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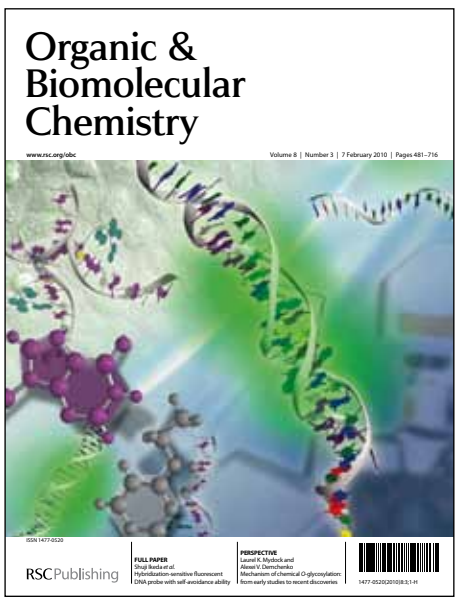

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Efficient pseudo-five-component coupling-Fiesselmann synthesis of luminescent oligothiophenes and their modification†‡

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Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
First published on the web Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

(Hetero)aryl bisacidchlorides and terminal alkynes, or likewise acidchlorides and terminal dialkynes, and ethyl 2-mercapto acetate can be reacted to give highly luminescent symmetrical terthiophenes and quinquethiophenes in the sense of a consecutive pseudo-five-component reaction in good to excellent yield. Further functionalization of the obtained oligomers can be readily achieved by halogenation followed by a metal-catalyzed coupling-reaction to give α,ω-diester substrates for subsequent transformations into highly functionalized materials.

Introduction

Thiophenes and oligothiophenes represent important building blocks in the synthesis of natural products[1] and pharmaceuticals.[2] Additionally, in recent years oligothiophenes have adopted a major role among functional π-electron systems,[3] in particular, as hole transport materials in organic light emitting diodes,[4] organic field-effect transistors,[5] and organic photovoltaics.[6] Besides the molecular structure especially the conformation and morphology of these electroactive oligomers exert a decisive influence on the bulk materials' properties.

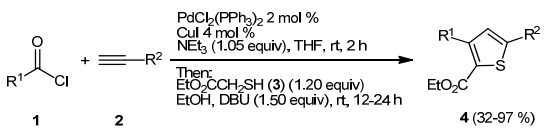
For a long time polythiophenes with a 2,5-linking pattern have efficiently been synthesized, e.g. by electropolymerisation.[7] Functionalized monomers can also be applied to improve the typically poor solubility of oligo- and polythiophenes as a necessary prerequisite for solution-based processing. In contrary to 2,5-linked polymers with variable polydispersity, the efficient synthesis of monodisperse well-defined oligothiophenes still remains a challenge. The latter are particularly interesting for vacuum deposition processing finally furnishing defectfree high-quality films.[8] Furthermore, functionalized oligo- and polythiophene scaffolds do not only influence the solubility or self-organization, but even more the photophysical and electronic molecular properties. In addition oligomer conformations largely depend on the substituent decoration and they are responsible for extended π-electron conjugation and for bulk charge transport properties.[3]

Particularly interesting are functionalities on oligothiophene scaffolds that can be addressed under mild enzymatic conditions. Thereby conformational organization of electronic functional oligothiophenes under kinetic control leading to highly tunable electronic materials can be enabled. Finally, the ease of synthetic accessibility of functional organic materials such as conjugated oligomers by diversity oriented synthesis[9] is a highly demanding methodological challenge, which can be efficiently reached by way of one-pot syntheses where all functionalities can be introduced in a very concise and convergent fashion.

In the past years we have developed rapid diversity-oriented accesses to functional chromophores[9] and electrophores based upon the productive concepts of consecutive multicomponent synthesis of heterocycles and domino transformations initiated by transition metal catalyzed alkyne coupling.[10] Furthermore rapid one-pot sequences to (oligo)thiophenes could be scouted and methodologically developed.[11] Now, we set out to expand our recently reported three-component coupling-Fiesselmann synthesis of 2,4-disubstituted thiophene 5-carboxylates to an access of functionalized oligothiophenes as electronically tunable extended π-system building blocks.[12] Here, we report on the synthesis and optical properties of selected oligothiophenes. In addition, we disclose various functionalizations of the multicomponent products for rapidly accessing interesting building blocks for materials syntheses.

