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Oligo(2,5-thienyleneethynylene)s with Terminal Donor-Acceptor Substitution

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Dedicated to Professor Horst Kunz on the occasion of his 65th birthday

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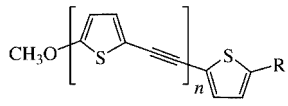
Five oligo(2,5-thienyleneethynylene) series (OTE, n = 1–5), namely the push-pull substituted compounds **1b**-**5b** and **1c**-**5c**, the purely donor substituted compounds **1a**-**5a** and two precursor series with protected and deprotected ethynyl end-groups, respectively, were obtained by a convergent synthetic strategy. The extension of the conjugated chromophores in the donor-acceptor OTE (DAOTE) series is superimposed by an intramolecular charge transfer (ICT), which decreases with an increasing number, n, of repeat units. The overall effect is studied by the convergence of the UV/Vis absorption maxima λ_{max} (n) → λ_∞ for $n \to \infty$.

Introduction

Conjugated oligomers are interesting target compounds for numerous applications in materials science. Among the variety of such compounds, push-pull systems D–π–A represent a special class which is characterized by typical electronic and optical properties.[1]

Several oligo(2,5-thienyleneethynylene)s (OTEs) (Scheme 1) were prepared in the past by applying C(sp)–C(sp^2) coupling reactions of the Sonogashira–Hagihara type.[2–15] Apart from normal end-groups, which are characteristic for this reaction, namly thienyl and/or free or protected ethynyl groups, some special end-groups such as formyl,[6] phenyl,[7] fluorene,[9] thioester,[7] fullerene[6] or 2,2′:6′,2′′-terpyridine[2,3] have been introduced. In order to improve the solubility, the repeat units normally contain alkyl substituents on the thiophene rings: 3-ethyl,[4,6–10,12] 3-hexyl,[5] or 3,4-dibutyl.[2,3]

We are studying push-pull OTE systems (DAOTE) with OCH_3 groups as terminal donor groups and CHO or NO_2 groups as terminal acceptor groups (Scheme 1). The purely donor-substituted series **1a**–**5a** (n = 1–5) shall be compared to the DAOTE series **1b**–**5b** (n = 1–5) and **1c**–**5c** (n = 1–5) in order to study the effect of the intramolecular charge transfer (ICT) when the conjugated chain is extended. Alkyl side chains were abandoned because they can enhance the torsional angles along the main chain of conjugated oligomers and therefore impair the conjugation to some extent.



R \ n	1	2	3	4	5
H	**1a**	**2a**	**3a**	**4a**	**5a**
CHO	**1b**	**2b**	**3b**	**4b**	**5b**
NO_2	**1c**	**2c**	**3c**	**4c**	**5c**

Scheme 1. Repeat unit in oligo- and poly(2,5-thienyleneethynylene)s and the target series **1**–**5**/**a**–**c**.

An exact comparison of the λ_{max} values of an oligomer series with alkyl substituents and the analogous series without alkyl substituents is difficult because electronic effects can be superimposed by possible torsional effects. In the present study of the ICT in DAOTEs, any additional deviation from the planarity of the chromophores would have a strong impact.

The ICT in conjugated oligomers with terminal donor-acceptor (DA) substitution depends not only on the strength of the donor and acceptor moieties, but also on the conjugated π-electron linker.[1] Benzene rings in the repeat units of the linker can lead to the unexpected effect that the long-wavelength absorption of the corresponding oligomer series exhibits a monotonously hypsochromic shift with increasing numbers of repeat units (increasing length of the chromophore). We established this effect for oligo-

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(phenyleneethynylene)s that have strong donor and strong acceptor groups (DAOPEs).[16,17] Since this effect is very important for the application of such rigid rods in nonlinear optics (NLO),[18] we are investigating OTEs as π-electron linkers. The crucial question is: how do 2,5-thienyleneethynylene repeat units tolerate the contribution of zwitterionic resonance structures, which are necessary for the ICT?[1]

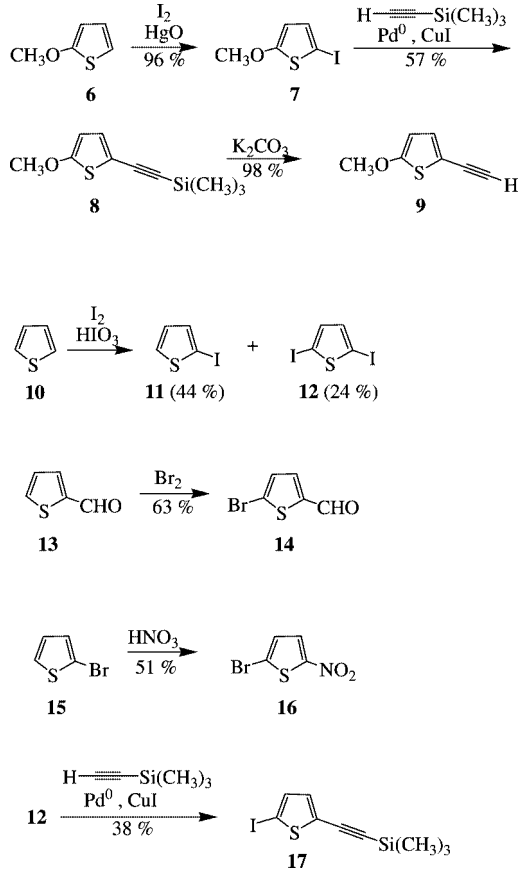
Results and Discussion

Synthesis

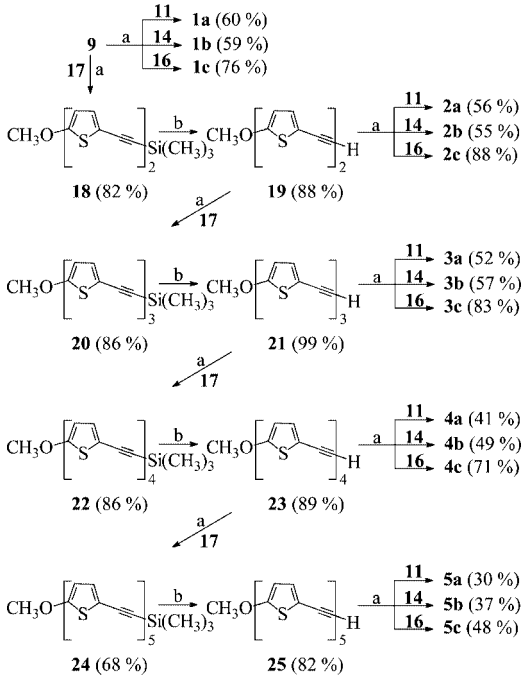
In order to minimize the number of reaction steps, convergent syntheses of the oligomers **1**–**5/a–c** were conceived. Scheme 2 summarizes the preparations of the components **9**, **11**, **14** and **16**, which contain the terminal donor and acceptor groups. 2-Methoxythiophene (**6**) was transformed to 2-iodo-5-methoxythiophene (**7**) by an oxidative iodination with I_2/HgO. The Sonogashira–Hagihara coupling of **7** and trimethylsilylethyne yielded compound **8**, which was deprotected to alkyne **9**. A related oxidative iodination of thiophene (**10**) furnished 2-iodothiophene (**11**) and 2,5-diiodothiophene (**12**). Bromination of thiophene-2-carbaldehyde (**13**) and nitration of 2-bromothiophene (**15**) afforded the components **14** and **16**, respectively. In addition, Scheme 2 contains the preparation of the reagent **17**, which serves for the extension of the conjugated chain. The Sonogashira–Hagihara reaction of the diiodo compound **12** and an equimolar amount of trimethylsilylethyne gave a mixture of **17** (38%), 2,5-bis(trimethylsilylethynyl)thiophene (31%) and unreacted **12**.[16]

Repetitive processes of Sonogashira–Hagihara reactions with the "extension reagent" **17** and deprotections afforded, alternatingly, two auxiliary series of oligo(2,5-thienyleneethynylene)s: **9** → **18** → **19** → **20** → **21** → **22** → **23** → **24** → **25** (Scheme 3); series **18**, **20**, **22** and **24** contains a trimethylsilylethynyl end-group, whereas series **19**, **21**, **23** and **25** has an ethynyl end-group. Both series have methoxy groups as electron donating groups attached to the other end of the conjugated chains. The target compounds are then reached by end-capping processes of **9**, **19**, **21**, **23** and **25** with **11**, **14** and **16**, respectively. Thus, the purely donor substituted OTE series **1a**–**5a** (n = 1–5) and the push-pull series **1b**–**5b** (n = 1–5) and **1c**–**5c** (n = 1–5) were obtained. The yields of the chain extension and the deprotection steps are usually high; the yields of the end-capping steps are lower−in particular for the reactions with **11** and **14**. On the whole, the efficiency of the reactions summarized in Scheme 3 decreases with increasing length of the oligomer chains.

