Push–Pull-Substituted Oligo(2,5-thienyleneethynylene)s

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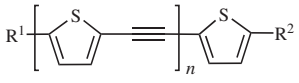
Abstract: Oligo(2,5-thienyleneethynylene)s (OTE) with terminal donor-acceptor substitution were synthesized by applying Sonogashira–Hagihara reactions and a protection group technique. The combination of the alkylthio and nitro substituents provides a DAOTE series, whose long-wavelength absorption shows a monotonous bathochromic effect for increasing numbers *n* of repeat units. The convergence limit is already reached for $n = 3$.

Key words: alkynes, conjugation, coupling, heterocycles, sulfur

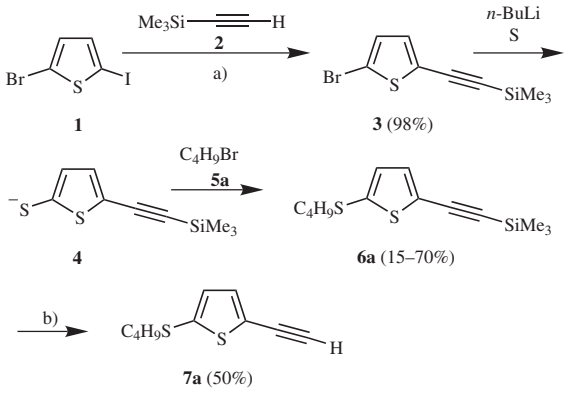
Because of their interesting linear and nonlinear optical (NLO) properties, donor-acceptor substituted conjugated oligomers and polymers (D–π–A) have attracted a lot of attention.[1] Our recent studies on such systems were focussed on oligo(2,5-thienyleneethynylene)s (OTE) (Figure 1). Different end-groups R^1 and R^2 such as 2,2′:6′,2″-terpyridine,[2,3] fullerene,[4] fluorene[5] and substituted benzene rings[6] have been introduced in OTEs. In continuation of our studies, we now became interested in the preparation of push-pull-substituted compounds. The Sonogashira–Hagihara reaction represents by far the most usual access to the conjugated chains of aryleneethynylenes.[1] This is also valid for 2,5-thienyleneethynylenes.[2–15] The majority of OTEs contains solubilizing alkyl groups attached to the thiophene rings. However, such groups enhance the torsional angles along the chain and therefore impair the conjugation. These side chains can be abandoned for $n \leq 5$, when solubilizing end-groups R^1 or R^2 or both are present.



OTE / PTE

Figure 1 Oligo- and poly(2,5-thienyleneethynylene)s

We decided to prepare donor-acceptor substituted oligo(2,5-thienyleneethynylene)s (DAOTE) with alkylthio groups R^1 and nitro groups R^2. Long alkylthio groups are weak electron donating, but highly solubilizing groups. Moreover, they can be cleaved to thiols and fixed on gold surfaces. Nitro groups are strong electron acceptors, which reduce the solubility. We first tried the combination C_4H_9S/NO_2. 2-Bromo-5-iodothiophene (**1**) was reacted chemoselectively in 5-position with trimethylsilylacetylene (**2**) by applying the Sonogashira–Hagihara reaction (Scheme 1). Compound **3,** the product of the C(sp^2)–C(sp) coupling, was obtained in an almost quantitative yield. The next step, namely the bromine/lithium exchange was followed by the introduction of sulfur (**3** → **4**) and the alkylation with the butyl group (**4** + **5a** → **6a**). The yield was disappointing when only the in situ formed 1-bromobutane (**3** + BuLi → **5a**) reacted; however, additionally added **5a** enhanced the yield to about 70%. Deprotection of **6a** with K_2CO_3 afforded **7a**, which could be used as component for the donor end of the conjugated DAOTE system.



Scheme 1 Preparation of 2-butylthio-5-ethynylthiophene (**7a**): *Reagents and conditions*: a) $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, Et_3N; b) K_2CO_3, MeOH–CH_2Cl_2 (1:1).

We varied then the synthetic sequence and attached first the alkylthio group to the thiophene ring (Scheme 2). Thiophene (**8**) was lithiated and treated with elemental sulfur[6] (**8** → **9**) and subsequently with 1-iodododecane (**9** + **5b** → **10**).[16] The oxidative iodination of **10** occurred selectively in 5-position and the obtained compound **11** was subjected to a Sonogashira–Hagihara reaction with **2**. The target component **7b** was then formed by the deprotection step **6b** → **7b**.

The convergent synthetic strategy for the DAOTE systems required then the use of extension reagent **12** and endcapping reagent **13** (Scheme 3). The donor components **7a**,**b** reacted with **13** to **14a**,**b**. The better solubilizing dodecyl group led thereby to a much better yield than the butyl group. Because of this advantage, only **7b** was used for the extension of the conjugated chain. An alternating sequence of Sonogashira–Hagihara reactions and deprotection steps afforded the oligomers **15b**, **16b**, **18b**,

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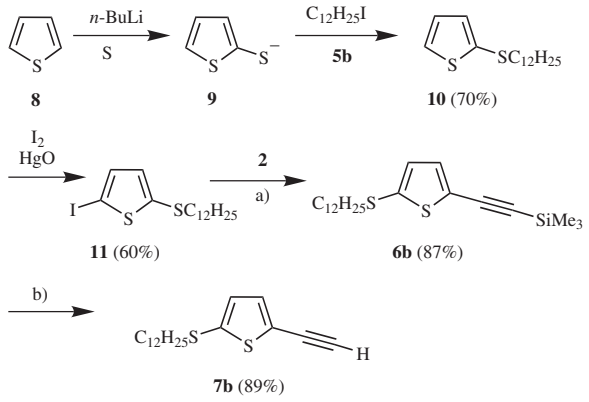


Scheme 2 Preparation of the donor component **7b**: *Reagents and conditions*: a) $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, Et_3N, toluene; b) K_2CO_3, MeOH–CH_2Cl_2 (1:1).

19b, **21b** and **22b**. The compounds **16b**, **19b** and **22b**, which contain a free ethynyl group, were then end-coupled with **13**. The yield of the products **17b**, **20b** and **23b** decreased with increasing length of the chain (increasing numbers *n* of repeat units).

