Thiophene–Phenylene/Naphthalene-Based Step-Ladder Copolymers

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ABSTRACT: A series of step-ladder copolymers based on thiophene–phenylene–thiophene **SL1**-**SL3** and thiophene–naphthylene–thiophene **SL4** repeat units with varying lengths of the oligothiophene segment has been designed and synthesized via a microwave-assisted Stille-type cross-coupling reaction followed by a polymer-analogous cyclization reaction. The optical properties of the step-ladder copolymers have been investigated in detail, in particular at low temperature and in the solid-state. © 2008 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 46: 7342–7353, 2008
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INTRODUCTION

Phenylene- and thiophene-based materials belong to the most extensively studied classes of conjugated molecules for use in organic electronic devices such as light-emitting diodes,[1,2] polymer lasers,[3] field-effect transistors,[4] and polymer solar cells[5,6] Unsubstituted oligomers of a certain length are generally completely insoluble in organic solvents and require vacuum deposition. However, for large area devices, solution-processable materials are needed.[7] The introduction of solubilizing side-chains can significantly increase the solubility, and therefore the processability, but may also induce steric hindrance resulting in a mutual distortion of the building blocks of the single-stranded molecules. This distortion often reduces the π-conjugation along the backbone and changes the optical and electronic properties of the polymer. To overcome or at least minimize the problem of reduced π-interactions much effort was devoted to rigidify the backbone partially or completely by the introduction of additional inter-ring bridges, which may furthermore bear the necessary solubilizing side-chains.[8] Because a soluble ladder-type poly(*para*-phenylene) (LPPP) was described in 1991 by Scherf and Müllen[9] much effort has been devoted to the tuning of the polymers properties and processability. Various types of bridges have been realized. For example, in addition to the original methylene bridges, ethane, or carbonyl bridges have been described as well as heteroatom bridges containing nitrogen or sulfur atoms, respectively.[10–24]

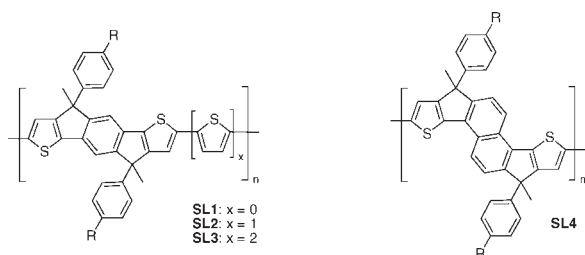Within this contribution the synthesis of a series of novel, partly rigidified, thiophene–

Figure 1. Structure of thiophene–thiophene (**SL1**-**SL3**) and thiophene–naphthylene–thiophene (**SL4**)-based step-ladder polymers

phenylene–thiophene, and thiophene–naphthylene–thiophene-based step-ladder copolymers is described. These alternating copolymers contain a central ladder-type building block that was synthesized in a ring closure reaction similar to the LPPP synthesis that was combined with oligothiophene segments of different length (Fig. 1).

THIOPHENE–PHENYLENE–THIOPHENE AND THIOPHENE–NAPHTHYLENE–THIOPHENE STEP LADDER COPOLYMERS—RESULTS AND DISCUSSION

The polymeric intermediates toward the desired step-ladder copolymers **SL1** and **SL2**, the polyke-

tones **PK1** and **PK2**, as shown in Scheme 1, were synthesized in a microwave-assisted Stille-type cross-coupling reaction from the terephthalophenone monomer **1** and the corresponding bis(trimethyl)stannyl oligothiophenes utilizing PdCl$_2$(dppf) as catalyst.[24,25] The resulting single-stranded polyketones **PK1** and **PK2** were purified by Soxhlet extraction with ethanol to remove low molecular weight fractions and yielded the polyketones in 44 and 47% yield, respectively. The next synthetic step was a polymer-analogous transformation of the keto groups into tertiary alcohols by reaction with lithium organyls (here: methyl lithium).[26] The progress of the conversion was monitored by IR-spectroscopy via the disappearance of the carbonyl band. The final Friedel–Crafts-type ring closure was achieved by addition of an excess of BF$_3$·Et$_2$O to a solution of the polyalcohol in dichloromethane.[27] This ring closure sequence allows for the introduction of a broad variety of substituents ranging from alkyl to alkylphenyl side groups via addition of different lithium organyls. To remove low molecular weight fractions all step-ladder polymers were again extracted with ethanol and subsequently precipitated into methanol to afford the step-ladder copolymers **SL1** and **SL2** in yields of 76 and 71%, respectively. The polymers were soluble in many
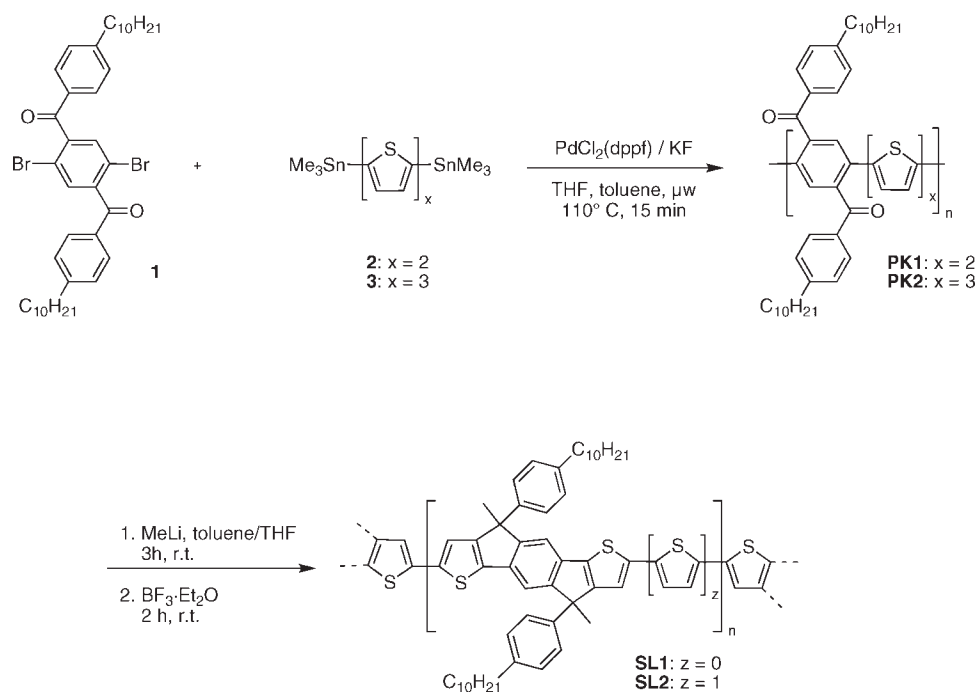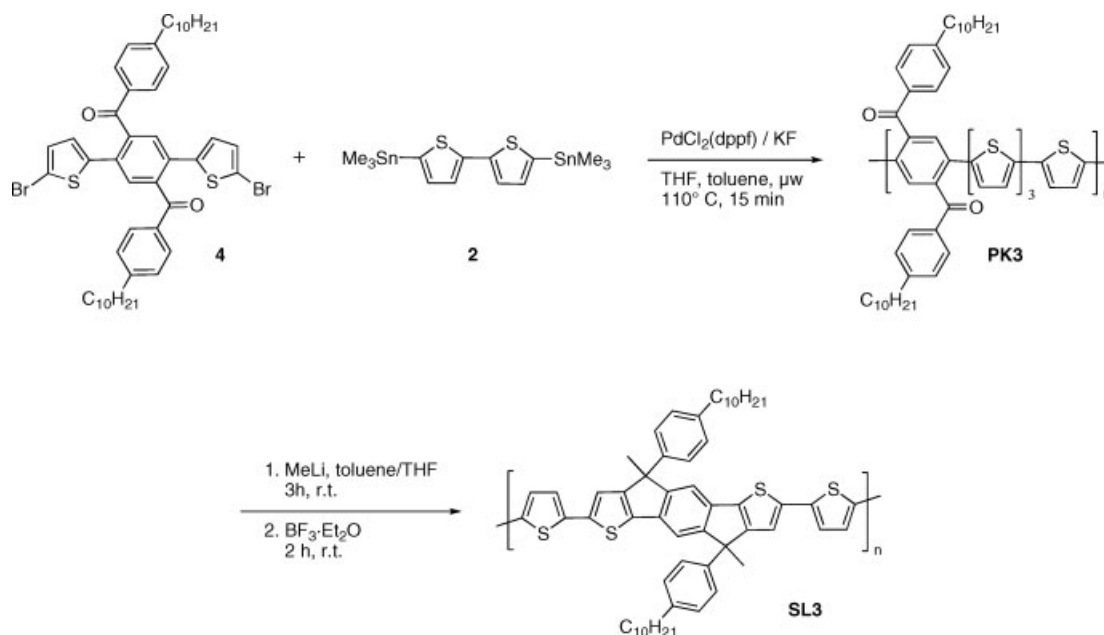