The Sonogashira–Hagihara reactions were performed under normal conditions with $Pd(PPh_3)Cl_2$ and CuI as cocatalysts; the only restriction is given by the fact that secondary amines like piperidine (**27**) can not be used because they add to the electrophilic triple bond. Therefore triethylamine was applied as the base. The cleavage of the trimethylsilylethynyl group was achieved by K_2CO_3 in CH_3OH/CH_2Cl_2 (1:1).

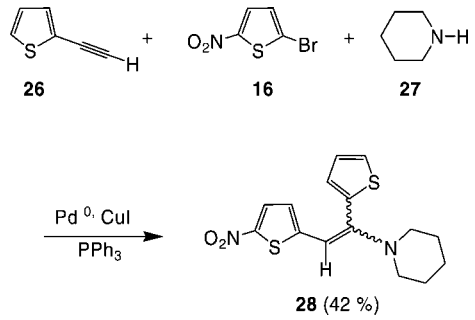


Scheme 2. Preparation of the components **9**, **11**, **14** and **16** for the donor and the acceptor ends and component **17** as a reagent for the extension of the chain.



Scheme 3. Preparation of the OTE series **1**–**5/a**–**c** by convergent and coupled syntheses based on the precursor series **18**, **20**, **22**, **24** and **19**, **21**, **23**, **25**: a) $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, $N(C_2H_5)_3$, toluene; b) K_2CO_3, CH_2Cl_2/CH_3OH.

Scheme 4 demonstrates the one-pot process that generates **28** from **26**, **16** and **27**; piperidine (**27**) adds in a regioselective mode to the expected coupling product of **26** and **16**, which can be detected as an intermediate.[19,20]



Scheme 4. Formation of 1-[2-(5-nitrothien-2-yl)-1-(thien-2-yl)vinyl]-piperidine (**28**).[21]

Spectroscopic Characterization

The terminal donor-acceptor substitution provokes a uniform polarization of conjugated chains. Studies on oligo(1,4-phenylenevinylene)s DAOPV[22–24] and oligo(1,4-phenyleneethynylene)s DAOPE[17] revealed an intramolecular charge transfer (ICT) from the donor group to the chain and from the chain to the acceptor group. The participation of a zwitterionic resonance structure D–π–A ↔ D^+–π–A^- becomes less and less relevant the longer the chain is.[1] Apart from the charge separation over a long distance, more and more benzenoid rings would aquire a *p*-quinoid character which is energetically unfavorable. Now, the question is, how do the heteroaromatic rings of an OTE chain behave in this context? Figure 1 reveals that the terminal DA substitution leads to a polarization which becomes evident in the δ (^{13}C) values; ^{13}C chemical shifts are very sensitive to partial charges on the corresponding nuclei. The polarization of the triple bond increases with increasing donor and acceptor strength; the sum of the $\Delta\delta$ values amounts to 6.2 + 2.3 = 8.5 ppm in **1b** and to 6.7 + 3.0 = 9.7 ppm in **1c**, because the NO_2 group is a stronger acceptor than the formyl group. Moreover, the comparison of the π–electron linkers in **1c** and **30** reveals that the 2,5-thienyleneethynylene unit is somewhat more prone to the ICT than the 1,4-phenyleneethynylene unit ($\Delta\delta$ = 9.7 ppm in **1c** vs. 8.5 ppm in **30**). The extension of the chain in the series **1c**, **2c**, **3c**, **4c** and **5c** gradually decreases the mutual interaction of donor group (OCH_3) and acceptor group (NO_2); consequently the ICT is weakened in this sequence. Accordingly the $\Delta\delta$ sum of the triple bond on the donor side decreases in the series **1c**–**4c** from 9.7 via 6.1 and 5.3 to 5.2 ppm.[25] Compound **4a** (lacking an NO_2 group) has a $\Delta\delta$ value of 5.0, indicating that the push-pull effect in **4c** is already very small. The analogous effect of a decreasing ICT with increasing numbers *n* of repeat units is found on the acceptor end of the DAOTEs. The polarization of the triple bonds in the center of the chain is always low. The ^{1}H and ^{13}C NMR spectroscopic data of **1**–**5/a**–**c** and the two precursor OTE series are summarized in the Tables 1, 2, 3, and 4.

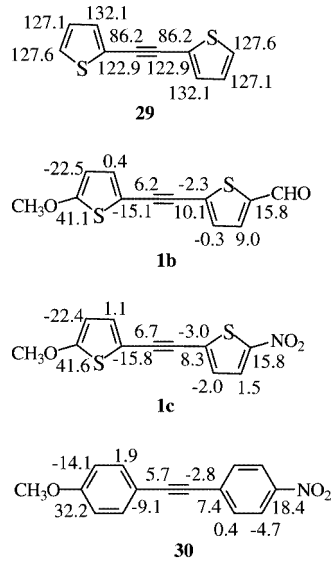


Figure 1. ^{13}C chemical shifts of 2,2′-ethynediylbisthiophene **29**[16] (δ values in $CDCl_3$), $\Delta\delta$ values induced by the push-pull effect in **1b** and **1c**, and $\Delta\delta$ values of **30**[16] related to unsubstituted diphenylacetylene. The assignment of the signals is based on 2D NMR measurements (HMQC, HMBC).

The band of the long-wavelength electron transition in D–π–A systems is called a charge-transfer band because the ICT provokes a decrease of the transition energy.[1] Figure 2 shows the UV/Vis absorptions of **1c** and **30** in $CDCl_3$. The incorporation of thiophene rings in the π-linker results in a considerable bathochromic shift: the λ_{max} value of **1c** is 70 nm greater than the λ_{max} value of **30**.

Table 5 summarizes the long-wavelength absorption maxima of the five OTE series presented here. The purely donor-substituted series **1a**–**5a**, as well as the two auxiliary series **8**, **18**, **20**, **22**, **24** and **9**, **19**, **21**, **23**, **25** exhibit the expected bathochromic shifts by extension of the conjugation (increasing number, *n*, of repeat units). Figure 3 demonstrates the approach $\lambda_{max} \rightarrow \lambda_\infty$ for $n \rightarrow \infty$. The exponential fit is given by Equation (1) and the effective conjugation length (ECL) by Equation (2).[1,26]

$$\lambda_{max}(n) = \lambda_\infty - (\lambda_\infty - \lambda_1)e^{-b(n-1)} \quad (1)$$

$$n_{ECL} = \frac{\ln(\lambda_\infty - \lambda_1)}{b} + 1 \quad (2)$$

The parameter *b* and the resulting values for λ_∞ and n_{ECL} are listed in Table 6. Figure 3 visualizes the convergence behavior.

Compared to the donor-substituted oligo(1,4-phenyleneethynylene) [OPE] series with a terminal dialkylamino group,[17,27] the three series of Table 2 have somewhat higher λ_{max} and n_{ECL} values. The effective conjugation length of 9 repeat units, which is valid for the OTE series **1a**–**5a**, resembles that of OPEs without electron-releasing donor groups, which have n_{ECL} = 10.[17,27]

The extrapolation of the DAOTE series **1b**–**5b** and **1c**–**5c** is difficult, because a second π–π* transition is shifted to

Table 1. ^1H and ^{13}C NMR spectroscopic data of the OTE series **8**, **18**, **20**, **22** and **24** in $CDCl_3$: δ values relative to TMS as internal standard, ^3J (H,H) coupling constants (Hz).