The spectroscopic characterization of the compounds was mainly based on ^1H and ^{13}C NMR measurements including heteronuclear 2 D spectra (HMQC and HMBC).[17] Figure 2 shows the assignment of the ^1H and ^{13}C chemical shifts of **14b**. The donor-acceptor substitution causes a polarization, which is clearly documented by the $\Delta\delta$ (^{13}C) values of the acetylenic carbon atoms. The ^{13}C chemical shifts are very sensitive towards partial charges. Extension of the conjugation (n = 2, 3, 4) leads to an increasing distance of D and A and therefore to a decreasing interaction of the partial dipole moments at the chain ends.[1a,18,19]

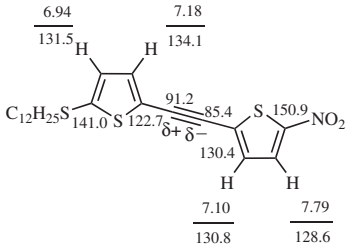
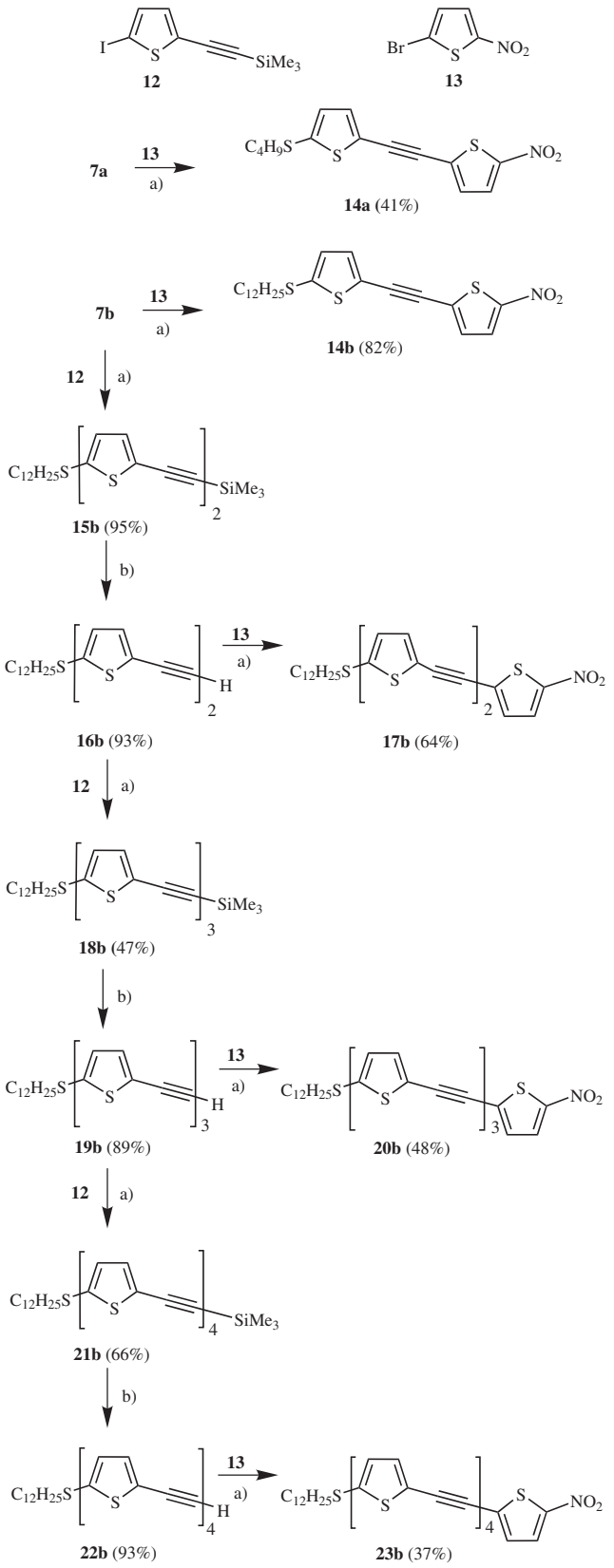


Figure 2 Assignment of the ^1H and ^{13}C chemical shifts of **14b** on the basis of 2D-NMR measurements (HMQC and HMBC) in $CDCl_3$

The uniform oligomeric structures of the two precursor series **6b**, **15b**, **18b**, **21b** and **7b**, **16b**, **19b**, **22b** as well as the target oligomer series **14b**, **17b**, **20b** and **23b** can be best assessed by the ^{13}C NMR data summarized in Table 1.

The intramolecular charge transfer (ICT) in the long-wavelength absorption, the so-called charge transfer band, provides a further criterion for the D–π–A interaction. The effect is strong for the small distance of D and A in **14b**. Whereas dithienylacetylene (Figure 1, $R^1 = R^2 = H$, n = 1) has in $CHCl_3$ a λ_{max} value of 317 nm,



Scheme 3 Preparation of the DAOTE series **14a**,**b**; **17b**; **20b**; **23b**: a) $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, NEt_3, toluene; b) K_2CO_3, MeOH–CH_2Cl_2 (1:1).

Table 1 ^{13}C Chemical Shifts of the Precursor Oligomer Series **6b**, **15b**, **18b**, **21b** and **7b**, **16b**, **19b**, **22b** and the DAOTEs **14b**, **17b**, **20b** and **23b** ($CDCl_3$/TMS, δ)