Scheme 1. Synthesis of the step-ladder copolymers **SL1** and **SL2** in a microwave-assisted Stille-type cross-coupling reaction and subsequent polymer-analogous cyclization.

Table 1. Yields and Molecular Weights of the Polyketones **PK1**, **PK2**, **PK3**, and **PK4** and Step-Ladder-Type Copolymers **SL1**, **SL2**, **SL3**, and **SL4** (GPC Analyses Performed on Solutions of the Copolymers in THF with PS Calibration)

Polymer	Yield [%]	M_n (g/mol)	M_w (g/mol)	PD
PK1	44	10,400	29,000	2.8
PK2	47	14,800	53,100	3.6
PK3	52	12,600	40,200	3.2
PK4	49	12,800	30,900	2.4
SL1	76	12,000	24,000	2.0
SL2	71	16,200	47,000	2.9
SL3	72	14,200	44,000	3.1
SL4	82	13,500	28,400	2.1

organic solvents like toluene, chloroform or dichloromethane thus allowing a full spectroscopic characterization. GPC analysis revealed M_n values of 12,000 g/mol (PD = 2.0) and 16,200 g/mol (PD = 2.9) for copolymers **SL1** and **SL2**, respectively (Table 1). The copolymers were fully characterized by ^{1}H/^{13}C-NMR spectroscopy. In the ^{13}C-NMR spectrum of the polyketone precursor **PK1** the carbon resonance of the carbonyl group was observed at ∂ = 196.7 ppm. Upon cyclization to **SL1**, the disappearance of the keto resonance and the appearance of a signal at ∂ = 53.2 ppm assigned to the newly formed quarternary carbon of the methylene bridge proved the complete for-

mation of the step-ladder structure. Similar features could be observed for the copolymers **PK2**/**SL2** with corresponding carbon signals at ∂ = 194.2 ppm (**PK2**) and ∂ = 54.1 ppm (**SL2**), respectively. Because of the very low solubility of unsubstituted 2,2′:5′,2″:5″,2‴-quaterthiophene, generation of the appropriate distannylated derivative was unfeasible. Therefore, an alternate synthetic route towards the step-ladder copolymer bearing four thiophene rings per repeat unit was established. The synthesis of monomer **4** started from the terephthalophenone monomer **1**, which was reacted with 2-(tributyl)stannyl thiophene following a microwave-assisted Stille-type coupling protocol as described previously.[28] Bromination of the monomer with NBS gave the dibromo monomer **4**,[29] which was copolymerized with bis(trimethyl)stannyl bithiophene **2** to the corresponding polyketone **PK3**. Reduction and cyclization with (i) methyl lithium and (ii) BF$_3$·Et$_2$O, respectively, as described before yielded the step-ladder copolymer **SL3** (Scheme 2).[27] After Soxhlet extraction with ethanol, a GPC analysis revealed an M_n of 14,200 g/mol (PD = 3.1) for the copolymer **SL3**. The copolymer was further characterized by ^{1}H/^{13}C-NMR spectroscopy. For the synthesis of the thiophene–naphthylene–thiophene step ladder copolymer **SL4** the naphthylene-based diketo monomer **5**[30] was coupled with the distannylated bithiophene monomer **2** in a similar

Scheme 2. Synthesis of the step-ladder copolymer **SL3** in a microwave-assisted Stille-type cross-coupling reaction and subsequent polymer-analogous cyclization.
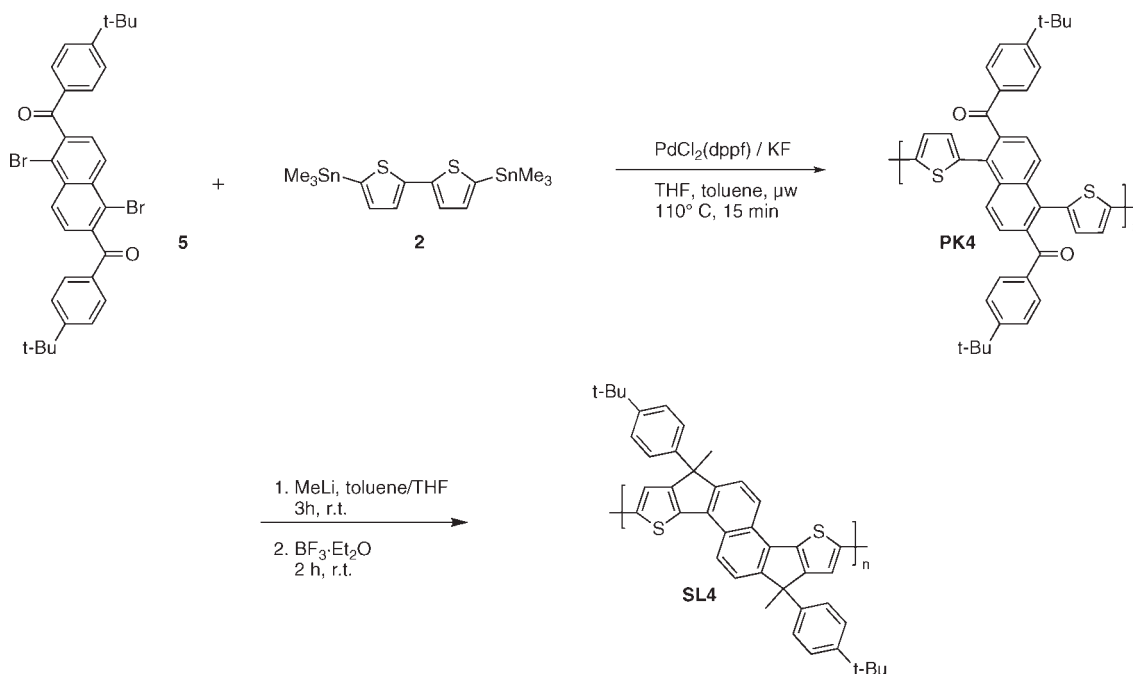
Scheme 3. Synthesis of step-ladder copolymer **SL4** in a microwave-assisted Stille-type cross-coupling reaction and subsequent polymer-analogous cyclization.

microwave-assisted Stille-type cross-coupling reaction (Scheme 3).[24,25] The reaction yielded the single-stranded precursor polymer **PK4**, which was purified by Soxhlet extraction with ethanol to remove low molecular weight fractions (yield: 49% after precipitation into methanol). Subsequently, the polyketone was applied to the already described polymer-analogous reaction sequence including (1) reduction with methyl lithium and (2) Friedel–Crafts-type ring-closure with an excess of $BF_3(Et_2O)$ in dichloromethane.[27] Again, the progress of the transformation was monitored by IR and NMR spectroscopy. After a final purification of the step-ladder copolymer **SL4** by Soxhlet extraction with ethanol and reprecipitation from chloroform into methanol the copolymer **SL4** was afforded in a yield of 82%. An M_n of 13,500 g/mol (PD = 2.1) was confirmed by GPC analysis and the polymer further characterized by ^1H and ^{13}C-NMR spectroscopy.