Comp.	CH_3O (s)	Thiophene rings (AB) sp^2-CH	sp^2-C_q	Triple bonds sp-C	$Si(CH_3)_3$ (s)
8	3.86	6.02/6.89 (4.1)			0.21
	60.1	103.8, 131.4	109.4, 167.1	96.3, 98.4	–0.1
18	3.88	6.08/6.94 (4.0), 7.01/7.06 (4.0)			0.24
	60.2	104.3, 131.3, 131.5, 132.5	108.6, 124.3, 124.6, 167.7	83.7, 87.9, 97.0, 100.1	–0.2
20	3.89	6.10/6.95 (4.0), 7.07/7.10 (3.7), 7.08 (s, 2 H)			0.23
	60.3	104.3, 131.5, 131.6, 132.0, 132.3, 132.6	108.5, 123.5, 123.8, 125.2, 125.4, 167.8	83.6, 86.7, 86.8, 88.6, 96.7, 100.6	–0.3
22	3.89	6.09/6.95 (4.1), 7.08/7.13 (4.0), 7.09 (s, 2 H), 7.14 (s, 2 H)			0.24
	60.2	104.3, 131.6, 131.6, 132.1, 132.3, 132.4, 132.4, 132.6	108.5, 123.4, 123.6, 124.4, 124.5, 125.3, 125.5, 167.9	83.7, 86.6, 86.8, 87.3, 87.4, 88.7, 96.7, 100.7	–0.2
24	3.89	6.09/6.95 (4.1), 7.07/7.14 (4.0), 7.09 (s, 2 H), 7.15 (s, 2 H)			0.23
	60.3	104.3, 131.6, 131.6, 132.2, 132.3, 132.4, 132.4, 132.4, 132.4, 167.9	108.5, 123.4, 123.6, 124.3, 124.4, 124.5, 124.6, 125.3, 125.5, 167.9	83.6, 86.5, 86.7, 87.2, 87.2, 87.3, 87.5, 88.7, 96.7, 100.7	–0.3

Table 2. ^1H and ^{13}C NMR spectroscopic data of the OTE series **9**, **19**, **21**, **23** and **25** in $CDCl_3$: δ values relative to TMS as internal standard, ^3J (H,H) coupling constants (Hz).

Comp.	CH_3O (s)	Thiophene rings (AB) sp^2-CH	sp^2-C_q	Triple bonds CH (s) sp-CH	sp-C
9	3.86	6.03/6.92 (4.1)		3.18	
	60.2	103.8, 131.9	108.2, 167.1	79.1	77.7
19	3.89	6.08/6.94 (4.0), 7.02/7.11 (3.9)		3.35	
	60.2	104.3, 131.2, 131.6, 132.9	108.5, 123.0, 125.1, 167.8	82.1	76.5, 83.5, 88.0
21	3.89	6.09/6.95 (4.1), 7.07/7.11 (4.0), 7.10, 7.13 (3.9)		3.41	
	60.2	104.3, 131.5, 131.6, 131.9, 132.4, 133.0	108.5, 123.5, 123.8, 124.5, 125.5, 167.9	82.5	76.3, 83.6, 86.5, 86.8, 88.6
23	3.89	6.09/6.95 (4.1), 7.08/7.13 (4.0), 7.14 (m, 4 H)		3.38	
	60.3	104.3, 131.6, 131.7, 132.0, 132.3, 132.4, 132.4, 133.0	108.5, 123.4, 124.0, 124.1, 124.3, 124.6, 125.5, 167.9	82.6	76.3, 83.6, 86.7, 87.0, 87.4, 88.7
25	3.89	6.09/6.95 (4.1), 7.07/7.13 (3.7), 7.14 (m, 6 H)		3.38	
	60.3	104.3, 131.6, 131.6, 132.1, 132.3, 132.4, 132.5, 132.5, 132.5, 133.0	108.5, 123.4, 124.0, 124.1, 124.3, 124.4, 124.5, 124.7, 125.5, 167.9	82.6	76.3, 83.6, 86.6, 86.7, 87.0, 87.1, 87.3, 87.5 88.7

longer wavelengths and for $n \geq 2$ partly overlaps with the charge-transfer band. Nevertheless, Table 5 reveals a bathochromic shift for **1b**–**5b** with increasing length of the chromophore (increasing numbers, *n*, of repeat units), whereas series **1c**–**5c** with the NO_2 group as a stronger acceptor exhibits a long-wavelength transition, which is virtually independent of the length of the chromophore ($\lambda_{max} \approx 430$ nm).

A comparison of the unsubstituted OTEs[11] (with λ_{max} values of 317, 360, 377 and 400 nm for $n = 1$–4) with the series **1a**–**5a**, **1b**–**5b** and **1c**–**5c** reveals that the terminal substitution provokes a bathochromic shift for each *n*; the effect is particularly strong for the push-pull substitution in **1b**–**5b** and even more so in **1c**–**5c**. The λ_{max} values increase from 317 nm to 329, 392 and 431 nm for the unsubstituted compounds ($n = 1$) **1a**, **1b** and **1c**, respectively; the greatest change in wavelength is 114 nm. A comparison of the unsubstituted series **1a**–**4a** with **1c**–**4c** ($n = 1$–4) shows that increasing numbers of repeat units diminish the change from 114 ($n = 1$) to 70 ($n = 2$), 48 ($n = 3$) and 22 nm ($n = 4$). The influence of the ICT becomes smaller and smaller as the π-electron linker is extended. Higher numbers ($n > 4$) of unsubstituted OTEs are not known. The very long series of oligo(3-ethyl-2,5-thienyleneethynylene)s[10,12] with

Table 3. ^{1}H NMR data of the OTE series **1**–**5/a**–**c**: δ values in $CDCl_3$, TMS as internal standard, ^3J and ^4J coupling constants (Hz).

Comp.	CH_3O (s)	Thiophene rings AM spin patterns or multiplets	AMX spin patterns[a]/CHO (s)
1a	3.88	6.08/6.93 (4.0)	6.97 (5.1, 3.5)/7.22 (3.5, 1.2)/7.25 (5.1, 1.2)
1b	3.90	6.12/7.01 (4.1), 7.22/7.62 (4.0)	9.82 (CHO)
1c	3.89	6.13/7.03 (4.1), 7.05/7.78 (4.4)	
2a	3.89	6.10/6.96 (4.1), 7.08/7.12 (3.9)	7.00 (5.1, 3.5)/7.28 (3.5, 1.2)/7.30 (5.1, 1.2)
2b	3.89	6.10/6.96 (4.1), 7.09/7.18 (3.9), 7.29/7.64 (4.1)	9.84 (CHO)
2c	3.89	6.10/6.96 (4.1), 7.09/7.20 (4.0), 7.12/7.79 (4.4)	
3a	3.89	6.09/6.95 (4.1), 7.08/7.13 (4.0), 7.14 (m, 2 H)	7.00 (5.2, 3.7), 7.28 (3.7, 1.1)/7.30 (5.2, 1.1)
3b	3.89	6.09/6.95 (4.0), 7.07/7.14 (3.9), 7.15/7.20 (4.0), 7.30/7.64 (4.0)	9.84 (CHO)
3c	3.90	6.10/6.96 (4.1), 7.08/7.15 (4.1), 7.17/7.24 (4.0), 7.15/7.81 (4.4)	
4a	3.89	6.09/6.95 (4.0), 7.07–7.16 (m, 6 H)	7.00 (5.1, 3.7), 7.29 (3.7, 0.8), 7.31 (5.1, 0.8)
4b	3.90	6.10/6.96 (4.1), 7.08–7.18 (m, 6 H), 7.31/7.65 (4.1)	9.86 (CHO)
4c	3.89	6.10/6.95 (4.0), 7.08–7.25 (m, 7 H), 7.80 (4.4, 1 H)	
5a	3.89	6.09/6.95 (4.0), 7.07–7.22 (m, 8 H)	7.00 (5.2, 3.7), 7.28 (3.7, 1.1), 7.31 (5.2, 1.1)
5b	3.89	6.09/6.95 (4.0), 7.07/7.14 (3.9), 7.15–7.22 (m, 8 H)	9.85 (CHO)
5c	3.90	6.09/6.97 (4.1), 7.08–7.25 (m, 9 H), 7.80 (4.4, 1 H)	

[a] The coupling constants (5.1 ± 0.1) Hz and (3.6 ± 0.1) Hz belong to 4-H, the values (3.6 ± 0.1) Hz and (1.0 ± 0.2) Hz to 3-H, and the values (5.1 ± 0.1) Hz and (1.0 ± 0.2) Hz to 5-H of the terminal thiophene ring of **1a**–**5a**.