Product	sp^2-C		sp-C		sp^3-C	
	CH	C_q	CH	C_q	CH_2	CH_3
6b	132.0, 132.8	125.6, 137.4		97.1, 99.04	22.7, 28.4, 29.1, 29.3, 29.4, 29.5, 29.6, 29.6, 29.7, 31.9, 38.9	–0.2, 14.1
15b	131.7, 132.1, 132.5, 132.7	124.0, 124.7, 125.0, 138.5		86.4, 86.7, 96.8, 100.5	22.6, 28.4, 29.1, 29.3, 29.4, 29.5, 29.6, 29.6, 29.7, 31.9, 38.6	–0.2, 14.1
18b	132.0, 132.1, 132.3, 132.6, 132.8, 132.8	123.7, 124.2, 124.6, 124.7, 125.3, 138.7		86.4, 86.6, 87.1, 87.4, 96.7, 100.7	22.6, 28.4, 29.1, 29.3, 29.4, 29.5, 29.6, 29.6, 29.6, 31.9, 38.6	–0.2, 14.1
21b	132.1, 132.1, 132.1, 132.4, 132.4, 132.4, 132.6, 132.8	123.6, 124.0, 124.4, 124.5, 124.6, 124.9, 125.3, 138.7		86.3, 86.5, 87.0, 87.2, 87.3, 87.5, 96.7, 100.7	22.6, 28.4, 29.1, 29.3, 29.4, 29.5, 29.5, 29.6, 29.6, 31.9, 38.6	–0.3, 14.1
7b	131.9, 133.3,	124.4, 137.8	81.7	77.2	22.7, 28.4, 29.1, 29.3, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9, 38.9	14.1
16b	131.6, 132.1, 132.7, 132.9	123.6, 124.6, 124.6, 138.6	82.4	76.5, 86.2, 86.8	22.6, 28.4, 29.1, 29.3, 29.4, 29.4, 29.5, 29.6, 29.7, 31.9, 38.6	14.1
19b	132.0, 132.0, 132.1, 132.4, 132.8, 133.0	123.9, 124.0, 124.1, 124.6, 124.8, 138.7	82.4	76.3, 86.3, 86.7, 86.9, 87.4	22.6, 28.4, 29.1, 29.3, 29.4, 29.5, 29.5, 29.6, 29.7, 31.9, 38.5	14.1
22b	132.1, 132.1, 132.1, 132.4, 132.4, 132.5, 132.8, 132.8	124.0, 124.1, 124.4, 124.5, 124.6, 124.9, 124.9, 138.7	82.6	76.3, 86.3, 86.6, 87.0, 87.0, 87.3, 87.4	22.7, 28.4, 29.1, 29.3, 29.4, 29.5, 29.5, 29.6, 29.6, 31.9, 38.6	14.1
14b	128.6, 130.8, 131.5, 134.1	122.7, 130.4, 141.0, 150.9		85.4, 91.2	22.7, 28.4, 29.1, 29.3, 29.4, 29.5, 29.6, 29.6, 29.7, 31.9, 38.4	14.1
17b	128.6, 131.2, 132.0, 132.3, 132.7, 133.8	122.7, 123.9, 124.3, 129.8, 141.0, 150.8		85.8, 86.3, 86.8, 90.6	22.7, 28.4, 29.1, 29.3, 29.4, 29.5, 29.6, 29.6, 29.7, 31.9, 38.4	14.1
20b	128.6, 131.2, 132.0, 132.3, 132.4, 132.5, 132.7, 133.8	122.7, 123.3, 123.9, 124.5, 125.1, 129.8, 141.0, 150.8		85.8, 86.3, 86.8, 87.5, 87.7, 90.6	22.7, 28.4, 29.1, 29.3, 29.4, 29.5, 29.6, 29.6, 29.7, 31.9, 38.5	14.1
23b	128.5, 131.2, 132.1, 132.1, 132.4, 132.5, 132.5, 123.7, 132.8, 133.7	122.9, 124.0, 124.1, 124.6, 124.9, 125.0, 126.1, 129.8, 138.8, 151.3		86.1, 86.3, 86.8, 86.9, 87.5, 87.5, 88.0, 90.8	22.7, 28.4, 29.1, 29.3, 29.4, 29.4, 29.5, 29.6, 29.7, 31.9, 38.6	14.1

14b exhibits an absorption maximum λ_{max} = 413 nm. The bathochromic shift decreases then very fast with increasing conjugation (increasing numbers *n* of repeat units) (Table 2 and Figure 3). The convergence value of the series $\lambda\infty$ = 428 ± 1 nm is already reached for the trimer;[1a,20] thus, the effective conjugation length n_{ECL} is extremely low for a linearly conjugated system.[18–22] Nevertheless, the DAOTE series with terminal NO_2 and $SC_{12}H_{25}$ groups is a monotonous bathochromic series[1a] – in contrast to the related DAOTE series with OCH_3 groups as stronger donor groups.[1a,20]

The UV/Vis spectra were obtained with a Zeiss MCS 320/340 spectrometer, the FT-IR spectra with a Perkin-Elmer GX/2000 spectrometer. The ^1H and ^{13}C NMR spectra were measured with the Bruker spectrometers AC 200 and AMX 400. $CDCl_3$ served as solvent and TMS as internal standard. The FD-MS measurements were performed on a Finnigan MAT 95 spectrometer. Silica gel (Merck,

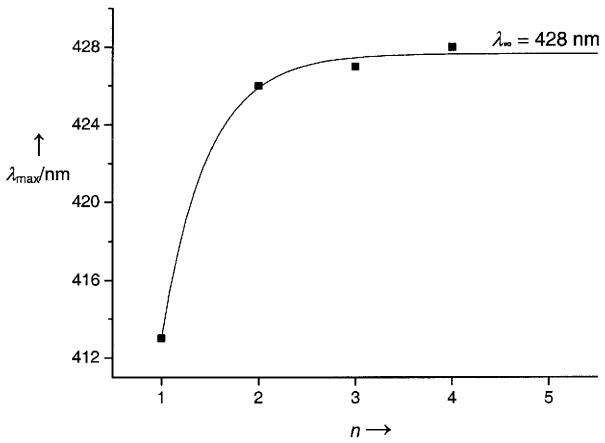


Figure 3 Long-wavelength absorption maxima of the DAOTE series **14b**, **17b**, **20b**, **23b** in $CHCl_3$ and their convergence to λ_∞ [The exponential fit corresponds to $\lambda(n) = \lambda_\infty - (\lambda_\infty - \lambda_1)e^{-2.12\ (n-1)}$].

Table 2 Long-Wavelength Absorption Maxima of the DAOTEs **14b**, **17b**, **20b**, **23b** in $CHCl_3$

Compound	*n*	λ_{max}[nm]	ε_{max}[$cm^2 \cdot mmol^{-1}$]
14b	1	413	24.2×10^3
17b	2	426	37.3×10^3
20b	3	427	45.6×10^3
23b	4	428	58.9×10^3

70–230 mesh ASTM) was used for column chromatography. Petroleum ether (PE) used refers to the fraction boiling at 40–70 °C.

The compounds **1**,[23] **12**[24] and **13**[24] were prepared according to literature; compounds **2**, **5a**, **5b** and **8** are commercially available.

Sonogashira–Hagihara Coupling; General Procedure A

Equivalent amounts of iodine component and ethynyl component were dissolved in an anhyd mixture of toluene and Et_3N (about 1:1). The solution was degassed and purged with argon. $Pd(PPh_3)_2Cl_2$ (ca. 0.025 equiv), CuI (ca. 0.05 equiv) and PPh_3 (ca. 0.05 equiv) were added under argon. (Twofold amounts of catalysts did not change the yields.) After stirring overnight at r.t., the volatile parts were evaporated in vacuo and the residue was dissolved in $CHCl_3$. The solution was washed with equal volumes of aq sat. NH_4Cl, $NaHCO_3$ and NaCl solutions. After drying (Na_2SO_4), the solvent was removed and the residue purified by column chromatography on SiO_2. The solvent used for elution depended on the chain lengths of the oligomer (see below). Solid products were purified by recrystallization from the solvent mentioned for each product.