The UV–vis absorption spectra of the copolymers **SL1**, **SL2** and **SL3** in dilute toluene solution at room temperature are shown in Figure 2 and summarized in Table 2. The UV–vis spectrum of **SL1** shows a long wavelength absorption band peaking at 480 nm with a shoulder at 523 nm and a steep absorption edge, consistent with the presence of a weakly distorted backbone structure. The incorporation of additional thiophene rings

between the step-ladder subunits leads to a 25 nm red-shift of the absorption maximum for **SL2** and a 28 nm red-shift for **SL3**, respectively. The bathochromic shift in **SL2** when compared to copolymer **SL1** reflects the lower band gap energy of (poly)thiophenes in comparison to (poly)phenylenes. However, a further increase of the length of the oligothiophene segment (when going from **SL2** to **SL3**) causes only a minor additional change of the absorption characteristics. The room temperature photoluminescence (PL) emission spectra of the novel step-ladder copolymers again exhibit the highest energy PL for copolymer **SL1**, with a maximum at 562 nm and a vibronic side-band at 600 nm. The copolymers **SL2** and **SL3** show a slight red-shift of the PL maxima (7 and 9 nm, respectively) and slightly better resolved vibronic side-bands. As already discussed for the absorption spectra, also the PL spectra of the two copolymers with the elongated oligothiophene segments do not show significant differences. Therefore, it is expected that a further elongation of the oligothiophene segments will not lead to significant changes of the optical spectra. Upon lowering the temperature to 77 K the absorption spectra become more structured with well-resolved 0–1 and, in case of copolymer **SL1**, also 0–2 progressions. The solid-state absorption spectra of thin films of the copolymers display a
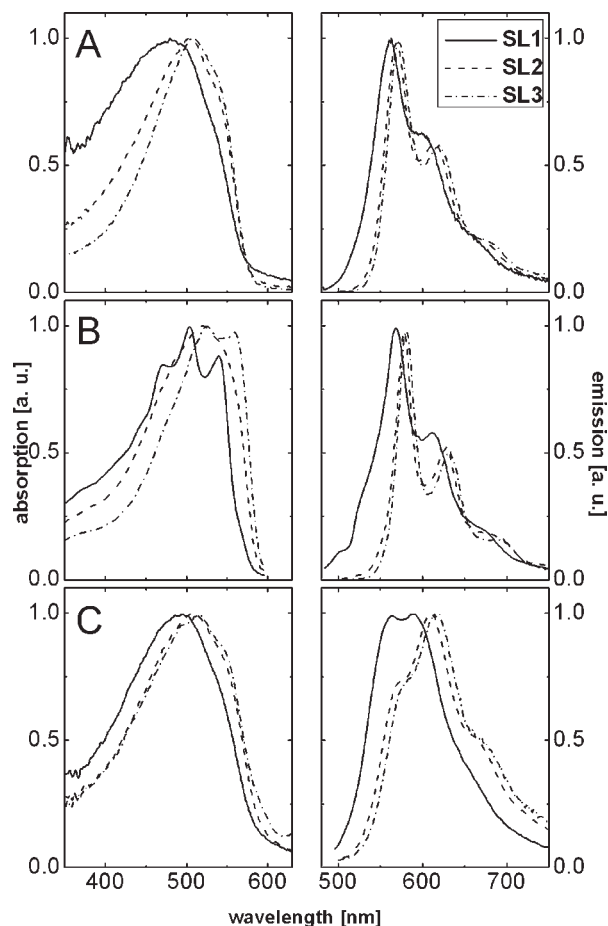
Figure 2. Absorption and photoluminescence (PL) emission spectra of the copolymers **SL1**, **SL2**, and **SL3** in dilute toluene solution at room temperature (A, 293 K), at low temperature (B, 77 K), and as thin films (C).

noticeable broadening of the absorption band. The maxima of the PL solid-state emission spectra experience a slight hypsochromic shift of 10–12 nm for all copolymers when compared with low temperature data. This finding can be related to a more rigid structure at low temperature. The thin film PL spectra show only small bathochromic shifts when compared with the spectra in dilute

solutions at room temperature (298 K). This implies that the copolymers in the solid state only show a low degree of interchain order. The amount of interchain order, leading to characteristic interchain π-interactions, is assumed to be responsible for the frequently observed red shifts of the optical spectra of conjugated polymers, especially oligothiophenes, in the solid state. The low intensity of the 0–0 PL transitions of the copolymers **SL1**, **SL2**, and **SL3** in the solid state is likely to be caused by self-absorption effects. The UV–vis absorption spectrum of the 1,5-naphthylene-based step-ladder copolymer **SL4** in toluene solution at room temperature shows an absorption maximum at 482 nm (Fig. 3 and Table 3). Copolymer **SL4** displays a more structured and narrower long wavelength absorption band when compared to copolymer **SL1** with its significantly broadened absorption band. This result might be caused by an ongoing aggregation of the less soluble copolymer **SL1** in toluene. Upon cooling to 77 K both absorption spectra become clearly structured and well-resolved 0–0, 0–1, and 0–2 transitions are visible. A distinct blue shift of 15 nm could be observed for copolymer **SL4** in relation to copolymer **SL1**. This finding can be rationalized by an increase of the energy difference between the benzoid (ground state) and quinoid (excited state) resonance structures when switching from 1,4-phenylene to 1,5-naphthylene leading to an increased excitation energy for **SL4**. The thin films absorption spectra of the two copolymers display less structured and broad absorption bands. The PL emission spectrum of the 1,5-naphthylene-based copolymer **SL4** in dilute toluene solution displays a similar spectral shape in relation to its 1,4-phenylene-based counterpart **SL1** apart from the blue-shift of the emission maximum of **SL4** of ~30 nm. At lower temperature (77 K) again an improved resolution of the vibronic progressions due to an increased molecular order is observed. Copolymer **SL4** shows well-resolved solid state PL emission bands with the 0–0

Table 2. Spectroscopic Data of the Step-Ladder-Type Copolymers **SL1**, **SL2**, and **SL3** in Toluene Solution at Room Temperature (293 K) and Low Temperature (77 K), as well as in the Solid State (Thin Film)

Polymer	λ_{max}^{abs} (nm) 293 K	λ_{max}^{abs} (nm) 77 K	λ_{max}^{abs} (nm) Film	λ_{max}^{abs} (nm) 293 K	λ_{max}^{abs} (nm) 77 K	λ_{max}^{abs} (nm) Film
SL1	480	470, *505*, 540	495	*562*, 600	569, 612	563, 590
SL2	505	520	510	*569*, 615	*578*, 627	576, *610*
SL3	508	*525*, 558	515	*572*, 620	*580*, 630	581, *615*

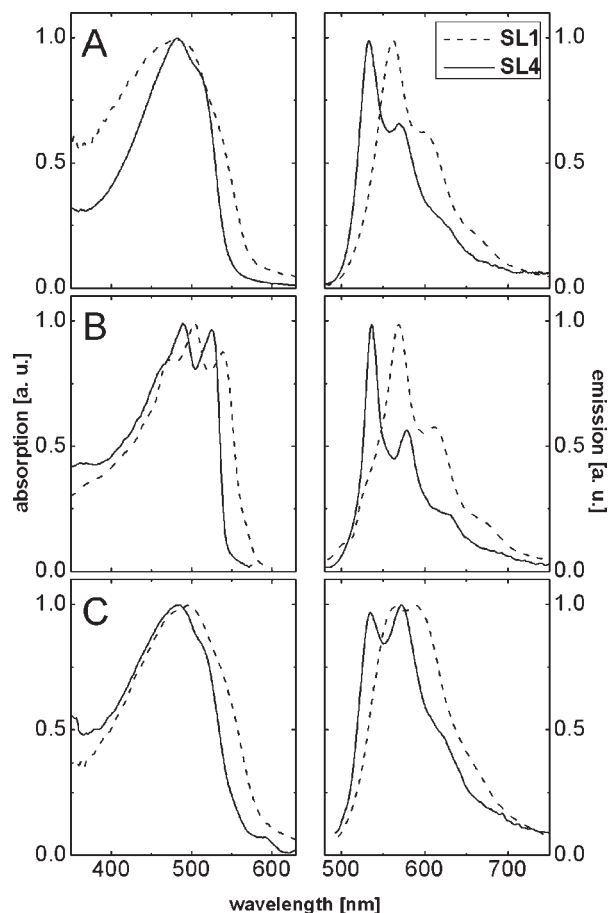The italicized wavelengths are the maxima with the highest intensity.