Table 4. ^{13}C NMR spectroscopic data of the OTE series **1**–**4/a–c**: δ values relative to TMS as internal standard.[a]

Comp.	CH_3O	sp^2-CH	sp^2-C_q	sp-C
1a	60.2	104.1, 127.0, 127.2, 131.0, 131.7	108.9, 123.2, 167.4	83.9, 86.9
1b	60.3	104.6, 131.8, 132.5, 136.1, 182.3 (CHO)	107.8, 133.0, 143.4, 168.7	83.9, 92.4
1c	60.3	104.7, 128.6, 130.1, 133.2	107.1, 131.2, 150.2, 169.2	83.2, 92.9
2a	60.2	104.3, 127.2, 127.9, 131.6, 131.6, 131.9, 132.4	108.6, 122.6, 124.0, 125.0, 167.8	83.8, 85.9, 87.3, 88.4
2b	60.3	104.3, 131.6, 131.7, 132.7, 133.1, 135.9, 182.2 (CHO)	108.3, 122.5, 126.4, 131.9, 144.2, 168.0	83.5, 86.5, 89.2, 90.7
2c	60.3	104.4, 128.5, 131.1, 131.6, 131.9, 133.7	108.2, 121.8, 127.1, 130.2, 151.1, 168.2	83.5, 85.7, 89.6, 91.2
3a	60.3	104.3, 127.2, 128.1, 131.6, 131.6, 132.0, 132.3, 132.4, 132.5	108.5, 122.4, 123.5, 124.1, 124.8, 125.4, 167.8	83.7, 85.7, 86.8, 87.2, 87.7, 88.6
3b	60.2	104.3, 131.6, 131.7, 132.3, 132.6, 132.8, 133.2, 135.9, 182.3 (CHO)	108.5, 123.2, 123.4, 125.6, 125.7, 131.8, 144.3, 167.9,	83.6, 86.6, 86.9, 87.9, 88.8, 90.5
3c	60.3	104.3, 128.5, 131.2, 131.6, 131.7, 132.3, 132.6, 133.7	108.4, 123.1, 123.9, 126.0, 126.4, 129.9, 151.2, 168.1	83.6, 85.9, 86.4, 88.3, 88.9, 90.8
4a	60.2	104.3, 127.2, 128.1, 131.6, 131.6, 132.0, 132.3, 132.3, 132.4, 132.4, 132.6	108.5, 122.4, 123.4, 123.9, 124.4, 124.6, 125.0, 125.5, 167.9	83.7, 85.7, 86.8, 87.0, 87.3, 87.5, 87.7, 88.7
4b	60.2	104.3, 131.6, 131.7, 132.4, 132.5, 132.5, 132.6, 132.8, 133.2, 135.9, 182.3 (CHO)	108.2, 123.3, 124.1, 124.9, 124.9, 125.4, 125.6, 131.8, 144.4, 167.9	83.6, 85.1, 86.6, 86.9, 87.6, 87.7, 88.7, 90.4
4c	60.2	104.3, 128.5, 131.2, 131.6, 131.7, 132.3, 132.4, 132.5, 132.7, 133.7	108.5, 122.8, 123.3, 123.8, 123.9, 125.0, 126.1, 129.9, 151.1, 168.2	86.0, 86.6, 86.8, 87.4, 87.6, 88.1, 88.7, 90.7

[a] The pentamers **5a**–**c** have insufficient solubility for the measurement of reliable ^{13}C NMR spectra.

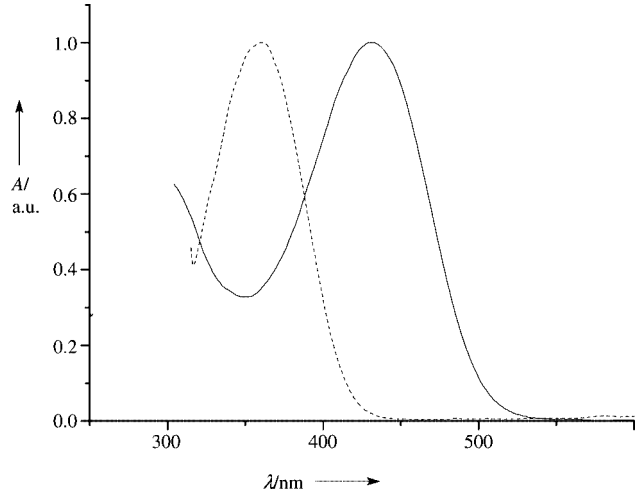


Figure 2. UV/Vis absorption of **1c** (−) and **30** (- - -) in $CHCl_3$.

Table 5. UV/Vis absorption maxima of the OTE series in $CHCl_3$.

Comp.	n	λ_{max}[nm]	log ε	Comp.	n	λ_{max}[nm]	log ε
8	1	297 ± 1	4.17	**9**	1	289 ± 1	4.08
18	2	359 ± 1	4.35	**19**	2	352 ± 1	4.35
20	3	389 ± 1	4.54	**21**	3	386 ± 1	4.60
22	4	399 ± 1	4.78	**23**	4	394 ± 1	4.73
24	5	407 ± 1	4.84	**25**	5	407 ± 1	4.75
1a	1	329 ± 1	4.43	**1b**	1	392 ± 1	4.30
2a	2	373 ± 1	4.49	**2b**	2	403 ± 2	4.47
3a	3	393 ± 1	4.67	**3b**	3	407 ± 3	4.63
4a	4	405 ± 1	4.82	**4b**	4	412 ± 5	4.77
5a	5	414 ± 1	4.86	**5b**	5	423 ± 5	5.00
1c	1	431 ± 1	4.25				
2c	2	430 ± 3	4.40				
3c	3	425 ± 6	4.61				
4c	4	422 ± 10	4.76				
5c	5	429 ± 6	5.00				

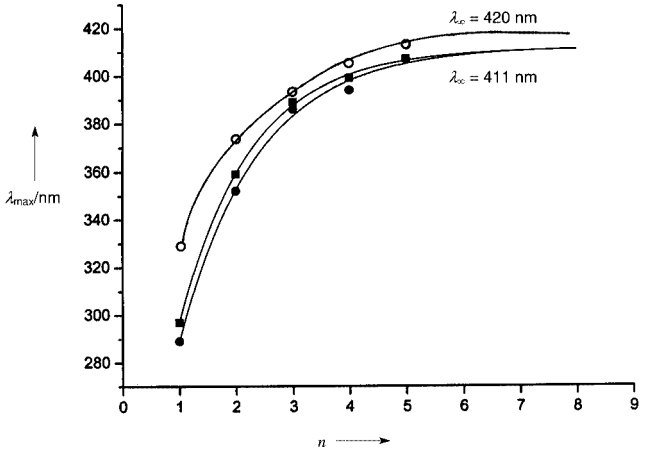


Figure 3. Convergence of the absorption maxima $\lambda(n) \rightarrow \lambda_\infty$ of **1a**–**5a** (-o-), **8**, **18**, **20**, **22**, **24** (-■-), and **9**, **19**, **21**, **23**, **25** (-●-) in $CDCl_3$.