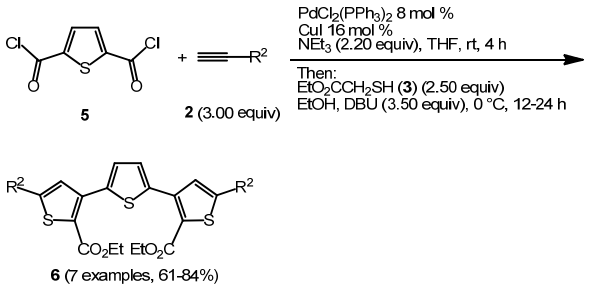
Results and discussion

Recently we communicated a concise, consecutive three-component transformation of (hetero)aroyl chlorides **1**, alkynes **2**, and ethyl 2-mercapto acetate (**3**) to give 2,4-disubstituted thiophene 5-carboxylates **4** in moderate to excellent yields in the sense of a coupling-Fiesselmann synthesis (Scheme 1).[12]



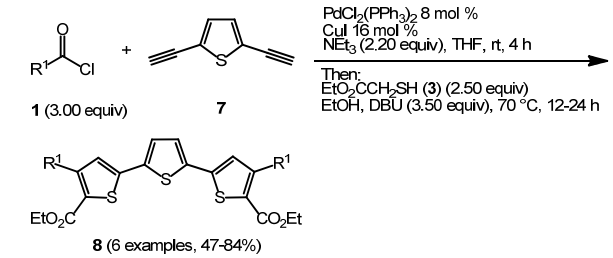
Scheme 1 Consecutive three-component Sonogashira alkynylation-Fiesselmann cyclocondensation synthesis of 2,4-disubstituted thiophene 5-carboxylates **4**.

This efficient methodology can be readily expanded to the synthesis of more extended conjugated oligomers. By choosing thiophene-2,5-dicarbonyl dichloride (**5**) as a coupling partner symmetrically substituted ter- and quinquethiophenes **6** can be synthesized in good yields in a one-pot fashion and in the sense of a pseudo-five-component reaction (Scheme 2, Figure 1).



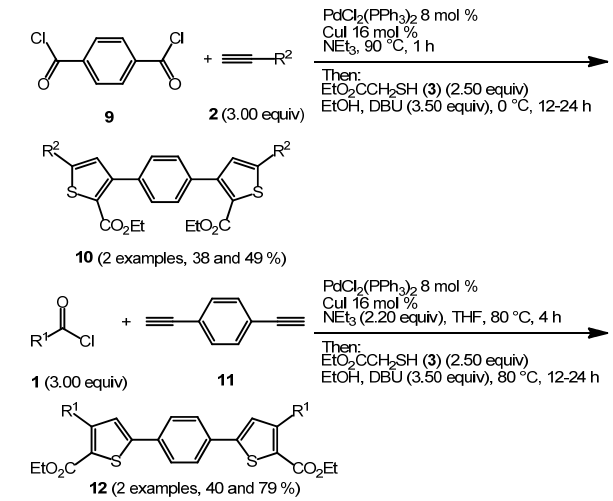
Scheme 2 Consecutive pseudo-five-component Sonogashira alkynylation-Fiesselmann cyclocondensation synthesis of symmetrically substituted ter- and quinquethiophenes **6**.

Likewise 2,5-diethynylthiophene (**7**) furnishes centrally α,α'-disubstituted ter- and quinquethiophenes **8** in good yields (Scheme 3, Figure 1). It should be noted that the use of dialkyne **7** is not trivial, since it is known to be very unstable and to decompose already at -25 °C. Only under nitrogen and upon exclusion of light it can be handled for a few hours.