Figure 3. Absorption and PL emission spectra of the copolymers **SL1** and **SL4** in dilute toluene solution at room temperature (A, 293 K), at low temperature (B, 77 K), and as thin films (C).

emission at 535 and its first vibronic progression at 572 nm. The 0–0 emission is significantly reduced due to self-absorption effects.

## SYNTHESIS AND CHARACTERIZATION OF A MODEL COMPOUND

To gain a detailed insight into the molecular structure of the bridged bis(2-thienyl)benzene

repeat units of the copolymers **SL1**, **SL2**, and **SL3**, synthesis and characterization of a related model compound was carried out. Scheme 4 depicts the synthesis of the dithienyl-substituted step-ladder thiophene-benzene-thiophene model compound. Diethyl 2,5-dibromoterephthalate **6** was reacted with 2.5 equiv. of 2,2′-bithio-phene-5-pinacol boronate **7** utilizing $Pd(PPh_3)_4$ as catalyst and K_2CO_3 as base in a microwave assisted Suzuki-type cross-coupling reaction yielding the diketo compound **8** in 76% yield.[28] The intramolecular cyclization towards the model compound **10** was achieved by addition of methyl lithium and applying the $BF_3 \cdot Et_2O$-catalyzed ring closure reaction as described previously.[27] Figure 4 shows the UV–vis absorption spectrum of the open-chain precursor **9** as well as of the cyclized model compound **10** in dilute chloroform solution. The cyclization of **9**–**10** is accompanied by a distinct red-shift of the optical spectra. The precursor **9** shows a featureless long-wavelength absorption band peaking at 389 nm, whereas upon ring-closure the absorption maximum is red-shifted to 424 nm. Furthermore, **10** displays a much steeper absorption edge and better resolved vibronic side-bands due to the increased rigidity of the molecule. The corresponding PL spectrum of **10** exhibits two well-resolved PL peaks for the 0–0 and 0–1 transitions at 475 and 502 nm, respectively, as well as a shoulder at 523 nm for the 0–2 transition. The molecular structure of model compound **10** was also investigated by X-ray single crystal analysis. Figure 5 shows the planarity of the π-conjugated core segment that is bridged by two sp^3 carbons. The four methyl side-groups are positioned orthogonal to the molecular plane. The attached thiophene substituents exhibit a slight out-of-plane twist of 20.05° relative to the planar core segment suggesting that the copolymers **SL1**, **SL2**, **SL3**, and **SL4** should also exhibit a similar weak distortion of the individual segments. The relatively small distortion is similar to the situation in unsubstituted oligo(*para*-phenylene)s (distortion angle: ~19°).[30] In contrast, a higher distortion

Table 3. Spectroscopic Data of the Step-Ladder-Type Copolymers **11** and **29** in Toluene Solution at Room Temperature (293 K) and at Low Temperature (77 K), as well as in the Solid State (Thin Film)

Polymer	λ_{max}^{Abs} (nm) 293 K	λ_{max}^{abs} (nm) 77 K	λ_{max}^{abs} (nm) Film	λ_{max}^{Fluo} (nm) 293 K	λ_{max}^{Fluo} (nm) 77 K	λ_{max}^{Fluo} (nm) Film
SL4	482	*490*, 525	485	*533*, 570	*536*, 577	535, *572*
SL1	480	470, *505*, 540	495	*562*, 600	*569*, 612	563, 590

The italicized wavelengths are the absorption and PL emission maxima with the highest intensity.
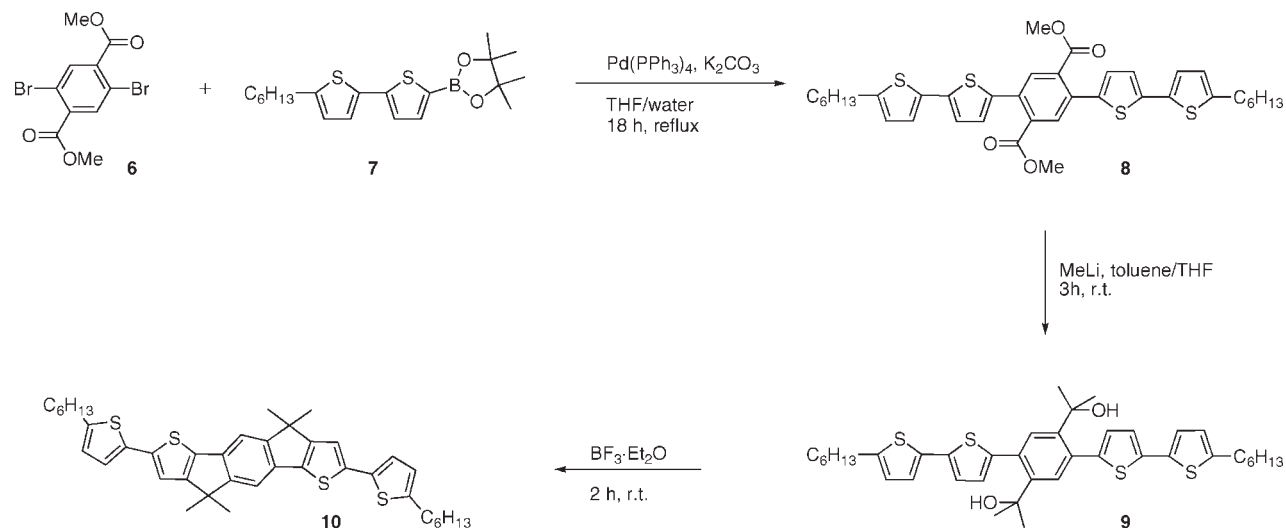
Scheme 4.   Synthetic route towards the model compound **10**.

angle is observed in regioregular poly(3-hexylthiophene) (P3HT, $\sim 30°$).[31,32] The weak distortion in oligomer **10** and the corresponding copolymers **SL1**, **SL2**, **SL3**, and **SL4** should allow a sufficient conjugative interaction along the oligomer and co-polymer backbones. Within the unit cell of the model compound **10** some intermolecular π-inter-action between the planarized oligomer molecules occurs (shortest distance between the molecular planes: 4.2 Å). It can be concluded that the copolymers **SL1**, **SL2**, **SL3**, and **SL4** should also allow some interchain π-π-interactions.