Table 6. Extrapolation of the long-wavelength absorption maxima of the series **1a**–**5a** and the precursor oligomers.

Series	Convergence parameter b	λ_∞ [nm]	n_{ECL}
1a–**5a**	0.63 ± 0.04	420 ± 3	9
8, **18**, **20**, **22**, **24**	0.77 ± 0.07	411 ± 2	7
9, **19**, **21**, **23**, **25**	0.79 ± 0.03	411 ± 4	7

λ_∞ = 433 nm (in THF) is not absolutely comparable, since the ethyl groups in each repeat unit cause an electronic change; however, the effect of the alkyl groups is rather small, as measurements of poly(thienyleneethynylene)s revealed.[28]

Conclusions

Conjugated oligomers normally show a systematic change of certain properties as linear and nonlinear optics with increasing chain length.[29] The λ_{max} values of long-wavelength absorption, for example, increase with increasing numbers of repeat units and monotonously approach a limiting value λ_∞. However, terminal push-pull substitution provokes an intramolecular charge transfer (ICT), which polarizes the molecules and has a strong influence on the absorption. The bathochromic shift λ_{max} $(n + 1) > \lambda_{max}$ (n) caused by the extension of the conjugation can be opposed by the decrease of ICT with increasing chain length. Thus, in principle different types of absorption behavior can be observed:[1]

a) a diminished monotonously bathochromic shift: λ_{max} $(n + 1) > \lambda_{max}$ (n)

b) a monotonously hypsochromic shift: λ_{max} $(n + 1) < \lambda_{max}$ (n)

c) a borderline case between a) and b): λ_{max} $(n + 1) \approx \lambda_{max}$ (n)

d) a maximum of λ_{max} for a certain number, n', followed by a hypsochromic shift: $\lambda_1 < \lambda (n') > \lambda (n + 1) > \lambda (n + 2)$, etc.

The type of absorption behaviour depends not only on the D-A pair, but also on the π–electron linker. The novelly prepared OTE series, discussed here, belong to the type a) with the exception of series **1c**–**5c**, in which the λ_{max} values are almost independent of n (type c). Since conjugated oligomers containing thiophene units have interesting nonlinear optical properties, we are anxious to study the NLO of the new systems **1**–**5/a**–**c**. The convergent and coupled synthetic strategy, outlined in the Scheme 2 and Scheme 3 renders these compounds easily accessible.

Experimental Section

General: The melting points were measured with a Büchi melting point apparatus and are uncorrected. The UV/Vis spectra were obtained with a Zeiss MCS 320/340 spectrometer, and the FT IR spectra with a Perkin–Elmer GX 2000 spectrometer. The ^1H and ^{13}C NMR spectra were recorded with the Bruker spectrometers AMX 400 and AC 300, respectively. $CDCl_3$ served as solvent unless otherwise noted, and TMS was used as the internal standard. The FD (field desorption) mass spectra were obtained with a Finnigan MAT 95 spectrometer. Elemental analyses were performed in the microanalytical laboratory of the Institute of Organic Chemistry at the University of Mainz, Germany.

2-Iodo-5-methoxythiophene (7): The solution of 2-methoxythiophene[30] (**6**, 2.0 g, 17.5 mmol) in dry benzene (40 mL) was cooled to 5 °C before yellow HgO (3.85 g, 17.8 mmol) and I_2 (4.59 g, 18.1 mmol)were added in small portions. The mixture was stirred at 0 °C until the color faded. The solvent was removed and the residue was purified by column chromatography (5 × 15 cm silica gel, petroleum b.p. 40–70 °C). The obtained product (4.03 g, 96%, 81%[31]) was a light yellow oil and was used directly for the next reaction step. ^1H NMR ($CDCl_3$): δ = 3.84 (s, 3 H, OCH_3), 5.91 (d, ^3J = 4.1 Hz, 1 H, 4-H), 6.88 (d, ^3J = 4.1 Hz, 1 H, 3-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 57.4 (C-2), 60.4 (OCH_3), 105.8 (C-4), 134.4 (C-3), 169.9 (C-5) ppm. FD MS: *m/z* (%) = 240 (100) [M^+].

General Procedure for the Sonogashira–Hagihara Reaction (Described for 7 → 8)

2-Methoxy-5-(trimethylsilylethynyl)thiophene (8): Compound **7** (4.11 g, 17.1 mmol), trimethylsilylacetylene (1.85 g, 18.8 mmol), $Pd(PPh_3)_2Cl_2$ (300 mg, 0.43 mmol), CuI (163 mg, 0.86 mmol) and triphenylphosphane (225 mg, 0.86 mmol) were added under Ar to an oxygen-free mixture of dry toluene (30 mL) and triethylamine (10 mL, 7.255 g, 71.7 mmol). After stirring overnight at room temperature, the volatile components were evaporated and the residue was dissolved in $CHCl_3$, filtered and washed with saturated aqueous solutions (50 mL each) of NH_4Cl, $NaHCO_3$ and NaCl. The organic layer was dried with Na_2SO_4 and the solvent was removed. The raw product was purified by column chromatography (8 × 20 cm SiO_2, petroleum b. p. 40–70 °C) to yield a colorless oil (2.14 g, 57%). FD MS: *m/z* (%) = 210 (100) [M^+]. $C_{10}H_{14}OSSi$ (210.1): calcd. C 57.10, H 6.71, S 15.24; found C 57.07, H 6.86, S 15.28.

General Procedure for the Deprotection of Ethynyl Groups (Described for 8 → 9)

2-Ethynyl-5-methoxythiophene (9): Compound **8** (4.12 g, 19.6 mmol) was treated at room temperature with K_2CO_3 (2.98 g, 21.5 mmol) in CH_3OH/ CH_2Cl_2 (1:1, 20 mL). After the end of the reaction (TLC control SiO_2/CH_2Cl_2), the solvent was removed and the residue was dissolved in $CHCl_3$. The solution was filtered and ex-

tracted with water (3 × 40 mL), dried with Na_2SO_4 and the solvents were evaporated. Column chromatography (8 × 20 cm SiO_2, petroleum b. p. 40–70 °C) gave the pure oily product (2.60 g, 98%). FD MS: *m/z* (%) = 138 (100) [M^+]. C_7H_6OS (138.0): calcd. C 60.84, H 4.38, S 23.20; found C 60.97, H 4.28, S 23.46.

2-Iodothiophene (11) and 2,5-Diiodothiophene (12): Preparation from **10**[30] was performed according to the literature.[32] **11**: oil. ^1H NMR ($CDCl_3$): δ = 6.80 (dd, ^3J = 3.3, ^3J = 5.1 Hz, 1 H, 4-H), 7.24 (dd, ^3J = 3.3, ^4J = 1.1 Hz, 1 H, 3-H), 7.35 (dd, ^3J = 5.1, ^4J = 1.1 Hz, 1 H, 5-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 73.1 (C-2), 128.9 (C-5), 131.5 (C-4), 136.9 (C-3) ppm. **12**: crystals, which melt at 42 °C (ref.[28] 42 °C). ^1H NMR ($CDCl_3$): δ = 6.91 (s, 2 H, 3-H, 4-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 76.1 (C-2, C-5), 138.7 (C-3, C-4) ppm.

5-Bromothiophene-2-carbaldehyde (14): Preparation from **13**[30] was performed according to the literature.[33] ^1H NMR ($CDCl_3$): δ = 7.12 (d, ^3J = 4.1 Hz, 1 H, 4-H), 7.47 (d, ^3J = 4.1 Hz, 1 H, 3-H), 9.71 (s, 1 H, CHO) ppm.

2-Bromo-5-nitrothiophene (16): The preparation of **16** was performed according to the literature by bromination of thiophene **10**[34] and subsequent nitration.[35] Yield: 51% of yellow crystals, m.p. 40 °C (ref.[35] 41 °C).