Scheme 3 Consecutive pseudo-five-component Sonogashira alkynylation-Fiesselmann cyclocondensation synthesis of centrally α,α'-disubstituted ter- and quinquethiophenes **8**

Terephthaloyl dichloride (**9**) reacts with alkynes **2** giving rise to the formation of the thienyl terminated dumbbells **10**, whereas 1,4-diethynylbenzene (**11**) and the acid chlorides **1** furnish the *p*-phenylene bridged symmetrical molecules **12** in moderate to good yields (Scheme 4, Figure 1).



Scheme 4 Consecutive pseudo-five-component Sonogashira alkynylation-Fiesselmann cyclocondensation synthesis of the dithienyl dumbbells **10** and **12**.

The structure of all compounds is unambiguously supported by NMR spectroscopy and MALDI spectrometry. Due to the inherent molecular C_2-symmetry all NMR spectra show only a half set of signals. The thiophene based systems **6** and **8** display two characteristical singlets with identical intensity in the aromatic region of the ^{1}H NMR spectra, whereas the phenylene analogues **10** and **12** exhibit two singlets with an integral ratio of 1:2. In all cases the typical triplet and quartet of the ethyl ester is most characteristically found. The MALDI spectra of all compounds likewise reveal a characteristic fragmentation pattern arising from the loss of an ethoxy radical from the molecular peak.

As previously shown for the synthesis of 2,4-disubstituted thiophene 5-carboxylates **4** the Fiesselmann thiophene synthesis[13,14] via the multicomponent approach to the oligothiophenes **6**, **8**, **10**, and **12** advantageously applies a small set of mono- and dialkynes or mono- and diacidchlorides. They are readily available or easily accessible substrates for rapidly creating a library of functional π-systems in a one-pot fashion. In the series of the derivatives **6** the electronic nature of the alkynes **2** was scouted to give that electron deficient, electroneutral, electron rich, heterocyclic and even cyclopropyl alkynes are equally well tolerated. Even the highly sensitive 2,5-diethynylthiophene (**7**) furnishes the corresponding symmetrical oligothiophenes **8** in an average isolated yield of 68 %, which equals a yield of 88 % per bond forming step.

The electronic properties of the oligothiophene derivatives **6**, **8**, **10**, and **12** were thoroughly studied by UV/vis and fluorescence spectroscopy (Table 1, Figure 2 and 3). Most strikingly, large Stokes shifts $\Delta\tilde{\nu}$ are observed for all representatives. In addition, the fluorescence quantum yields Φ_f were determined with coumarin 1 ($\Phi_f = 0.73$) as a standard. Expectedly, the absorption maxima $\lambda_{max,abs}$ of the oligothiophenes **6** are blueshifted by 2700-7600 cm^{-1} in comparison to the bands of the analogous oligothiophenes **8**. Only the oligothiophenes **6** can be finetuned in their absorption behavior by the electronic nature of the remote terminal substituents, displaying $\lambda_{max,abs}$ in the range from 307 to 359 nm. In contrast the absorption maxima $\lambda_{max,abs}$ of the analogous oligothiophenes **8** are found around 395 nm. Interestingly, all compounds **6** and **8** display emission maxima around 445 nm, independent of both the ligation and the substitution pattern. The common structural feature of all oligothiophene derivatives is the conjugated terthienyl moiety symmetrically substituted with ethyl carboxylate functionalities **6** and **8**. It can be concluded that the vibrationally relaxed excited state structures of both series are geometrically very similar, presumably, other than in the electronic ground state, with extended coplanarity of all three thienyl units. Since significant deviations from coplanarity are known for 2,5-linked oligothiophenes with sterically crowded substituents causing a twisting of the conjugated backbone,[15] it is obvious that second redshifted emission shoulders are detected around 471 nm for the systems **8** (Figure 2). The occurrence of this additional redshifted emission might indeed arise from a planarized excited state geometry with increased overall delocalization and thereby lowering the vibrationally relaxed excited state.