Deprotection of the Ethynyl Groups; General Procedure B

To the trimethylsilylethynyl compound (1 equiv) dissolved in CH_2Cl_2–MeOH (1:1), was added K_2CO_3 (ca. 1.1 equiv). The stirred reaction mixture was kept at r.t. until the TLC (SiO_2/toluene) indicated the end of the cleavage. The solvent was removed in vacuo, the residue dissolved in $CHCl_3$, washed with H_2O (3 ×) and dried (Na_2SO_4). Evaporation led to the crude product, which was purified by column chromatography (SiO_2/solvent described for each case) and/or recrystallization.

2-Bromo-5-(trimethylsilylethynyl)thiophene (3)

A mixture of **1** (30.00 g, 104 mmol), **2** (10.3 g, 105 mmol), $Pd(PPh_3)_2Cl_2$ (1.03 g, 2.6 mmol), CuI (0.99 g, 5.2 mmol) and PPh_3 (1.36 g, 5.2 mmol) was reacted in toluene/Et_3N (130 mL) according to the general procedure A. Column chromatography (10 × 20 cm SiO_2, PE) yielded 26.32 g (98%) of a viscous oil.

^{1}H NMR ($CDCl_3$): δ = 0.23 (s, 9 H, CH_3), 6.87/6.94 (AB, ^3J = 4.0 Hz, 2 H, 3-H, 4-H).

^{13}C NMR ($CDCl_3$): δ = –0.2 (CH_3), 96.4, 101.1 (C≡C), 113.1 (C-2), 125.0 (C-5), 129.8, 132.8 (C-3, C-4).

FD-MS: *m*/*z* (%) = 260/258 (100, M^+, Br isotope pattern).

Anal. Calcd for $C_9H_{11}BrSSi$ (259.2): C, 41.70; H, 4.28; S, 12.37. Found: C, 41.31; H, 3.96; S, 12.50.

2-Butylthio-5-(trimethylsilylethynyl)thiophene (6a)

To 2-bromo-5-(trimethylsilylethynyl)thiophene (**3**; 9.0 g, 34.7 mmol) in anhyd Et_2O (25 mL), was added dropwise a 2.5 M solution of *n*-BuLi in *n*-hexane (13.8 mL, 34.7 mmol) at –78 °C. After stirring for 1 h under argon, powdered sulfur (1.4 g, 43.7 mmol) was added and the reaction stopped after 2 h at 0 °C. H_2O (10 mL) was slowly added and the mixture stirred for 30 min. To the filtered mixture was added CH_2Cl_2 (50 mL). After extraction with H_2O (2 × 50 mL), the organic layer was dried (Na_2SO_4) and evaporated. Column chromatography (3 × 30 cm SiO_2, PE) afforded 1.44 g (15%) of a viscous oil. The yield was enhanced to about 70% when equimolar amounts of **5a** were added after the addition of sulfur and stirring was continued overnight at r.t.

^{1}H NMR ($CDCl_3$): δ = 0.25 (s, 9 H, CH_3), 0.87 (t, ^3J = 6.7 Hz, 3 H, CH_3), 1.32–1.44 (m, 2 H, CH_2), 1.52–1.62 (m, 2 H, CH_2), 2.80 (t, ^3J = 7.3 Hz, 2 H, SCH_2), 7.05 (d, ^3J = 3.3 Hz, 1 H, 3-H), 7.21 (d, ^3J = 3.3 Hz, 1 H, 4-H).

^{13}C NMR ($CDCl_3$): δ = –0.2 [$Si(CH_3)_3$], 13.5 (CH_3), 21.5 (CH_2), 31.4 (CH_2), 38.3 (SCH_2), 85.0/85.4 (C≡C), 128.6 (C-5), 133.4, 133.5 (C-3, C-4), 144.1 (C-2).

FD-MS: *m*/*z* (%) = 268 (100, M^+).

Anal. Calcd for $C_{13}H_{20}S_2Si$ (268.5): C, 58.15; H, 7.51; S, 23.88. Found: C, 58.22; H, 7.43; S, 23.60.

2-Butylthio-5-ethynylthiophene (7a)

Following the general procedure B, **6a** (1.44 g, 5.4 mmol) and K_2CO_3 (0.85 g, 5.9 mmol) in CH_2Cl_2–MeOH (20 mL, 1:1) afforded a colorless oil, which was purified by column chromatography (4 × 40 cm SiO_2, PE); yield: 0.53 g (50% based on **6a**).

^{1}H NMR ($CDCl_3$): δ = 0.88 (t, ^3J = 6.7 Hz, 3 H, CH_3), 1.33–1.44 (m, 2 H, CH_2), 1.52–1.63 (m, 2 H, CH_2), 2.80 (t, ^3J = 7.3 Hz, 2 H, SCH_2), 3.34 (s, 1 H, C≡CH), 6.90 (d, ^3J = 3.6 Hz, 1 H, 3-H), 7.10 (d, ^3J = 3.6 Hz, 1 H, 4-H).

^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 21.5 (CH_2), 31.4 (CH_2), 38.3 (SCH_2), 77.2/81.7 (C≡C), 124.4 (C-5), 131.9, 133.3 (C-3, C-4), 137.8 (C-2).

FD-MS: *m*/*z* (%) = 196 (100, M^+).

Anal. Calcd for $C_{10}H_{12}S_2$ (196.3): C, 61.18; H, 6.16; S, 32.66. Found: C, 61.34; H, 6.08; S, 32.50.

2-(Dodecylthio)thiophene (10)

To thiophene (**8**; 5.0 g, 59.5 mmol) in anhyd THF (20 mL), was added dropwise a 2.5 M solution of *n*-BuLi in *n*-hexane (23.8 mL, 59.5 mmol) at –10 °C. After stirring for 1 h under argon, powdered sulfur (2.56 g, 80.0 mmol) was added and the mixture warmed within 2 h to r.t. 1-Iodododecane (**5b**; 17.6 g, 59.5 mmol) was added and the stirring continued for 16 h. The volatile parts of the reaction mixture were evaporated and the residue was dissolved in CH_2Cl_2. The filtered solution was extracted with H_2O (3 × 50 mL), dried (Na_2SO_4) and distilled to give a viscous oil; yield: 10.5 g (70%); bp 154 °C/200 Pa.