2-Iodo-5-(trimethylsilylethynyl)thiophene (17): 2,5-diiodothiophene (**12**, 4.0 g, 11.9 mmol), trimethylsilylacetylene (1.17 g, 11.9 mmol), $Pd(PPh_3)_2Cl_2$ (209 mg, 0.29 mmol), CuI (114 mg, 0.59 mmol) and PPh_3 (157 mg, 0.59 mmol) reacted in dry toluene (10 mL) and dry triethylamine (3 mL, 2.177 g, 21.5 mmol) according to the procedure **7** → **8** described above. A colorless oil (1.38 g, 38%) was obtained. ^1H NMR ($CDCl_3$): δ = 0.24 [s, 9 H, $Si(CH_3)_3$], 6.85 (d, ^3J = 4.1 Hz, 1 H, 4-H), 7.05 (d, ^3J = 4.1 Hz, 1 H, 3-H) ppm. ^{13}C NMR ($CDCl_3$): δ = –0.1 [$Si(CH_3)_3$], 74.9 (C-2), 96.3, 100.9 (acetyl. C), 129.5 (C-5), 133.8 (C-4), 136.8 (C-3) ppm. FD MS: *m/z* (%) = 306 (100) [M^+]. $C_9H_{11}ISSi$: (305.9): calcd. C 35.30, H 3.62, S 10.47; found C 35.25, H 3.72, S 10.33.

2-(5-Methoxythien-2-ylethynyl)-5-(trimethylsilylethynyl)thiophene (18): Compound **9** (750 mg, 5.43 mmol), compound **17** (1660 mg, 5.43 mmol), $Pd(PPh_3)_2Cl_2$ (95 mg, 0.14 mmol), CuI (52 mg, 0.27 mmol) and PPh_3 (71 mg, 0.27 mmol) reacted in dry toluene (30 mL) and dry triethylamine (10 mL, 7.255 g, 71.7 mmol) according to the procedure **7** → **8** described above. Column chromatography (5 × 25 cm SiO_2, petroleum b. p. 40–70 °C/CH_2Cl_2, 3:1) afforded **18** (1400 mg, 82%) as a colorless oil. FD MS: *m/z* (%) = 316 (100) [M^+]. $C_{16}H_{16}OS_2Si$ (316.0): calcd. C 60.72, H 5.10, S 20.26; found C 60.96, H 5.31, S 20.17.

2-Ethynyl-5-(5-methoxythien-2-ylethynyl)thiophene (19): Deprotection as described for **8** → **9** yielded of **19** (1.22 g, 88%) from **18** (1.79 g, 5.66 mmol). Column chromatography (8 × 20 cm SiO_2 with petroleum b. p. 40–70 °C/CH_2Cl_2, 3:1) led to an almost colorless viscous oil, which was analytically pure. FD MS: *m/z* (%) = 244 (100) [M^+]. $C_{13}H_8OS_2$ (244.0): calcd. C 63.91, H 3.30, S 26.24; found C 64.07, H 3.44, S 26.15.

Trimer 20: Compound **19** (900 mg, 3.69 mmol), compound **17** (1130 mg, 3.69 mmol), $Pd(PPh_3)_2Cl_2$ (65 mg, 0.092 mmol), CuI (35 mg, 0.18 mmol) and PPh_3 (48 mg 0.18 mmol) reacted in dry triethylamine (10 mL, 7.255 g, 71.7 mmol) and dry toluene (10 mL) according to the procedure **7** → **8** described above. Column chromatography (8 × 30 cm SiO_2, petroleum b. p. 40–70 °C/CH_2Cl_2, 3:1) afforded yellow crystals (1.35 g, 86%), m.p. 81 °C. FD MS: *m/z* (%) = 528 (100) [M^+]. $C_{28}H_{20}OS_4Si$ (528.0): calcd. C 63.60, H 3.81, S 24.25; found C 63.85, H 3.93, S 24.36.

Trimer 21: Preparation was according to the general procedure as described for **8** → **9**. Compound **20** (1.34 g, 3.17 mmol) yielded **21** (1.1 g, 99%) as yellow crystals, m.p. 63 °C. FD MS: *m/z* (%) = 350 (100) [M^+]. $C_{19}H_{10}OS_3$ (350.0): calcd. C 65.12, H 2.88, S 27.44; found C 65.09, H 2.85, S 27.49.

Tetramer 22: Compound 22 was prepared according to the general procedure for **7** → **8**. Compound **21** (900 mg, 2.57 mmol), compound **17** (780 mg, 2.57 mmol), $Pd(PPh_3)_2Cl_2$ (45 mg, 0.064 mmol), CuI (25 mg, 0.128 mmol) and PPh_3 (34 mg, 0.128 mmol) reacted in dry $N(C_2H_5)_3$ (10 mL, 7.255 g, 71.7 mmol) and dry toluene (10 mL). Column chromatography (8 × 30 cm SiO_2, petroleum b. p. 40–70 °C/CH_2Cl_2, 1:1) yielded yellow crystals (1170 mg, 86%), m.p. 112 °C. FD MS: *m/z* (%) = 528 (100) [M^+]. $C_{28}H_{20}OS_4Si$ (528.0): calcd. C 63.60, H 3.81, S 24.25; found C 63.58, H 3.93, S 24.36.

Tetramer 23: The procedure described for **8** → **9** afforded **23** as yellow crystals (310 mg, 89%) from **22** (400 mg, 0.76 mmol). After recrystallization from CH_2Cl_2/CH_3OH,[36] the compound melted at 102 °C. FD MS: *m/z* (%) = 456 (100) [M^+]. $C_{25}H_{12}OS_4$ (456.0): calcd. C 65.76, H 2.65, S 28.09; found C 65.92 H 2.53, S 27.92.

Pentamer 24: According to the general procedure **7** → **8**, compound **23** (830 mg, 1.82 mmol), compound **17** (560 mg, 1.82 mmol), $Pd(PPh_3)_2Cl_2$ (32 mg, 0.045 mmol), CuI (17 mg, 0.091 mmol) and PPh_3 (24 mg, 0.091 mmol) reacted in dry $N(C_2H_5)_3$ (5 mL, 3.63 g, 35.85 mmol) and dry toluene (10 mL). Column chromatography (8 × 30 cm SiO_2, petroleum b. p. 40–70 °C/CH_2Cl_2, 1:1) and subsequent recrystallization from the same mixture of solvents yielded **24** as red crystals (780 mg, 68%), m.p. 145 °C. FD MS: *m/z* (%) = 635 (100) [M +H^+]. $C_{34}H_{22}OS_5Si$ (634.0): calcd. C 64.32, H 3.49, S 25.25; found C 64.24, H 3.60, S 25.51.

Pentamer 25: The procedure described for **8** → **9** gave **25** (450 mg, 82%) from **24** (640 mg, 0.98 mmol). After recrystallization from petroleum b. p. 40–70 °C/CH_2Cl_2 (1:1) the orange crystals melted at 111 °C. FD MS: *m/z* (%) = 563 (100) [M +H^+]. $C_{31}H_{14}OS_5$ (562.0): calcd. C 66.16, H 2.51, S 28.49; found C 66.08, H 2.43, S 28.57.

2-Methoxy-5-(thien-2-ylethynyl)thiophene (1a): According to the general procedure **7** → **8**, compound **9** (250 mg, 1.8 mmol), compound **11** (380 mg, 1.8 mmol), $Pd(PPh_3)_2Cl_2$ (32 mg, 0.045 mmol), CuI (17 mg, 0.09 mmol) and PPh_3 (24 mg, 0.09 mmol) reacted in dry $N(C_2H_5)_3$ (10 mL, 7.255 g, 71.7 mmol) and dry toluene (10 mL). Column chromatography (3 × 50 cm SiO_2, petroleum b. p. 40–70 °C/CH_2Cl_2, 4:1) afforded a viscous oil (240 mg, 60%). FD MS: *m/z* (%) = 220 (100) [M^+]. IR (neat): $\tilde{\nu}$ = 2191 cm^{-1} (C≡C). $C_{11}H_8OS_2$ (220.0): calcd. C 59.97, H 3.66, S 29.22; found C 59.82, H 3.76, S 29.51.