CONCLUSIONS

A series of thiophene–phenylene–thiophene and thiophene–naphthylene–thiophene-based step-ladder copolymers with varying lengths of the oligothiophene segment has been synthesized in Stille-type cross-coupling reactions to give single-stranded precursor polymers followed by a polymer-analogous cyclization sequence. The increased energy difference between benzoid and quinoid resonance structures for the 1,5-naphthy-lene-based copolymer leads to a 15–30 nm blue shift of its absorption and emission spectra (both in dilute solution at different temperature and in the solid state). The optical spectra were recorded both in dilute solution at different temperatures and in the solid state and revealed a spectral red-
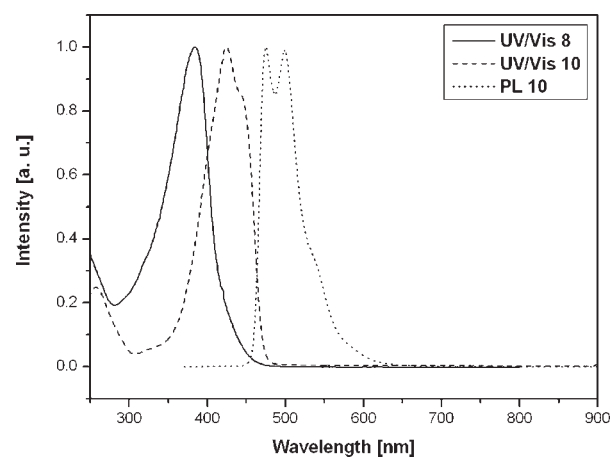

Figure 4.   UV–vis absorption spectra of **8** and model compound **10** in dilute chloroform solution; as well as the PL spectrum of **10** in dilute chloroform solution (excitation wavelength: 445 nm).
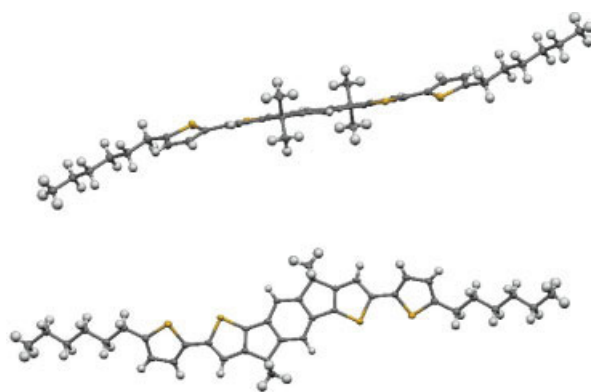

Figure 5.   X-ray single crystal structure of model compound **10**: View in-plane and perpendicular to the plane of the planarized core segment.

shift of the absorption and emission maxima with increasing numbers of thiophene building blocks in the corresponding repeat unit. The planar structure of the step-ladder core segment was confirmed by X-ray single crystal analysis of a related model compound.

EXPERIMENTAL

Materials and Characterization

Unless otherwise indicated, all reagents were obtained from commercial suppliers and were used without further purification. The solvents used were commercial p.a. quality. The reactions were carried out under argon with the use of standard and Schlenk techniques. The vials for the microwave-assisted reactions were filled in a glove box. ^{1}H- and ^{13}C-NMR data were obtained on a Bruker ARX 400-spectrometer. The UV–vis and fluorescence spectra were recorded on a Jasco V-550 spectrophotometer and a Varian-Cary Eclipse photoluminescence spectrometer, respectively. Gel permeation chromatographic analysis (GPC) utilized PS-columns (two columns, 5 μm gel, pore widths mixed bed linear) connected with UV/vis and RI detection. All GPC analyses were performed on solutions of the polymers in THF at 30 °C (concentration of the polymer: about 1.5 g/L). The calibration was based on polystyrene standards with narrow molecular weight distribution. Microwave-assisted syntheses were performed using a CEM Discover microwave system. The monomers **1**,[9] **2**,[33] **3**,[33] and **5**[29] have been synthesized according to literature procedures.

4′,4″-Didecyl-2,5-bis(5′-bromothien-2′-yl) terephthalophenone (4)

a. 1,4-Bis(4,4′-decyl-benzoyl)-2,5-dibromobenzene (2.0 g, 2.76 mmol), 2-(tributyl-stannyl)thiophene (2.36 g, 6.34 mmol), potassium fluoride (1.6 g, 27.6 mmol), and bis(triphenyl-phosphine)-palladium(II)chloride (194 mg, 10 mol %) were mixed in a Schlenk tube under argon atmosphere. THF (50 mL) was added and the reaction mixture was stirred for 2 days at 90 °C. Afterwards the reaction mixture was extracted with a mixture of water and chloroform. The organic layer was extensively washed with water, dried with Na$_2$SO$_4$ and the solvent was removed *in vacuo*. The crude product was purified by column chromatography on silica (hexane/ethyl acetate:99/1

v:v) and recrystallized from ethanol to give 1.16 g (58%) of white crystals.

^{1}H-NMR (400 MHz, CDCl$_3$): δ [ppm] = 7.70 (d, 4H, J = 8.2 Hz), 7.61 (s, 2H), 7.18 (s, 2H), 7.16 (d, 4H, J = 7.9 Hz), 7.00 (d, 2H, J = 3.5 Hz), 6.84 (dd, 2H, J = 3.7 Hz, J = 5.0 Hz), 2.60 (m, 4H), 1.65 (m, 8H), 1.36 (m, 24H), 0.93 (t, 6H, J = 7.3 Hz). ^{13}C-NMR (100 MHz, CDCl$_3$): δ [ppm] = 197.3, 149.5, 140.4, 140.0, 134.2, 131.8, 130.1, 129.4, 128.5, 127.9, 127.6, 126.7, 36.0, 31.8, 30.9, 29.5, 29.5, 29.4, 29.2, 29.1, 22.6, 13.5. FT-mass: m/z (calc) = 730.5 (731.1) Anal. Calcd. for C$_{48}$H$_{58}$O$_2$S$_2$: C, 78.86; H, 8.00; S, 8.77. Found: C, 78.45; H, 7.70; S, 8.79.

b. A solution of 4′,4″-didecyl-2,5-bis(2′-thienyl)-terephthalophenone (1.0 g, 1.4 mmol) in DMF (25 mL) was protected from light and cooled down to −20 °C. To this solution a mixture of NBS (0.61 g, 3.4 mmol, 2.5 eq) in DMF (25 mL) was added dropwise. The mixture was stirred at −20 °C for 30 min, and then allowed to warm up to room temperature. The mixture was stirred for another 8 h at room temperature, and then poured onto ice and extracted with dichloromethane. The combined organic layers were dried over Na$_2$SO$_4$. Afterwards the solvents were removed *in vacuo*. The crude product was purified by column chromatography on silica (hexane/ethyl acetate: 90/10 v:v) and recrystallized from ethanol. Yield: 700 mg.

^{1}H-NMR (400 MHz, C$_2$D$_2$Cl$_4$): δ [ppm] = 7.61 (d, 4H, J = 8.2 Hz), 7.44 (s, 2H), 7.14 (m, 4H), 6.77 (d, 2H, J = 3.8 Hz), 6.67 (d, 2H, J = 3.9 Hz), 2.56 (m, 4H), 1.53 (s, 8H), 1.19 (m, 24H), 0.80 (t, 6H, J = 6.8 Hz). ^{13}C-NMR (100 MHz, C$_2$D$_2$Cl$_4$): δ [ppm] = 197.5, 150.0, 140.5, 140.1, 134.3, 132.1, 130.4, 129.8, 128.9, 128.2, 128.1, 127.2, 36.3, 32.1, 31.1, 29.8, 29.8, 29.7, 29.6, 29.5, 23.0, 14.5. FT-mass: m/z (calc) = 887.6 (888.9). FTIR (neat): v [cm^{-1}] = 2920, 2850, 1653, 1603, 1570, 1466, 1432, 1415, 1375, 1310, 1282, 1239, 1178, 1145, 1119, 1078, 997, 963, 921, 894, 846, 808, 757, 718, 699. Anal. Calcd. for C$_{48}$H$_{56}$Br$_2$O$_2$S$_2$: C, 64.84; H, 6.35; S, 7.21. Found: C, 64.76; H, 6.13; S, 7.11.