^{1}H NMR ($CDCl_3$): δ = 0.88 (t, ^3J = 6.6 Hz, 3 H, CH_3), 1.12–1.38 (m, 18 H, CH_2), 1.54–1.63 (m, 2 H, CH_2), 2.77 (t, ^3J = 7.4 Hz, 2 H, SCH_2), 6.94 (dd, ^3J = 5.4 Hz, ^3J = 3.7 Hz, 1 H, 4-H), 7.08 (dd, ^3J = 3.7 Hz, ^4J = 1.1 Hz, 1 H, 3-H), 7.29 (dd, ^3J = 5.4 Hz, ^4J = 1.1 Hz, 1 H, 5-H).

^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 28.4, 28.5, 29.1, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (CH_2), 38.9 (SCH_2), 127.4 (C-3), 128.8 (C-5), 133.1 (C-4), 135.1 (C-2).

FD-MS: *m*/*z* (%) = 284 (100, M^+).

Anal. Calcd for $C_{16}H_{28}S_2$ (284.5): C, 67.54; H, 9.92; S, 22.54. Found: C, 67.67; H, 9.85; S, 22.42.

2-Dodecylthio-5-iodothiophene (11)

To compound **10** (1.0 g, 3.5 mmol) in anhyd benzene (10 mL), were slowly added yellow HgO (0.77 g, 3.5 mmol) and I_2 (0.92 g, 3.6 mmol) at 0 °C. The mixture was vigorously stirred till the color (caused by the I_2) faded, filtered and the solvent removed. Purification by column chromatography (5 × 30 cm SiO_2, PE) yielded 0.87 g (60%) of a yellow oil.

^{1}H NMR ($CDCl_3$): δ = 0.87 (t, ^3J = 6.7 Hz, 3 H, CH_3), 1.12–1.38 (m, 18 H, CH_2), 1.53–1.64 (m, 2 H, CH_2), 2.74 (t, ^3J = 7.4 Hz, 2 H, SCH_2), 6.76 (d, ^3J = 3.7 Hz, 1 H, 3-H), 7.06 (d, ^3J = 3.7 Hz, 1 H, 4-H).

^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7/28.3/28.3/29.1/29.3/29.4/29.5/29.6/29.6/31.9 (CH_2), 39.1 (SCH_2), 75.1 (C-5), 134.8 (C-3), 137.4 (C-4), 140.6 (C-2).

FD-MS: *m*/*z* (%) = 410 (100, M^+).

Anal. Calcd for $C_{16}H_{27}IS_2$ (410.4): C, 46.82; H, 6.63; S, 15.62. Found: C, 46.59; H, 6.74; S, 15.55.

2-Dodecylthio-5-(trimethylsilylethynyl)thiophene (6b)

Following the general procedure A, a mixture of **11** (0.51 g, 1.24 mmol), **2** (0.12 g, 1.24 mmol), $Pd(PPh_3)_2Cl_2$ (11.8 mg, 0.03 mmol), CuI (11.8 mg, 0.06 mmol), PPh_3 (16.3 mg, 0.06 mmol) and Et_3N (5 mL, 3.63 g, 35.87 mmol) in toluene (5 mL) yielded **6b** as a viscous colorless oil. Column chromatography (3 × 40 cm SiO_2, PE) afforded 0.50 g (87%) of analytically pure product.

^{1}H NMR ($CDCl_3$): δ = 0.24 [s, 9 H, $Si(CH_3)_3$], 0.87 (t, ^3J = 6.7 Hz, 3 H, CH_3), 1.12–1.38 (m, 18 H, CH_2), 1.50–1.63 (m, 2 H, CH_2), 2.79 (t, ^3J = 7.4 Hz, 2 H, SCH_2), 7.05 (d, ^3J = 3.3 Hz, 1 H, 3-H), 7.21 (d, ^3J = 3.3 Hz, 1 H, 4-H).

FD-MS: *m*/*z* (%) = 380 (100, M^+).

Anal. Calcd for $C_{21}H_{36}S_2Si$ (380.7): C, 66.25; H, 9.53; S, 16.84. Found: C, 66.06; H, 9.67; S, 16.58.

2-Dodecylthio-5-ethynylthiophene (7b)

Reaction of **6b** (2.10 g, 5.52 mmol) and K_2CO_3 (0.84 g, 6.06 mmol) in MeOH–CH_2Cl_2 (20 mL, 1:1) afforded – according to the general procedure B described above – a viscous oil, which was purified by column chromatography (8 × 30 cm SiO_2, PE); yield: 1.51 g (89%).

^{1}H NMR ($CDCl_3$): δ = 0.87 (t, ^3J = 6.8 Hz, 3 H, CH_3), 1.12–1.38 (m, 18 H, CH_2), 1.50–1.64 (m, 2 H, CH_2), 2.79 (t, ^3J = 7.4 Hz, 2 H, SCH_2), 3.33 (s, 1 H, C≡CH), 6.89 (d, ^3J = 3.7 Hz, 1 H, 3-H), 7.09 (d, ^3J = 3.7 Hz, 1 H, 4-H).

FD-MS: *m*/*z* (%) = 308 (100, M^+).

Anal. Calcd for $C_{18}H_{28}S_2$ (308.5): C, 70.07; H, 9.15; S, 20.78. Found: C, 69.89; H, 9.22; S, 20.66.

2-[5-(Butylthio)thien-2-ylethynyl]-5-nitrothiophene (14a)

Following the general procedure A, a mixture of **7a** (0.53 g, 2.7 mmol), **13** (0.56 g, 2.7 mmol), $Pd(PPh_3)_2Cl_2$ (0.028 g, 0.07 mmol), CuI (0.026 g, 0.14 mmol), PPh_3 (0.037 g, 0.14 mmol) in Et_3N–toluene (12 mL, 1:1) afforded a red oil, which was purified by column chromatography (3 × 50 cm SiO_2, PE); yield: 0.36 g (41%).

IR (neat): 2189 cm^{-1} (C≡C).

^{1}H NMR ($CDCl_3$): δ = 0.89 (t, ^3J = 6.7 Hz, 3 H, CH_3), 1.37–1.47 (m, 2 H, CH_2), 1.55–1.65 (m, 2 H, CH_2), 2.86 (t, ^3J = 7.4 Hz, 2 H, SCH_2), 6.95 (d, ^3J = 3.8 Hz, 1 H, 4-$H_{thienyl}$), 7.10 (d, ^3J = 4.4 Hz, 3-H), 7.19 (d, ^3J = 3.8 Hz, 1 H, 3-$H_{thienyl}$), 7.80 (d, ^3J = 4.4 Hz, 1 H, 4-H).