5-(5-Methoxythien-2-ylethynyl)thiophene-2-carbaldehyde (1b): Compound **9** (180 mg, 1.3 mmol), compound **14** (248 mg, 1.3 mmol), $Pd(PPh_3)_2Cl_2$ (23 mg, 0.033 mmol), CuI (12 mg, 0.065 mmol) and PPh_3 (17 mg, 0.065 mmol) reacted in dry $N(C_2H_5)_3$ (5 mL, 35.85 mmol) and dry toluene (10 mL). Column chromatography (5 × 30 cm SiO_2, petroleum b. p. 40–70 °C/CH_2Cl_2, 1:1) afforded yellow crystals (190 mg, 59%), m.p. 65 °C. FD MS. *m/z* (%) = 248 (100) [M^+]. IR (KBr): $\tilde{\nu}$ = 2184 cm^{-1} (C≡C). $C_{12}H_8O_2S_2$ (248.0): calcd. C 58.04, H 3.25, S 25.82; found C 58.32, H 3.17, S 25.89.

2-(5-Methoxythien-2-ylethynyl)-5-nitrothiophene (1c): Compound **9** (163 mg, 1.19 mmol), compound **16** (247 mg, 1.19 mmol), $Pd(PPh_3)_2Cl_2$ (21 mg, 0.03 mmol), CuI (11 mg, 0.06 mmol) and PPh_3 (15 mg, 0.06 mmol) reacted in dry $N(C_2H_5)_3$ (10 mL, 7.255 g, 71.7 mmol) and dry toluene (10 mL). Column chromatography (5 × 25 cm SiO_2, petroleum b. p. 40–70 °C/CH_2Cl_2, 1:1) yielded red crystals (240 mg,

76%), m.p. 88 °C. FD MS: *m/z* (%) = 265 (100) [M+]. IR (KBr): $\tilde{\nu}$ = 2183 cm^{-1} (C≡C). $C_{11}H_7NO_3S_2$ (265.3): calcd. C 49.80, H 2.66, N 5.28, S 24.17; found C 49.86, H 2.64, N 5.17, S 24.01.

2-(5-Methoxythien-2-ylethynyl)-5-(thienylethynyl)thiophene (2a): Compound **18** (200 mg, 0.82 mmol), compound **11** (172 mg, 0.82 mmol), $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol), CuI (7.7 mg, 0.04 mmol) and PPh_3 (10.7 mg, 0.04 mmol) reacted in dry $N(C_2H_5)_3$ (5 mL, 3.628 g, 35.8 mmol) and dry toluene (5 mL). Column chromatography (8 × 20 cm SiO_2, petroleum b. p. 40–70 °C) afforded a viscous yellow oil (150 mg, 56%). FD MS: *m/z* (%) = 326 (100) [M+]. IR (neat): $\tilde{\nu}$ = 2184 cm^{-1} (C≡C). $C_{17}H_{10}OS_3$ (326.0): calcd. C 62.55, H 3.09, S 29.46; found C 62.44, H 3.19, S 29.30.

5-[5-(5-Methoxythien-2-ylethynyl)thien-2-ylethynyl]thiophene-2-carbaldehyde (2b): Compound **19** (180 mg, 0.61 mmol), compound **14** (129 mg, 0.61 mmol), $Pd(PPh_3)_2Cl_2$ (10.7 mg, 0.015 mmol), CuI (5.8 mg, 0.031 mmol) and PPh_3 (8.1 mg, 0.031 mmol) reacted in dry $N(C_2H_5)_3$ (5 mL, 3.628 g, 35.8 mmol) and dry toluene (10 mL). Column chromatography (5 × 30 cm SiO_2, petroleum b. p. 40–70 °C/CH_2Cl_2, 1:1) yielded red crystals (120 mg, 55%), m.p. 81 °C. FD MS: *m/z* (%) = 354 (100) [M+]. IR (KBr): $\tilde{\nu}$ = 2178 cm^{-1}. $C_{18}H_{10}O_2S_3$ (354.0): C 60.99, H 2.84, S 27.3; found C 60.49, H 2.68, S 27.11.

2-(5-Methoxythien-2-ylethynyl)-5-(5-nitrothienylethynyl)thiophene (2c): Compound **19** (150 mg, 0.61 mmol), **16** (127 mg, 0.61 mmol), $Pd(PPh_3)_2Cl_2$ (11 mg, 0.015 mmol), CuI (5.8 mg, 0.031 mmol) and PPh_3 (8.0 mg, 0.031 mmol) reacted in dry $N(C_2H_5)_3$ (5 mL, 3.628 g, 35.8 mmol) and dry toluene (10 mL). Column chromatography (5 × 30 cm SiO_2, petroleum b. p. 40–70 °C/CH_2Cl_2, 1:1) afforded red crystals (200 mg, 88%), m.p. 100 °C. FD MS: *m/z* (%) = 371 (100) [M+]. $C_{17}H_9NO_3S_3$ (371.0): calcd. C 54.97, H 2.44, N 3.77, S 25.89; found C 54.77, H 2.46, N 3.69, S 25.86.

Trimer 3a: Compound **21** (118 mg, 0.34 mmol), compound **11** (71 mg, 0.34 mmol), $Pd(PPh_3)_2Cl_2$ (5.9 mg, 0.0084 mmol), CuI (3.2 mg, 0.017 mmol) and PPh_3 (4.4 mg, 0.017 mmol) reacted in dry $N(C_2H_5)_3$ (5 mL, 3.628 g, 35.8 mmol) and dry toluene (6 mL). Column chromatography (3 × 40 cm SiO_2, petroleum b. p. 40–70 °C/CH_2Cl_2, 3:1) yielded a viscous, yellow oil (76 mg, 52%). FD MS: *m/z* (%) = 432 (100) [M+]. IR (neat): $\tilde{\nu}$ = 2183 cm^{-1} (C≡C). $C_{23}H_{12}OS_4$ (432.0): calcd. C 63.86, H 2.80, S 29.64; found C 63.70, H 2.95, S 29.61.

Trimer 3b: Compound **21** (200 mg, 0.57 mmol), compound **14** (107 mg, 0.63 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 0.014 mmol), CuI (5.4 mg, 0.028 mmol) and PPh_3 (7.5 mg, 0.028 mmol) reacted in dry $N(C_2H_5)_3$ (5 mL, 3.628 g, 35.8 mmol) and dry toluene (5 mL). Column chromatography (5 × 40 cm SiO_2, petroleum b. p. 40–70 °C/CH_2Cl_2, 1:1) afforded orange crystals (150 mg, 57%), m.p. 102 °C. FD MS: *m/z* (%) = 460 (100) [M+]. IR (KBr): $\tilde{\nu}$ = 2178 cm^{-1} (C≡C). $C_{24}H_{12}O_2S_4$ (460.0): calcd. C 62.58, H 2.63, S 27.84; found C 62.37, H 2.51, S 27.53.

Trimer 3c: Compound **21** (150 mg, 0.43 mmol), compound **16** (89 mg, 0.43 mmol), $Pd(PPh_3)_2Cl_2$ (7.5 mg, 0.011 mmol), CuI (4.0 mg, 0.022 mmol) and PPh_3 (5.6 mg, 0.022 mmol) reacted in dry $N(C_2H_5)_3$ (5 mL, 3.628 g, 35.8 mmol) and dry toluene (10 mL). Column chromatography (5 × 40 cm SiO_2, petroleum b. p. 40–70 °C/CH_2Cl_2, 1:1) yielded red crystals (170 mg, 83%), m.p. 155 °C. FD MS: *m/z* (%) = 477 (100) [M+]. IR (KBr): $\tilde{\nu}$ = 2178 cm^{-1} (C≡C). $C_{23}H_{11}NO_3S_4$ (477.0): calcd. C 57,84, H 2.32, N 2.93, S 26.85; found C 57.59, H 2.46, N 2.81, S 26.37.