2,5-Bis(5-hexyl-2,2′-bithiophene)-5′-yldimethylterephthalate (8)

A 250-mL two-necked round-bottom flask was charged with 2,5-dibromo-dimethylterephthalate (1.50 g, 4.25 mmol), potassium carbonate (2.9 g, 8.5 mmol, 4 equiv.), Pd(PPh3)4 (0.49 g, 10%), THF (60 mL), and water (20 mL). 5-Hexyl-5′-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2′-bithiophene

(4 g, 10.6 mmol, 2.5 equiv.) was dissolved in degassed THF (20 mL) and added dropwise to the solution via a syringe. The solution was refluxed for 24 h. The reaction mixture was diluted with chloroform and washed with aqueous 2 N HCl, saturated aqueous $NaHCO_3$ and NaEDTA solutions and brine. The organic phase was dried over Na_2SO_4 and the solvent removed *in vacuo*. The crude product was purified by column chromatography on silica (Hex/EA:85/15 v:v) and recrystallized from ethanol. Yield: 76%.

^{1}H-NMR (400 MHz, CDCl$_3$): δ [ppm] = 7.72 (s, 2H), 7.01 (d, 2H, J = 3.7 Hz), 6.96 (d, 2H, J = 3.5 Hz), 6.92 (d, 2H, J = 3.7 Hz), 6.64 (d, 2H, J = 3.5 Hz), 2.73 (t, 4H, J = 7.6 Hz), 1.64-1.50 (m, 4H), 1.33–1.29 (m, 1H), 1.27–1.18 (m, 12H), 0.83 (t, 6H, J = 7.0 Hz). ^{13}C-NMR (100 MHz, CDCl$_3$): δ [ppm] = 168.3, 146.4, 139.6, 138.3, 134.3, 133.5, 132.9, 131.8, 128.1, 125.2, 124.1, 123.7, 53.1, 31.8, 31.8, 30.4, 29.0, 22.8, 14.4. FT-mass: m/z (calc) = 690,4 (691) UV/vis (CHCl$_3$): λ_{max} [nm] = 384. Anal. Calcd. for $C_{38}H_{42}O_4S_4$: C, 66.05; H, 6.13; S, 18.56. Found: C, 65.79; H, 5.83; S, 18.09.

Step-Ladder Model Compound (10)

A 40-fold excess of MeLi (7 mL, 11.2 mmol, 1.6M) was added to a solution of the previously synthesized diketone **8** (1.4 g, 0.2 mmol) in toluene (30 mL) at room temperature and stirred for 30 min. Afterwards THF (20 mL) was added and the mixture stirred for additional 12 h. The reaction was stopped with ethanol, chloroform (100 mL) added, and the solution washed with aqueous 2 N HCl and brine. The organic phase was dried over Na_2SO_4 and the solvent removed *in vacuo*. The crude product was dissolved in dichloromethane (30 mL) and treated with an excess of boron trifluoride etherate (4 mL, 31.8 mmol). The solution was stirred for 3 h, and then a mixture of ethanol/water (2:1) added. The organic layer was diluted with chloroform and extracted several times with water. The organic phase was dried over Na_2SO_4 and the solvent removed *in vacuo*. The residue was purified by column chromatography on silica (Hex/EA:80/20 v:v) and recrystallized from ethanol. Yield: 78%.

^{1}H-NMR(400 MHz, C$_2$D$_2$Cl$_4$): δ [ppm] = 7.50 (d, 2H, J = 3.7 Hz)), 7.25 (s, 2H), 6.98 (s, 2H), 6.63 (d, 2H, J = 3.9 Hz), 2.72 (m, 12H), 1.66–1.57 (m, 4H, J = 7.6 Hz), 1.52–1.50 (m, 4H),1.35–1.21 (m, 12H), 0.82 (t, 6H, J = 6.8 Hz). ^{13}C-NMR (100 MHz, C$_2$D$_2$Cl$_4$): δ [ppm] = 159.1, 155.7, 145.4, 140.0, 138.7, 136.0, 134.3, 125.0, 123.0, 117.1,

113.1, 45.9, 31.7, 31.6, 30.4, 28.9, 26.4, 22.7, 14.2. FD-mass: m/z (calc.) = 654.8 (655.1). UV/vis (CHCl$_3$): λ_{max} [nm] = 425, 444 (shoulder). Anal. Calcd. for $C_{40}H_{46}S_4$: C, 73.34; H, 7.08; S, 19.58. Found: C, 73.04; H, 6.55; S, 19.33.

General Procedure for Microwave-Assisted Stille-Type Polymerizations

Equimolar amounts of the bis(trimethylstannyl) oligothiophene and 4′,4″-didecyl-2,5-bis(5′-bromo-thien-2′-yl)terephthalophenone (15), 10 equiv. of potassium fluoride, and 10 mol % PdCl$_2$(dppf) were mixed in a sealed 10 mL vial under glove box conditions. Dry toluene (2 mL) and dry DMF (1 mL) were added and the solutions irradiated with microwaves (300 W, 110 °C) for 15 min. The reaction mixture was diluted with chloroform and washed with aqueous 2 N HCl, saturated aqueous $NaHCO_3$ and NaEDTA solutions and brine. The organic phase was dried over Na_2SO_4 and the solvent removed *in vacuo*. The residue was dissolved in chloroform, reprecipitated into methanol, filtered, and dried.

Synthesis of Polyketone PK1

Yield: 44%. GPC (vs. polystyrene standards in THF) M_n = 10,400 g/mol, M_w/M_n = 2.8.

^{1}H-NMR (400 MHz, C$_2$D$_2$Cl$_4$): δ [ppm] = 7.67-7.61 (m, 4H), 7.51–7.48 (bs, 2H), 7.17–7.11 (m, 4H), 6.86–6.75 (m, 4H), 2.61–2.53 (m, 4H), 1.59–1.49 (m, 8H), 1.29–1.17 (m, 24H), 0.87–0.79 (m, 6H). ^{13}C-NMR (100 MHz, C$_2$D$_2$Cl$_4$): δ [ppm] = 196.7, 149.9, 140.4, 139.5, 138.3, 134.5, 131.5, 130.3, 129.5, 129.0, 128.8, 124.9, 36.2, 32.0, 30.8, 29.7, 29.6, 29.5, 29.4, 29.3, 22.8, 14.2. UV/vis (CHCl$_3$): λ_{max} [nm] = 492. FTIR (neat): v [cm^{-1}] = 2922, 2851, 1659 (C=O), 1603, 1572, 1529, 1485, 1462, 1414, 1371, 1309, 1279, 1244, 1178, 1146, 1119, 1068, 1019, 984, 928, 893, 849. Anal. Calcd. for $C_{48}H_{56}O_2S_2$: C, 79.07; H, 7.74; S, 8.80. Found: C, 78.99; H, 7.54; S, 8.49.

Synthesis of Polyketone PK2

Yield: 47%. GPC (vs. polystyrene standards in THF) M_n = 14,800 g/mol, M_w/M_n = 3.6.
^{1}H-NMR (400 MHz, C$_2$D$_2$Cl$_4$): δ [ppm] = 7.66–7.59 (m, 4H), 7.49–7.44 (bs, 2H), 7.12-7.01 (m, 6H), 6.82–6.74 (m, 4H), 2.58–2.51 (m, 4H), 1.62–1.47 (m, 8H), 1.33–1.16 (m, 24H), 0.88–0.79 (m, 6H). ^{13}C-NMR (100 MHz, C$_2$D$_2$Cl$_4$): δ [ppm] = 194.2, 149.1, 140.4, 140.2, 138.0, 134.6, 134.5,

131.5, 130.1, 129.4, 129.2, 129.1, 128.6, 124.5, 36.2, 32.1, 30.5, 29.7, 29.6, 29.5, 29.4, 29.2, 23.1, 14.3. UV/VIS (CHCl$_3$): λ_{max} [nm] = 494. FTIR (neat): v [cm^{-1}] = 2922, 2849, 1663 (C=O), 1599, 1575, 1538, 1455, 1416, 1371, 1309, 1279, 1256, 1173, 1133, 1075, 990, 927. Anal. Calcd. for C$_{52}$H$_{58}$O$_2$S$_3$: C, 76.99; H, 7.21; S, 11.86. Found: C, 76.88; H, 6.98; S, 11.42.