^{13}C NMR ($CDCl_3$): δ = 13.5 (CH_3), 21.6 (CH_2), 31.4 (CH_2), 38.1 (SCH_2), 85.4, 91.2 (C≡C), 122.8, 130.4, 140.9, 150.9 (C_q), 128.6, 130.8, 131.6, 134.1 (CH).

FD-MS: *m*/*z* (%) = 323 (100, M^+).

Anal. Calcd for $C_{14}H_{13}NO_2S_3$ (323.5): C, 51.99; H, 4.05; S, 29.74. Found: C, 52.04; H, 4.08; S, 29.88.

2-[5-(Dodecylthio)thien-2-ylethynyl]-5-nitrothiophene (14b)

Following the general procedure A, a mixture of **7b** (0.36 g, 1.16 mmol), **13** (0.24 g, 1.16 mmol), $Pd(PPh_3)_2Cl_2$ (11.2 mg, (0.028 mmol), CuI (10.7 mg, 0.056 mmol), and PPh_3 (14.7 mg, 0.056 mmol) in a Et_3N (20 mL, 14.52 g, 143 mmol)/toluene (20 mL) afforded a viscous red oil, which was purified by column chromatography (4 × 40 cm SiO_2, PE–CH_2Cl_2, 1:1); yield: 0.40 g (82%).

IR (neat): 2189 cm^{-1} (C≡C).

^{1}H NMR ($CDCl_3$): δ = 0.85 (t, ^3J = 6.7 Hz, 3 H, CH_3), 1.12–1.37 (m, 18 H, CH_2), 1.59–1.69 (m, 2 H, CH_2), 2.84 (t, ^3J = 7.4 Hz, 2 H, SCH_2), 6.94 (d, ^3J = 3.9 Hz, 1 H, 4-$H_{thienyl}$), 7.10 (d, ^3J = 4.4 Hz, 1 H, 3-H), 7.18 (d, ^3J = 3.9 Hz, 1 H, 3-$H_{thienyl}$), 7.79 (d, ^3J = 4.4 Hz, 1 H, 4-H).

FD-MS: *m*/*z* (%) = 435 (100, M^+).

Anal. Calcd for $C_{22}H_{29}NO_2S_3$ (435.7): C, 60.65; H, 6.71; N, 3.21; S, 22.08. Found: C, 60.48; H, 6.97; N, 3.14; S, 21.98.

2-[5-(Dodecylthio)thien-2-ylethynyl]-5-trimethylsilylethynylthiophene (15b)

Following the general procedure A, a mixture of **7b** (200 mg, 0.65 mmol), **12** (190 mg, 0.65 mmol), $Pd(PPh_3)_2Cl_2$ (6.3 mg, 0.016 mmol), CuI (6.1 mg, 0.032 mmol) and PPh_3 (8.4 mg, 0.032 mmol) in Et_3N (5 mL, 3.63 g, 35.87 mmol)/toluene (5 mL) afforded a yellowish viscous oil, which was purified by column chromatography (8 × 25 cm SiO_2, PE–CH_2Cl_2, 2:1); yield: 300 mg (95%).

^{1}H NMR ($CDCl_3$): δ = 0.23 [s, 9 H, $Si(CH_3)_3$], 0.86 (t, ^3J = 6.6 Hz, 3 H, CH_3), 1.12–1.37 (m, 18 H, CH_2), 1.57–1.67 (m, 2 H, CH_2), 2.81 (t, ^3J = 7.4 Hz, 2 H, SCH_2), 6.92 (d, ^3J = 3.7 Hz, 1 H, 4-$H_{thienyl}$), 7.04 (d, ^3J = 3.9 Hz, 1 H, 3-H), 7.07 (d, ^3J = 3.9 Hz, 1 H, 4-H), 7.10 (d, ^3J = 3.7 Hz, 1 H, 3-$H_{thienyl}$).

FD-MS: *m*/*z* (%) = 486 (100, M^+).

Anal. Calcd for $C_{27}H_{38}S_3Si$ (486.9): C, 66.61; H, 7.87; S, 19.76. Found: C, 66.49; H, 7.68; S, 19.56.

2-[5-(Dodecylthio)thien-2-ylethynyl]-5-ethynylthiophene (16b)

Following the general procedure B, reaction of **15b** (300 mg, 0.62 mmol) with K_2CO_3 (90 mg, 0.65 mmol) in MeOH–CH_2Cl_2 (20 mL, 1:1) afforded a yellowish viscous oil, which was purified by column chromatography (8 × 30 cm SiO_2, PE–CH_2Cl_2, 3:1); yield: 240 mg (93%).

^{1}H NMR ($CDCl_3$): δ = 0.86 (t, ^3J = 6.7 Hz, 3 H, CH_3), 1.11–1.36 (m, 18 H, CH_2), 1.57–1.67 (m, 2 H, CH_2), 2.81 (t, ^3J = 7.4 Hz, 2 H, SCH_2), 3.36 (s, 1 H, C≡CH), 6.93 (d, ^3J = 4.1 Hz, 1 H, 4-$H_{thienyl}$), 7.07 (d, ^3J = 3.7 Hz, 1 H, 3-H), 7.10 (d, ^3J = 4.1 Hz, 1 H, 3-$H_{thienyl}$), 7.12 (d, ^3J = 3.7 Hz, 1 H, 4-H).

FD-MS: *m*/*z* (%) = 414 (100, M^+).

Anal. Calcd for $C_{24}H_{30}S_3$ (414.7): C, 69.51; H, 7.29; S, 23.20; Found: C, 69.38; H, 7.22; S, 23.08.

Dimer 17b

Following the general procedure A, a mixture of **16b** (0.25 g, 0.60 mmol), **13** (0.13 g, 0.60 mmol), $Pd(PPh_3)_2Cl_2$ (5.9 mg, 0.015 mmol), CuI (5.5 mg, 0.029 mmol), PPh_3 (7.9 mg, 0.03 mmol) in Et_3N (5 mL, 3.63 g, 35.87 mmol)/toluene (5 mL) afforded red crystals, which were purified by column chromatography (3 × 40 cm SiO_2, PE–CH_2Cl_2, 1:1) and recrystallization from PE; yield: 0.21 g (64%); mp 38 °C.

IR (KBr): 2184 cm^{-1} (C≡C).

^{1}H NMR ($CDCl_3$): δ = 0.85 (t, ^3J = 6.7 Hz, 3 H, CH_3), 1.10–1.37 (m, 18 H, CH_2), 1.57–1.68 (m, 2 H, CH_2), 2.84 (t, ^3J = 7.4 Hz, 2 H, SCH_2), 6.94/7.10 (AB, ^3J = 4.1 Hz, 2 H, thiophene, donor side), 7.18 (m, 2 H, thiophene, center), 7.18/7.80 (AB, ^3J = 4.4 Hz, 2 H, thiophene, acceptor side).