Tetramer 4a: Compound **23** (140 mg, 0.31 mmol), compound **11** (71 mg, 0.34 mmol), $Pd(PPh_3)_2Cl_2$ (5.4 mg, 0.0076 mmol), CuI (2.9 mg, 0.015 mmol) and PPh_3 (4.0 mg, 0.015 mmol) reacted in dry $N(C_2H_5)_3$ (5 mL, 3.628 g, 35.8 mmol) and dry toluene (10 mL). Column chromatography (3 × 40 cm SiO_2, petroleum b. p. 40–70 °C/CH_2Cl_2, 1:1) afforded yellow crystals (68 mg, 41%), m.p. 57 °C. FD MS: *m/z* (%) = 539 (100) [M + H+]. IR (KBr): $\tilde{\nu}$ = 2190 cm^{-1} (C≡C). $C_{29}H_{14}OS_5$ (538.0): calcd. C 64.66, H 2.62, S 29.76; found C 64.50, H 2.79, S 29.82.

Tetramer 4b: Compound **23** (157 mg, 0.34 mmol), **14** (66 mg, 0.34 mmol), $Pd(PPh_3)_2Cl_2$ (6.0 mg, 0.0086 mmol), CuI (3.3 mg, 0.017 mmol) and PPh_3 (4.5 mg, 0.017 mmol) reacted in dry $N(C_2H_5)_3$ (5 mL, 3.628 g, 35.8 mmol) and dry toluene (10 mL). Column chromatography (5 × 40 cm SiO_2, petroleum b. p. 40–70 °C/CH_2Cl_2, 1:1) and recrystallization from CH_2Cl_2/CH_3OH[36] yielded orange crystals (96 mg, 49%), m.p. 121 °C. FD MS: *m/z* (%) = 567 (100) [M + H+]. IR: $\tilde{\nu}$ = 2177 cm^{-1} (C≡C). $C_{30}H_{14}O_2S_5$ (566.0): calcd. C 63.58, H 2.49, S 28.28; found C 63.43, H 2.51, S 28.16.

Tetramer 4c: Compound **23** (150 mg, 0.33 mmol), compound **16** (68 mg, 0.33 mmol), $Pd(PPh_3)_2Cl_2$ (5.7 mg, 0.008 mmol), CuI (3.1 mg, 0.016 mmol) and PPh_3 (4.3 mg, 0.016 mmol) reacted in dry $N(C_2H_5)_3$ (5 mL, 3.628 g, 35.8 mmol) and dry toluene (10 mL). Column chromatography (8 × 20 cm SiO_2, petroleum b. p. 40–70 °C/CH_2Cl_2, 1:1) and recrystallization from CH_2Cl_2/CH_3OH (1:1) afforded red crystals (140 mg, 71%), m.p. 169 °C. FD MS: *m/z* (%) = 584 (100) [M + H+]. IR (KBr): $\tilde{\nu}$ = 2180 cm^{-1} (C≡C). $C_{29}H_{13}NO_3S_5$ (583.0): calcd. C 59.67, H 2.24, N 2.40, S 27.46; found C 59.85, H 2.48, N 2.13, S 27.32.

Pentamer 5a: Compound **25** (130 mg, 0.23 mmol), compound **11** (48 mg, 0.23 mmol), $Pd(PPh_3)_2Cl_2$ (4.1 mg, 0.006 mmol), CuI (2.2 mg, 0.012 mmol) and PPh_3 (3.0 mg, 0.012 mmol) reacted in dry $N(C_2H_5)_3$ (10 mL, 71.7 mmol) and dry toluene (10 mL). Column chromatography (3 × 50 cm SiO_2, petroleum b. p. 40–70 °C/$CHCl_3$, 1:3) and twofold recrystallization from CH_2Cl_2/CH_3OH (1:1) yielded yellow crystals (45 mg, 30%), m.p. 121 °C. FD MS: *m/z* (%) = 645 (100) [M + H+]. IR (KBr): $\tilde{\nu}$ = 2170 cm^{-1}. $C_{35}H_{16}OS_6$ (644.0): calcd. C 65.19, H 2.50, S 29.83; found C 65.25, H 2.43, S 29.99.

Pentamer 5b: Compound **25** (180 mg, 0.32 mmol), compound **14** (61 mg, 0.32 mmol), $Pd(PPh_3)_2Cl_2$ (5.6 mg, 0.008 mmol), CuI (3.0 mg, 0.016 mmol) and PPh_3 (4.2 mg, 0.016 mmol) reacted in dry $N(C_2H_5)_3$ (5 mL, 35.8 mmol) and dry toluene (10 mL). Column chromatography (5 × 40 cm SiO_2, petroleum b. p. 40–70 °C/CH_2Cl_2, 1:1) and recrystallization from the same solvent mixture afforded orange crystals (80 mg, 37%), m.p. 157 °C. FD MS: *m/z* (%) = 673 (100) [M + H+]. IR (KBr): $\tilde{\nu}$ = 2170 cm^{-1} (C≡C). $C_{36}H_{16}O_2S_6$ (672.9): calcd. C 64.26, H 2.40, S 28.59; found C 64.08, H 2.33, S 28.44.

Pentamer 5c: Compound **25** (100 mg, 0.18 mmol), compound **16** (37 mg, 0.18 mmol), $Pd(PPh_3)_2Cl_2$ (3.1 mg, 0.004 mmol), CuI (1.7 mg, 0.009 mmol) and PPh_3 (2.3 mg, 0.009 mmol) reacted in dry $N(C_2H_5)_3$ (5 mL, 3.628 g, 35.8 mmol) and dry toluene (10 mL). Column chromatography (8 × 20 cm SiO_2, petroleum b. p. 40–70 °C/CH_2Cl_2, 1:1) and recrystallization from this solvent mixture yielded red crystals (60 mg, 48%), m.p. 183 °C. FD MS: *m/z* (%) = 690 (100) [M + H+]. IR (KBr): $\tilde{\nu}$ = 2190 cm^{-1}. $C_{35}H_{15}NO_3S_6$ (689.9): calcd. C 60.94, H 2.19, N 2.03; found C 60.88, H 2.28, N 1.88.

1-[2-(5-Nitrothien-2-yl)-1-(thien-2-yl)vinyl]piperidine (28): Compound **28** was obtained by applying the normal procedure for the Sonogashira–Hagihara reaction with piperidine (**27**) instead of NEt_3. Compound **26** (0.50 g, 4.62 mmol), compound **16** (0.96 g,

4.62 mmol), $Pd(PPh_3)_2Cl_2$ (0.081 g, 0.12 mmol), CuI (0.044 g, 0.23 mmol) and PPh_3 (0.061 g, 0.23 mmol) reacted in piperidine (10 mL, 8.606 g, 1.011 mol) to yield **28** (0.62 g, 42%) as a red-violet wax. The purification was performed by column chromatography (3×50 cm SiO_2, petroleum b. p. 40–70 °C/toluene, 5:1). ^{1}H NMR ($CDCl_3$): δ = 1.61 (m, 6 H, CH_2), 3.12 (m, 4 H, NCH_2), 5.83 (s, 1 H, olefin H), 6.40 (d, ^3J = 4.7 Hz, 1 H, 3 H, nitrothienyl), 7.06 (dd, ^3J = 3.5, ^3J = 1.2 Hz, 1 H, 3-H, thienyl), 7.15 (dd, ^3J = 5.1, ^3J = 3.5 Hz, 1 H, 4-H, thienyl), 7.60 (m, 2 H, 4-H, nitrothienyl and 5-H, thienyl) ppm. ^{13}C NMR ($CDCl_3$): δ = 24.3 (CH_2), 25.7 (CH_2), 49.3 (NCH_2), 97.5 (olefin. CH), 122.2, 128.5, 129.5, 129.9, 130.2, (CH), 135.0, 144.9, 147.5, 154.8 (C_q) ppm. FD MS: *m*/*z* (%) = 320 (100) [M^+]. $C_{15}H_{16}N_2O_2S_2$ (320.1): calcd. C 56.23, H 5.03, N 8.74, S 20.01; found C 56.12, H 4.96, N 8.88, S 19.83.

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