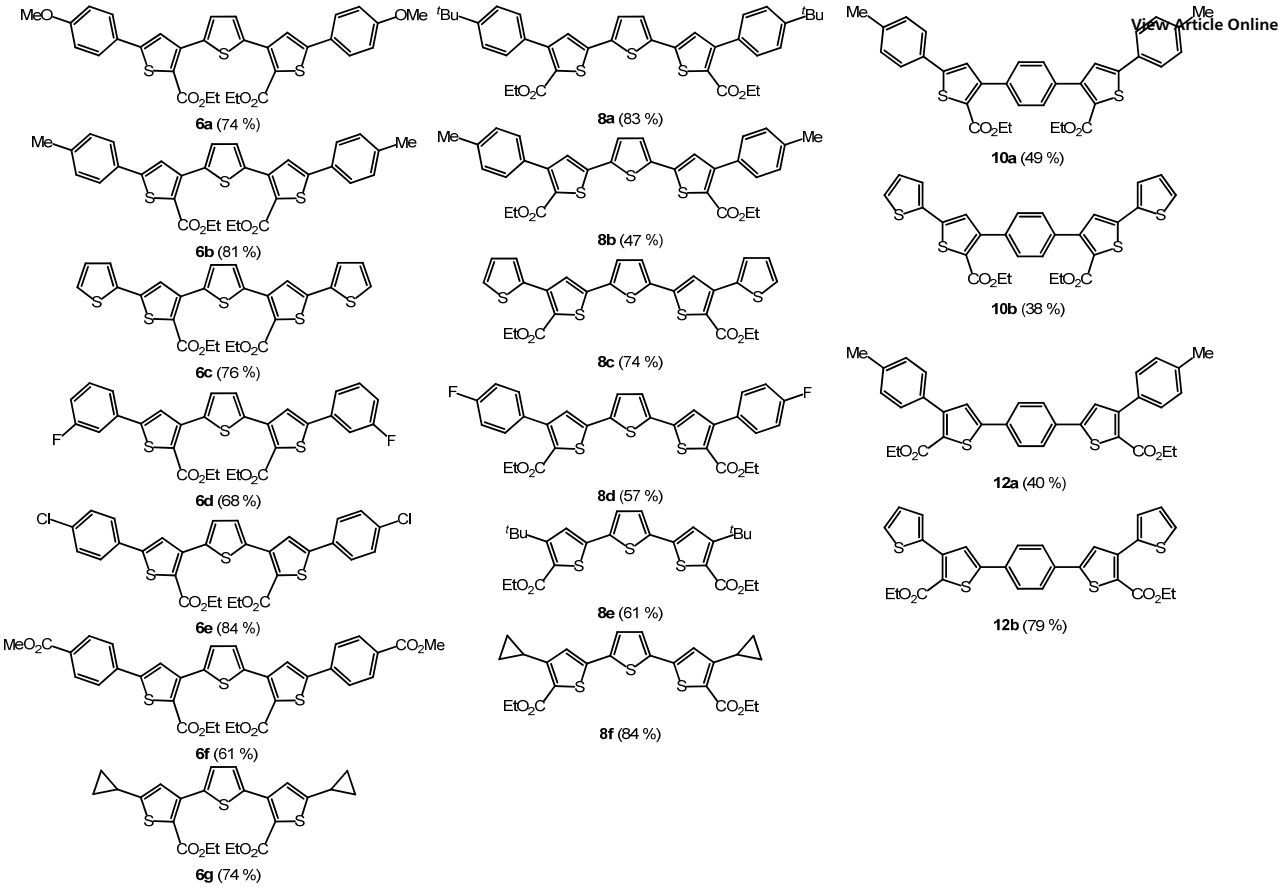


Figure 1 Symmetrically substituted oligothiophenes **6**, **8**, **10**, and **12** synthesized by consecutive pseudo-five-component Sonogashira alkynylation-Fiesselmann cyclocondensation synthesis (all yields are isolated yields after chromatographic purification).

Table 1 Selected absorption and emission data of the compounds **6**, **8**, **10**, and **12**.