Synthesis of Polyketone PK3

Yield: 52%. GPC (versus polystyrene standards in THF) M_n = 12,600 g/mol, M_w/M_n = 3.2.

^{1}H-NMR (400 MHz, C$_2$D$_2$Cl$_4$): δ [ppm] = 7.69–7.60 (m, 4H), 7.56–7.44 (m, 2H), 7.18–7.10 (m, 4H), 7.04–6.71 (m, 8H), 2.59–2.51 (m, 4H), 1.58–1.43 (m, 8H), 1.26–1.11 (m, 24H), 0.85–0.75 (m, 6H). ^{13}C-NMR (100 MHz, C$_2$D$_2$Cl$_4$): δ [ppm] = 196.9, 150.0, 140.5, 135.0, 134.6, 131.8, 131.7, 130.3, 129.1, 128.9, 127.9, 127.6, 125.0, 124.9, 124.8, 124.7, 36.2, 32.0, 30.9, 29.8, 29.7, 29.6, 29.5, 29.4, 22.8, 14.2. UV/vis (CHCl$_3$): λ_{max} [nm] = 495. FTIR (neat): v [cm^{-1}] = 2919, 2850, 1661 (C=O), 1603, 1489, 1456, 1414, 1337, 1280, 1251, 1178, 1146, 1101, 1067, 926, 893, 850, 788. Anal. Calcd. for C$_{56}$H$_{60}$O$_2$S$_4$: C, 75.29; H, 6.77; S, 14.36. Found: C, 75.02; H, 6.55; S, 13.98.

Synthesis of Polyketone PK4

The herein utilized method was slightly modified with respect to the general procedure: 1,5-dibromo-2,5-bis(4-tert-butyl-benzoyl)naphthalene (100 mg, 0.16 mmol), 5,5′-bis(trimethylstannyl)-2,2′-bithiophene (81.1 mg, 0.16 mmol), potassium fluoride (95.8 mg, 1.6 mmol), and 1,1-bis(diphenylphosphino)ferrocene-dichloropalladium(II) (12.1 mg, 10 mol %) were transferred into a 10 mL microwave vial. Afterwards the microwave vial was sealed, evacuated, and flushed with argon. Toluene (2 mL) and 1 mL of DMF were added via a syringe and the mixture irradiated with microwaves (300 W, 120 °C) for 12 min until black palladium metal precipitated out. The mixture was filtered to remove the metallic palladium, diluted with chloroform, and washed with aqueous 2 N HCl, saturated aqueous NaHCO$_3$ and NaEDTA solutions and brine. The organic phase was dried over Na$_2$SO$_4$ and the solvent removed in vacuo. The residue was dissolved in chloroform, reprecipitated into methanol, filtered and dried. Yield: 49%. GPC (vs. polystyrene standards in THF) M_n = 12,800 g/mol, M_w/M_n = 2.4.

^{1}H-NMR (C$_2$D$_2$Cl$_4$, 400 MHz): δ [ppm] = 8.20–8.12 (m, 2H), 7.57–7.52 (m, 4H), 7.33–7.27 (m, 4H), 6.92–6.88 (m, 2H), 6.87–6.83 (m, 2H), 1.27–1.21 (m, 18H). ^{13}C-NMR (C$_2$D$_2$Cl$_4$, 100 MHz): δ [ppm] = 197.4, 157.3, 140.3, 139.1, 136.7, 135.1, 133.9, 131.5, 130.0, 128.0, 125.9, 125.3, 124.2, 123.9, 35.2, 31.2. FTIR (neat): v [cm^{-1}] = 2925, 2852, 1671, 1603, 1461, 1408, 1362, 1332, 1259, 1193, 1164, 1108, 1026, 976, 866, 847, 794, 772, 719, 701. Anal. Calcd. for C$_{40}$H$_{34}$O$_2$S$_2$: C, 78.65; H, 5.61; S, 10.50; Found C, 78.19; H, 6.23; S, 9.96.

General Procedure for the Cyclization Sequence

A 40-fold excess of MeLi (3.5 mL, 5.6 mmol, 1.6 M) was added at room temperature to a solution of the previously synthesized diketo polymer (0.1 mmol) in toluene (30 mL) and stirred for 30 min. Afterwards THF (20 mL) was added and the mixture stirred at room temperature for additional 12 h. The reaction was quenched with ethanol, chloroform added, and the solution was washed with aqueous 2 N HCl and brine. The organic phase was dried over Na$_2$SO$_4$ and the solvent removed in vacuo. The crude product was dissolved in dichloromethane (30 mL) and treated with an excess of borontrifluoride etherate (2 mL, 15.9 mmol). The solution was stirred for 3 h and then a mixture of ethanol/water (2:1) was added. The organic layer was diluted with chloroform and extracted several times with water. The organic phase was dried over Na$_2$SO$_4$ and the solvent removed in vacuo. The residue was dissolved in chloroform and precipitated into methanol to give the cyclized step-ladder copolymers.

Synthesis of the Step-Ladder Copolymer SL1

Yield: 76%. GPC (vs. polystyrene standards in THF) M_n = 12,000 g/mol, M_w/M_n = 2.0.

^{1}H-NMR (400 MHz, C$_2$D$_2$Cl$_4$): δ [ppm] = 7.61 (d, 4H, J = 8 Hz), 7.45 (s, 2H), 7.11 (d, 4H, J = 8 Hz), 6.76 (bs, 2H), 2.58-2.44 (m, 4H), 1.88–1.80 (bs, 6H, CH3 bridge), 1.52–1.48 (m, 8H), 1.21–1.11 (m, 24H), 0.81–0.75 (m, 6H). ^{13}C-NMR (100 MHz, C$_2$D$_2$Cl$_4$): δ [ppm] = 140.9, 140.0, 136.9, 136.3, 133.9, 133.0 130.9, 128.8, 128.2, 126.1, 125.8, 53.2, 36.1, 32.2, 31.0, 29.7, 29.6, 29.5, 29.4, 29.3, 23.0, 14.2, 13.5. UV/vis (CHCl$_3$): λ_{max} (nm) = 492. FTIR (neat): v (cm^{-1}) = 2920, 2850, 1510, 1455, 1414, 1374, 1322, 1242, 1187, 1123, 1059, 1018, 990, 960, 871, 822, 720, 698, 674, 658. Anal.

Calcd. for $C_{50}H_{60}S_2$: C, 82.82; H, 8.34; S, 8.84. Found: C, 82.60; H, 7.99; S, 8.61.

Synthesis of the Step-Ladder Copolymer SL2

Yield: 71%. GPC (vs. polystyrene standards in THF) M_n = 16,200 g/mol, M_w/M_n = 2.9. ^{1}H-NMR (400 MHz, $C_2D_2Cl_4$): δ [ppm] = 7.25–7.12 (m, 6H), 7.08–6.85 (m, 8H), 2.57–2.42 (m, 4H), 1.95–1.75 (m, 6H, CH3 bridge), 1.65–1.45 (m, 8H), 1.35–1.05 (m, 24H), 0.90–0.74 (m, 6H). ^{13}C-NMR (100 MHz, $C_2D_2Cl_4$): δ [ppm] = 140.2, 138.4, 137.1, 136.5, 136.1, 133.3, 130.7, 129.8, 129.4, 128.7, 128.2, 125.0, 124.9, 54.1, 36.2, 32.0, 31.1, 29.7, 29.6, 29.5, 29.4, 29.3, 22.9, 14.2, 13.5. UV/vis (CHCl$_3$): λ_{max} [nm] = 508. FTIR (neat): v [cm^{-1}] = 2922, 2851, 1606, 1511, 1455, 1410, 1374, 1293, 1260, 1170, 1064, 1018, 904, 827, 790, 716, 692. Anal. Calcd. for $C_{54}H_{62}S_3$: C, 80.34; H, 7.74; S, 11.92. Found: C, 79.84; H, 7.26; S, 11.72.

