_n [g/mol] = 2700, M_w [g/mol] = 3000, M_p [g/mol] = 3100, PDI = 1.14.

General Procedure for the Cyclization of **5** into Ladder-Type Oligomers **6**

To a solution (1 mmol/L) of **5** in chloroform, an excess of boron trifluoride diethyl etherate (30 equiv.) was added. The reaction was stirred overnight under light exclusion and then quenched with ethanol. The reaction mixture was concentrated in vacuo and then washed with water and brine. Subsequently, the organic phase was dried over magnesium sulphate, and the solvent was removed in vacuo to obtain the product mixture **6** as a yellow solid in nearly quantitative yield.

Chloroform fraction: IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 2953 (m), 2922 (s), 2853 (s), 1648 (w, br), 1510 (w). ¹H NMR (600 MHz, C₂D₂Cl₄) δ [ppm] = 7.65–6.22 (m, 28H), 3.02–2.09 (m, 12H), 2.08–1.58 (m, 12H), 1.58–1.37 (m, 12H), 1.37–0.99 (m, 52H), 0.99–0.68 (m, 18H). ¹³C NMR (151 MHz, C₂D₂Cl₄) δ [ppm] = 152.6, 143.1, 140.6, 138.2, 132.4, 128.4, 126.7, 54.2, 35.8, 32.2, 32.0, 31.9, 31.6, 31.5, 31.3, 30.5, 29.9, 29.7, 29.6, 25.7, 23.3, 23.1, 23.0, 22.9, 14.6, 14.5. UV/vis (CHCl₃): $\lambda_{\text{max.}}$ [nm] = 242, 420, 442. PL (CHCl₃, $\lambda_{\text{exc.}}$ [nm] = 442): $\lambda_{\text{max.}}$ [nm] = 454, 482. SEC (THF): M_n [g/mol] = 6000, M_w [g/mol] = 8500, M_p [g/mol] = 3900, PDI = 1.43.

Acetone fraction: UV/vis (CHCl₃): $\lambda_{\text{max.}}$ [nm] = 242, 379, 399, 424. PL (CHCl₃, $\lambda_{\text{exc.}}$ [nm] = 424): $\lambda_{\text{max.}}$ [nm] = 429, 456. SEC (THF): M_n [g/mol] = 2700, M_w [g/mol] = 3400, M_p [g/mol] = 3000, PDI = 1.25.

Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0040-1710348>.

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