Entry	Compound	Absorption [a] $\lambda_{max,abs}$ [nm] (ε, M^{-1} cm^{-1})	Emission [b] $\lambda_{max,em}$ [nm] (Φ_f) [c]	Stokes shift $\Delta\tilde{\nu}$ [d] [cm^{-1}]
1	**6a**	340 (54800)	443 (0.08)	6800
2	**6b**	328 (51500)	442 (0.09)	7900
3	**6c**	344 (63800)	445 (0.11)	6600
4	**6d**	305 (42300)	444 (0.07)	10300
5	**6e**	307 (43300)	445 (0.10)	10100
6	**6f**	321 (55500)	449 (0.10)	8900
7	**6g**	359 (21500)	440 (0.08)	5100
8	**8a**	398 (30900)	449, 472 (<0.01)	2900
9	**8b**	396 (42200)	449, 472 (<0.01)	3000
10	**8c**	397 (35300)	450, 472 (<0.01)	3000
11	**8d**	395 (30800)	449, 470 (<0.01)	3000
12	**8e**	395 (42000)	451, 473 (<0.01)	3100
13	**8f**	395 (41300)	446, 470 (<0.01)	2900
14	**10a**	318 (42000)	396 (<0.01)	6200
15	**10b**	328 (43200)	408 (<0.01)	6000
16	**12a**	361 (43000)	404, 425 (<0.01)	2900
17	**12b**	347 (37300)	408, 428 (<0.01)	4300

[a] Recorded in CH_2Cl_2, T = 293 K, $c_0 = 10^{-3}$ M. [b] Recorded in CH_2Cl_2, T = 293 K, $c_0 = 10^{-6}$ M. [c] Fluorescence quantum yields were determined relative to Coumarin 1 (Φ_f = 0.73) as a standard in ethanol. [d] $\Delta\tilde{\nu} = 1/\lambda_{max,abs} - 1/\lambda_{max,em}$ [cm^{-1}].

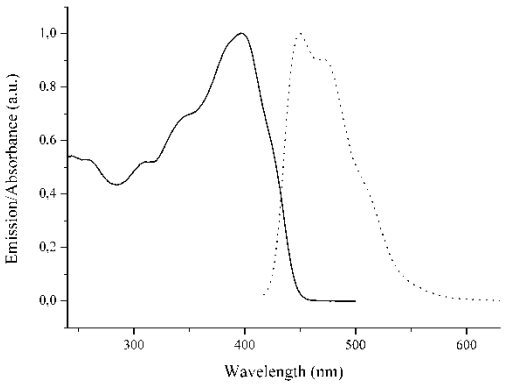


Figure 2 Normalized absorption (solid line) and emission spectra (dotted line) of compound **8c** (recorded in CH_2Cl_2, T = 293 K, $\lambda_{max,exc}$ 397 nm).

Likewise, the phenylene bridged dumbbells **12**, obtained from 1,4-diethynyl benzene (**11**), display two emissions (around 405 and 425 nm) as the thienyl bridged systems **8**, whereas the emission of the dumbbells **10** behaves similarly to the oligothiophenes **6** and only possess a single maximum around 400 nm (Table 1).

Among the synthesized series of oligothiophenes only the

derivatives **6** reveal substantial quantum yields Φ_f ranging from 7 to 11 %, whereas all other systems **8**, **10**, and **11** are only weakly fluorescent with quantum yields below 1 %.

In comparison to their solution luminescence all oligothiophenes display a pronounced red-shifted emission as a film and in the solid state. This effect is most remarkable for the series **6**, as illustrated for the emission of quinquethiophene **6c** in solution, in film and in solid state (Figure 3). Since packing largely influences the preferred ground state conformation in favor of planarization an extended π-conjugation rationalizes the red shift of the emission. In addition, it is known from 2,5-linked oligothiophenes that stacking in the solid state occurs directly or via herringbone packing.[16]

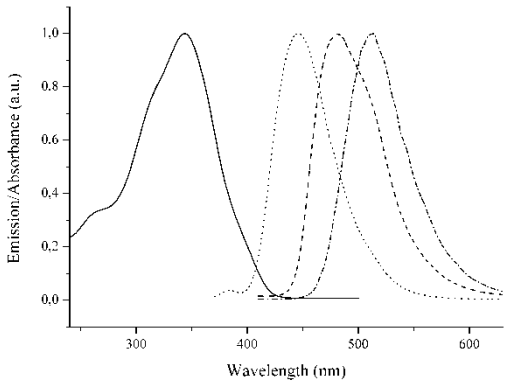


Figure 3 Normalized absorption (solid line), and emission spectra of compound **6c** in solution (dotted line), as a film (dashed line), and as a solid (dotted-dashed line) (recorded at T = 293 K, $\lambda_{max,exc}$ = 344 nm).