Synthesis of the Step-Ladder Copolymer SL3

Yield: 72%. GPC (vs. polystyrene standards in THF) M_n = 14,200 g/mol, M_w/M_n = 3.1. ^{1}H-NMR (400 MHz, $C_2D_2Cl_4$): δ [ppm] = 7.23–7.18 (m, 2H), 7.18–7.11 (m, 4H), 7.07–6.97 (m, 6H), 6.97–6.93 (m, 4H), 2.56–2.44 (m, 4H), 1.90-1.77 (m, 6H, CH3 bridge), 1.58–1.39 (m, 8H), 1.33–1.06 (m, 24H), 0.87–0.74 (m, 6H). ^{13}C-NMR (100 MHz, $C_2D_2Cl_4$): δ [ppm] = 140.4, 138.2, 137.6, 137.0, 136.4, 136.5, 133.7, 133.6, 130.4, 129.9, 128.8, 128.1, 125.4, 125.1, 124.9, 56.3, 36.1, 32.1, 31.4, 29.7, 29.6, 29.5, 29.4, 29.3, 22.8, 14.2, 13.6. UV/vis (CHCl$_3$): λ_{max} (nm) = 509. FTIR (neat): v [cm^{-1}] = 2920, 2850, 1510, 1455, 1414, 1374, 1322, 1187, 1171, 1122, 1100, 1058, 1018, 871, 825, 787. Anal. Calcd. for $C_{58}H_{64}S_4$: C, 78.33; H, 7.25; S, 14.42. Found: C, 77.82; H, 6.98; S, 14.11.

Synthesis of the Step-Ladder Copolymer SL4

Yield: 82%. GPC (vs. polystyrene standards in THF) M_n = 13,500 g/mol, M_w/M_n = 2.1. ^{1}H-NMR ($C_2D_2Cl_4$, 400 MHz): δ [ppm] = 8.01–7.94 (m, 4H), 7.92 (s, 2H), 7.56–7.49 (m, 4H), 7.25–7.15 (m, 4H), 1.99–1.90 (m, 6H, CH$_3$ bridge), 1.24 (s, 18H). ^{13}C-NMR (100 MHz, $C_2D_2Cl_4$): δ [ppm] = 149.1, 140.2, 134.4, 133.8, 133.6, 132.8, 131.0, 127.7, 126.1, 126.0 125.8, 125.7, 125.5, 55.4, 34.5, 31.2, 13.2. UV/vis (CHCl$_3$): λ_{max} [nm] = 485. FT-IR (neat): v [cm^{-1}] = 2959, 2924, 2862, 1674, 1560, 1512, 1455, 1407, 1384, 1361, 1332, 1260, 1217, 1200, 1114, 1087, 1061, 1014, 984, 927, 839, 810, 747, 724, 698, 668, 654. Anal. Calcd. for $C_{42}H_{38}S_2$: C, 83.12; H, 6.31; S, 10.57; Found: C, 83.01; H, 6.22; S, 10.37.

REFERENCES AND NOTES

1. Kraft, A.; Grimsdale, A. C.; Holmes, A. B. Angew Chem Int Ed 1998, 37, 402–428.
2. Anthony, J. E. Chem Rev 2006, 106, 5028–5048.
3. McGehee, M. D.; Heeger, A. J. Adv Mater 2000, 12, 1655–1668.
4. Dimitrakopoulos, C. D.; Malenfant, P. R. L. Adv Mater 2002, 14, 99–117.
5. Brabec, C. J.; Shaheen, S. E.; Fromherz, T.; Padinger, F.; Hummelen, J. C.; Dhanabalan, A.; Janssen, R. A. J.; Sariciftci, N. S. Synth Met 2001, 121, 1517–1520.
6. Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. Adv Funct Mater 2001, 11, 15–26.
7. Sheats, J. R. J Mater Res 1974, 19, 1974–1989.
8. Grimsdale, A. C.; Müllen, K. Macromol Rapid Commun 2007, 28, 1676–1702.
9. Scherf, U.; Müllen, K. Macromol Rapid Commun 1991, 12, 489–497.
10. Pietrangelo, A.; MacLachlan, M. J.; Wolf, M. O.; Patrick, B. O. Org Lett 2007, 9, 3571–3573.
11. Cicoira, F.; Santato, C.; Melucci, M.; Favaretto, L.; Gazzano, M.; Muccini, M.; Barbarella, G. Adv Mater 2006, 18, 169–174.
12. Li, X. C.; Sirringhaus, H.; Garnier, F.; Holmes, A. B.; Moratti, S. C.; Feeder, N.; Clegg, W.; Teat, S. J.; Friend, R. H. J Am Chem Soc 1998, 120, 2206–2207.
13. Takimiya, K.; Kunugi, Y.; Konda, Y.; Niihara, N.; Otsubo, T. J. Am Chem Soc 2004, 126, 5084–5085.
14. Wang, B.; Shen, F.; Lu, P.; Tang, S.; Zhang, W.; Pan, S.; Liu, M.; Liu, L.; Qiu, S.; Ma, Y. J Polym Sci Part A: Polym Chem 2008, 46, 3120–3127.
15. Wex, B.; Kaafarani, B. R.; Schroeder, R.; Majewski, L. A.; Burckel, P.; Grell, M.; Neckers, D. C. J Mater Chem 2006, 16, 1121–1124.
16. Xiao, K.; Liu, Y.; Qi, T.; Zhang, W.; Wang, F.; Gao, J.; Qiu, W.; Ma, Y.; Cui, G.; Chen, S.; Zhan, X.; Yu, G.; Qin, J.; Hu, W.; Zhu, D. J Am Chem Soc 2005, 127, 13281–13286.
17. Liao, L.; Cirpan, A.; Chu, Q.; Karasz, F. E.; Pang, Y. J Polym Sci Part A: Polym Chem 2007, 45, 2048–2058.
18. Yamamoto, T.; Takimiya, K. J Am Chem Soc 2007, 129, 2224–2225.
19. Li, Y. N.; Wu, Y. L.; Gardner, S.; Ong, B. S. Adv Mater 2005, 17, 849–853.
20. Wu, Y. L.; Li, Y. N.; Gardner, S.; Ong, B. S. J Am Chem Soc 2005, 127, 614–618.
21. Kalinin, A. V.; Reed, M. A.; Norman, B. H.; Snieckus, V. J Org Chem 2003, 68, 5992–5999.
22. Forster, M.; Scherf, U. Macromol Rapid Commun 2000, 21, 810–813.

23. Chmil, K.; Scherf, U. Makromol Chem Rapid Commun 1993, 14, 217–222.
24. Nehls, B. S.; Fuldner, S.; Preis, E.; Farrell, T.; Scherf, U. Macromolecules 2005, 38, 687–694.
25. Schlüter, A. D. J Polym Sci Part A: Polym Chem 2001, 39, 1533–1556.
26. Scherf, U. J. Mater Chem 1999, 9, 1853–1864.
27. Scherf, U.; Bohnen, A.; Müllen, K. Macromol Chem 1992, 193, 1127–1133.
28. Melucci, M.; Barbarella, G.; Sotgiu, G. J Org Chem 2002, 67, 8877–8884.
29. Preis, E.; Scherf, U. Macromol Rapid Commun 2006, 27, 1105–1109.
30. Sasaki, S.; Yamamoto, T.; Kanbara, T.; Morita, A.; Yamamoto, T. J Polym Sci Part B: Polym Phys 1992, 30, 293–297.
31. Kobashi, M.; Takeuchi, H. Macromolecules 1998, 31, 7272–7278.
32. Chen, S. A.; Lee, S. J Synth Met 1995, 72, 253–260.
33. Furuta, P.; Fréchet, J. M. J. J Am Chem Soc 2003, 125, 13173–13181.