FD-MS: *m*/*z* (%) = 542 (100, M^+).

Anal. Calcd for $C_{28}H_{31}NO_2S_4$ (541.8): C, 62.07; H, 5.77; N, 2.59; S, 23.67. Found: C, 61.89; H, 5.79; N, 2.34; S, 23.78.

Trimer 18b

Following the general procedure A, a mixture of **16b** (0.13 g, 0.31 mmol), **12** (0.10 g, 0.31 mmol), $Pd(PPh_3)_2Cl_2$ (3.1 mg, 0.008 mmol), CuI (2.9 mg, 0.015 mmol), PPh_3 (3.9 mg, 0.015 mmol) in Et_3N (5 mL, 3.63 g, 35.87 mmol)/toluene (5 mL) afforded yellow crystals, which were purified by column chromatography (8 × 25 cm SiO_2, PE–CH_2Cl_2, 9:1); yield: 0.09 g (47%); mp 84 °C.

^{1}H NMR ($CDCl_3$): δ = 0.24 (s, 9 H, CH_3), 0.86 (t, ^3J = 6.7 Hz, 3 H, CH_3), 1.12–1.36 (m, 18 H, CH_2), 1.57–1.68 (m, 2 H, CH_2), 2.82 (t, ^3J = 7.3 Hz, 2 H, SCH_2), 6.93/7.12 (AB, ^3J = 3.7 Hz, 2 H, $SC_{12}H_{25}$-substituted thiophene ring), 7.08 ('s', 2 H, central thiophene ring), 7.11/7.13 (AB ^3J = 3.7 Hz, 2 H, thiophene).

Anal. Calcd for $C_{33}H_{40}S_4Si$ (593.0): C, 66.84; H, 6.80; S, 21.63. Found: C, 66.73; H, 6.92; S, 21.70.

Trimer 19b

Cleavage of **18b** (0.088 g, 0.15 mmol) with K_2CO_3 (0.023 g, 0.16 mmol) in CH_2Cl_2–MeOH (10 mL, 1:1) according to the general procedure B, gave 0.080 g (98%) of **19b**. Recrystallization from the same solvent mixture yielded yellow crystals; mp 62 °C.

^{1}H NMR ($CDCl_3$): δ = 0.86 (t, ^3J = 6.7 Hz, 3 H, CH_3), 1.11–1.35 (m, 18 H, CH_2), 1.57–1.68 (m, 2 H, CH_2), 2.81 (t, ^3J = 7.4 Hz, 2 H, SCH_2), 3.36 (s, 1 H, C≡CH), 6.94 (d, ^3J = 3.7 Hz, 1 H, $C_{12}H_{25}$S-substituted thiophene ring), 7.10–7.15 (m, 5 H, thiophene rings).

FD-MS: *m*/*z* (%) = 520 (100, M^+).

Anal. Calcd for $C_{30}H_{32}S_4$ (520.8): C, 69.18; H, 6.19; S, 24.62. Found: C, 69.03; H, 6.30; S, 24.55.

Trimer 20b

A mixture of **19b** (0.25 g, 0.60 mmol), **13** (0.13 g, 0.60 mmol), $Pd(PPh_3)_2Cl_2$ (5.9 mg, 0.015 mmol), CuI (5.5 mg, 0.029 mmol) and PPh_3 (7.9 mg, 0.030 mmol) was reacted in Et_3N (5 mL, 3.63 g, 35.87 mmol)/toluene (5 mL) according to the general procedure A. Column chromatography (3 × 40 cm SiO_2, PE–CH_2Cl_2, 1: 1) and recrystallization of the product from PE afforded 0.21 g (48%) of red crystals; mp 76 °C.

IR (KBr): 2180 cm^{-1} (C≡C).

^{1}H NMR ($CDCl_3$): δ = 0.85 (t, ^3J = 6.7 Hz, 3 H, CH_3), 1.12–1.38 (m, 18 H, CH_2), 1.58–1.70 (m, 2 H, CH_2), 2.84 (t, ^3J = 7.4 Hz, 2 H, SCH_2), 6.94/7.10 (AB, ^3J = 4.1 Hz, 2 H, $C_{12}H_{25}$S-substituted thiophene ring), 7.16 (m, 4 H, inner thiophene rings), 7.16/7.80 (AB, ^3J = 4.4 Hz, 2 H, NO_2-substituted thiophene ring).

FD-MS: *m*/*z* (%) = 648 (100, $[M + H^+]$).

Anal. Calcd for $C_{34}H_{33}NO_2S_5$ (648.0): C, 63.03; H, 5.13; N, 2.16; S, 24.74. Found: C, 62.88; H, 5.39; N, 2.34; S, 24.70.

Tetramer 21b

A mixture of **19b** (0.077 g, 0.15 mmol), **12** (0.046 g, 0.15 mmol), $Pd(PPh_3)_2Cl_2$ (1.6 mg, 0.004 mmol), CuI (1.5 mg, 0.008 mmol), and PPh_3 (2.1 mg, 0.008 mmol) was reacted according to the general procedure A in Et_3N (5 mL, 3.63 g, 35.87 mmol)/toluene (5 mL). Column chromatography (8 × 30 cm SiO_2, PE–CH_2Cl_2, 3:1) afforded 0.069 g (66%) of yellow crystals; mp 109 °C.

^{1}H NMR ($CDCl_3$): δ = 0.22 (s, 9 H, CH_3), 0.86 (t, ^3J = 6.7 Hz, 3 H, CH_3), 1.10–1.37 (m, 18 H, CH_2), 1.56–1.66 (m, 2 H, CH_2), 2.82 (t, ^3J = 7.4 Hz, 2 H, SCH_2), 6.94/7.15 (AB, ^3J = 3.7 Hz, 2 H, $C_{12}H_{25}$S-substituted thiophene ring), 7.08–7.16 (m, 6 H, thiophene rings).

Anal. Calcd for $C_{39}H_{42}S_5Si$ (699.2): C, 67.00; H, 6.05; S, 22.93 Found: C, 66.85; H, 5.95; S, 23.02

Tetramer 22b

Cleavage of **21b** (69 mg, 0.10 mmol) with K_2CO_3 (15 mg, 0.11 mmol) in CH_2Cl_2–MeOH (10 mL, 1:1) according to the general procedure B afforded yellow crystals which were recrystallized from CH_2Cl_2–MeOH (1:1); yield: 53 mg (85%); mp 93 °C.