With this efficient, diversity-oriented synthetic access to oligothiophenes in hands the stage was set for various post-MCR modifications. Here, we particularly focused on the α,ω-functionalization of quinquethiophenes. Provided with functional groups, e.g. for further ligation, these bifunctional π-systems can represent valuable building blocks for the synthesis of organic materials.

The terminal dibromation of the oligothiophenes **4a** and **6c** can be achieved in excellent yields with NBS as an electrophilic brominating agent in a mixture of glacial acetic acid and chloroform furnishing the dibromo derivatives **13** and **14** (Scheme 5).[17]

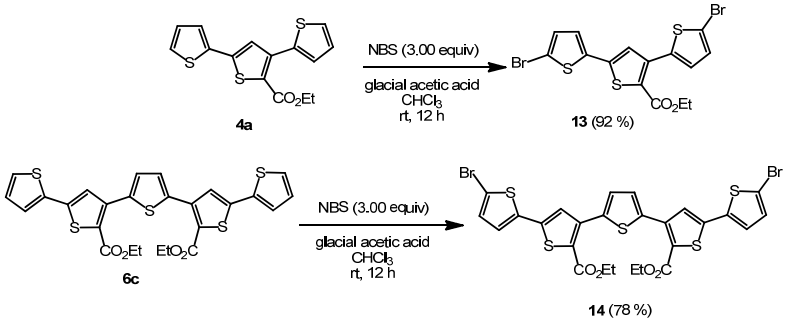
By Sonogashira coupling of the dibromides **13** and **14** with the ethyl hept-6-ynoate as a coupling partner almost quantitative yields of ω,ω'-bisethoxycarboxylates **15** and **16** containing conjugated alkynyl moieties were obtained (Scheme 6). These functionalized oligothiophenes display intense longest wavelength absorption bands at 340 and 363 nm (**15**) and 366 nm (**16**), respectively. The emission maxima are comparable to the α,ω-unsubstituted precursors **4a** and **6c** ($\lambda_{max,em}$ around 445 nm) and they are found as unstructured bands around 445 nm with fluorescence efficiencies Φ_f of 0.05 and 0.08, i.e. also comparable to **4a** and **6c**. By introducing long chain aliphatic substituents, the solubility of the targets in most organic solvents significantly increases and allows an easy processing from solution, e.g. in transesterification reactions.

Conclusions

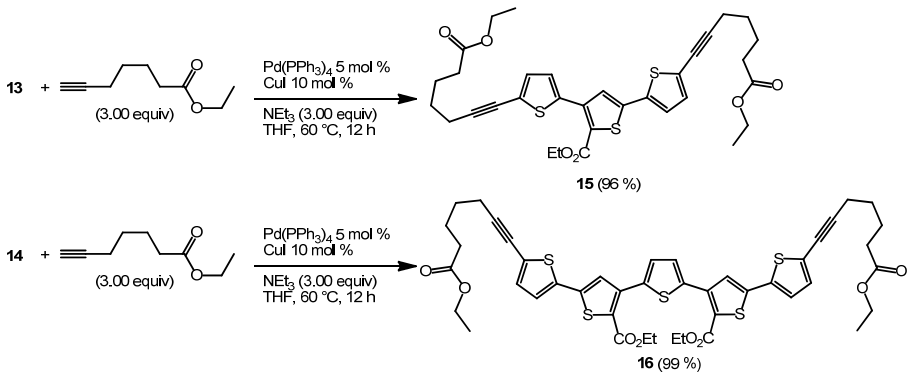
In conclusion, we have disclosed an efficient consecutive pseudo-five-component synthesis of oligothiophenes, in particular, symmetrically disubstituted ter- and quinquethiophenes and phenylene analogues in good to excellent yields. All represenatives are luminescent, yet, with variable fluorescence efficiency. Furthermore, these systems can be readily modified in post-MCR transformations to valuable halogenated substrates for metal-catalyzed reactions. For illustration Sonogashira coupling of dibrominated ter- and quinquethiophenes with an ω-carboethoxy functionalized alkyne furnishes ω,ω'-diesters, suitable substrates for polymerizations and enzymatic transformations. Further synthetic and photophysical studies with these building blocks are currently underway.