^{1}H NMR ($CDCl_3$): δ = 0.85 (t, ^3J = 6.6 Hz, 3 H, CH_3), 1.10–1.36 (m, 18 H, CH_2), 1.58–1.68 (m, 2 H, CH_2), 2.82 (t, ^3J = 7.4 Hz, 2 H, SCH_2), 3.38 (s, 1 H, C≡C), 6.94/7.15 (AB, ^3J = 4.0 Hz, 2 H, $C_{12}H_{25}$S-substituted thiophene ring), 7.11–7.16 (m, 6 H, thiophene rings).

Anal. Calcd for $C_{36}H_{34}S_5$ (627.0): C, 68.97; H, 5.47; S, 25.57. Found: C, 68.80; H, 5.65; S, 25.49.

Tetramer 23b

A mixture of **22b** (58.6 mg, 0.09 mmol), **13** (19.5 mg, 0.09 mmol), $Pd(PPh_3)_2Cl_2$ (0.8 mg, 0.002 mmol), CuI (0.9 mg, 0.005 mmol), and PPh_3 (1.3 mg, 0.005 mmol) was reacted in Et_3N (5 mL, 3.63 g, 35.87 mmol)/toluene (5 mL) according to the general procedure A. Purification by column chromatography (8 × 20 cm SiO_2, PE–CH_2Cl_2 1:3) and recrystallization from CH_2Cl_2–MeOH (1:1) yielded 26 mg (37%) red crystals; mp 117 °C.

IR (KBr): 2176 cm^{-1} (C≡C).

^{1}H NMR ($CDCl_3$): δ = 0.86 (t, ^3J = 6.6 Hz, 3 H, CH_3), 1.09–1.37 (m, 18 H, CH_2), 1.58–1.69 (m, 2 H, CH_2), 2.82 (t, ^3J = 7.4 Hz, 2 H, SCH_2), 6.94 (d, ^3J = 3.7 Hz, 1 H, $C_{12}H_{25}$S-substituted thiophene ring), 7.81 (d, ^3J = 4.4 Hz, 1 H, NO_2-substituted thiophene ring), 7.12–7.23 (m, 8 H, remaining H of thiophene rings).

FD-MS: *m*/z (%) = 754 (100, $[M + H^+]$).

Anal. Calcd for $C_{40}H_{35}NO_2S_6$ (754.1): C, 63.71; H, 4.68; N, 1.86; S, 25.51. Found: C, 63.57; H, 4.77; N, 1.69; S, 25.24.

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References

(1) (a) Meier, H. *Angew. Chem. Int. Ed.* **2005**, *44*, 2482; *Angew. Chem.* **2005**, *117*, 2536; and references cited therein. (b) Martin, R. E.; Diederich, F. *Angew. Chem. Int. Ed.* **1999**, *38*, 1350; *Angew. Chem.* **1999**, *111*, 1440. (c) *Electronic Materials: The Oligomer Approach*; Müllen, K.; Wegner, G., Eds.; Wiley-VCH: Weinheim, **1998**.
(2) Ringenbach, C.; De Nicola, A.; Ziessel, R. *J. Org. Chem.* **2003**, *68*, 4708.
(3) De Nicola, A.; Ringenbach, C.; Ziessel, R. *Tetrahedron Lett.* **2003**, *44*, 183.
(4) Obara, Y.; Takimiya, K.; Aso, Y.; Otsubo, T. *Tetrahedron Lett.* **2001**, *42*, 6877.
(5) Wu, R.; Schumm, J. S.; Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1996**, *61*, 6906.
(6) Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1376.
(7) Fujitsuka, M.; Makinoshima, T.; Ito, O.; Obara, Y.; Aso, T.; Otsubo, T. *J. Phys. Chem. B* **2003**, *107*, 739.
(8) Li, J.; Liao, L.; Pang, Y. *Tetrahedron Lett.* **2002**, *43*, 391.
(9) Pearson, D. L.; Jones, L. II; Schumm, J. S.; Tour, J. M. *Synth. Met.* **1997**, *84*, 303.
(10) Samuel, I. D. W.; Ledoux, I.; Delporte, C.; Pearson, D. L.; Tour, J. M. *Chem. Mater.* **1996**, *8*, 819.
(11) Geisler, T.; Petersen, J. C.; Bjoernholm, T.; Fischer, E.; Larsen, J.; Dehn, C.; Brédas, J.-L.; Tormos, G. V.; Nugara, P. N.; Lakshikantham, M. V.; Cava, M. P. *Synth. Met.* **1993**, *53*, 271.
(12) Pearson, D. L.; Schumm, J. S.; Tour, J. M. *Macromolecules* **1994**, *27*, 2348.

(13) Tormos, G. V.; Nugara, P. N.; Lakshikantham, M. V.; Cava, M. P. *Synth. Met.* **1993**, *53*, 271.
(14) Carpita, A.; Lessi, A.; Rossi, R. *Synthesis* **1984**, 571.
(15) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605; and references cited therein.
(16) (a) Higgins, R. W.; Garrett, R. *J. Org. Chem.* **1961**, *27*, 2168. (b) Jones, E.; Moodie, I. M. *Tetrahedron* **1965**, *21*, 2413. (c) Gronowitz, S. *Arkiv Kemi* **1958**, *13*, 269; *Chem. Abstr.* **1959**, *53*, 15056e.
(17) HMQC and HMBC contour plots for **14a** are depicted in: Hesse, M.; Meier, H.; Zeeh, B. *Spektroskopische Methoden in der organischen Chemie*, 7th ed.; Thieme: Stuttgart, **2005**, 193.
(18) Meier, H.; Gerold, J.; Kolshorn, H.; Mühling, B. *Chem. Eur. J.* **2004**, *10*, 360.
(19) Meier, H.; Mühling, B.; Kolshorn, H. *Eur. J. Org. Chem.* **2004**, 1033.
(20) Mühling, B. *Ph.D. Dissertation*; University of Mainz: Germany, **2004**.
(21) Meier, H.; Stalmach, U.; Kolshorn, H. *Acta Polym.* **1997**, *48*, 379.
(22) Ickenroth, D.; Weissmann, S.; Rumpf, N.; Meier, H. *Eur. J. Org. Chem.* **2002**, 2808.
(23) Raber, D. J. *J. Am. Chem. Soc.* **1971**, *93*, 4821.
(24) Meier, H.; Mühling, B.; Oehlhof, A.; Theisinger, S.; Kirsten, E. *Eur. J. Org. Chem.* **2006**, 405.