Acknowledgments

The support of this work by CLIB graduate cluster (scholarship for M. T.) and the Fonds der Chemischen Industrie is gratefully acknowledged.



Scheme 5 Halogenation of oligothiophenes **4a** and **6c** via NBS bromination.



Scheme 6 Diterminal functionalization of the dibromides **13** and **14** by Sonogashira coupling.

Experimental

General considerations

All reactions involving palladium-copper catalysis were performed in degassed oxygen-free solvents under an argon atmosphere in sealed reaction vessels. All starting materials were purchased from Aldrich, Fluka, Merck, Acros or ABCR and used without further purification. Solvents were dried by the solvent purification system: MBraun MB SPS-800. Column chromatography: silica gel 60 (Merck, Darmstadt), mesh 230-400, Biotage SP-4. TLC: silica gel plates (60 F_{254} Merck, Darmstadt). ^{1}H, ^{13}C and DEPT NMR spectra were recorded with a 500 MHz NMR spectrometer by using $CDCl_3$ and DMSO-d_6 as solvent. The assignments of quaternary C, CH, CH_2 and CH_3 have been made by using DEPT spectra. IR: Perkin-Elmer Lambda 3. UV/vis and fluorescence: Perkin-Elmer Model Lambda 16 and LS-55. Mass spectra were recorded with quadruple spectrometer. Elemental analyses were carried out in the microanalytical laboratory of the Pharmazeutisches Institut of the Heinrich-Heine-Universität Düsseldorf.

General Procedure (GP) for the pseudo-five-component Sonogashira alkynylation - Fiesselmann cyclocondensation of thiophene-2,5-dicarbonyl dichloride (5) with alkyne 2 to give oligothiophenes 6

$Pd(PPh_3)_4$ (92 mg, 0.08 mmol), CuI (30 mg, 0.16 mmol), and dry THF (15 mL) were successively placed in the reaction vessel under nitrogen at room temp and stirred for 5 min. After the addition of thiophene-2,5-dicarbonyldichloride (**5**) (209 mg, 1.00 mmol), the alkyne **2** (3.00 mmol), and triethylamine (223 mg, 2.20 mmol) the reaction mixture was stirred at room temp for 4 h (for experimental details see Table 2). Then, ethanol (2 mL), ethyl 2-mercapto acetate (**3**) (300 mg, 2.50 mmol), and DBU (533 mg, 3.50 mmol) were successively added at 0 °C and the solution was stirred for 20 h and allowed to come to room temp. For workup, the volatiles were removed under reduced pressure. The crude product was extracted three times with a mixture of CH_2Cl_2 and aqueous 1M HCl. The combined organic layers were dried with anhydrous $MgSO_4$, absorbed on celite®, and purified by automated column chromatography on fine silica gel (*n*-hexane/THF, gradient: 20 % to 35 %, 15 column volumes, 100 g) to give the compounds **6** as yellow to orange solids. Further purification can easily be achieved by recrystallization from ethanol.

Table 2 Experimental details for the synthesis of the oligothiophenes **6**.

entry	alkyne **2** [mg] (mmol)	oligothiophene **6** [mg] (yield)
1	396 (3.00) of **2a**	327 (74 %) of **6a**
2	348 (3.00) of **2b**	452 (81 %) of **6b**
3	324 (3.00) of **2c**	312 (76 %) of **6c**
4	360 (3.00) of **2d**	385 (68 %) of **6d**
5	410 (3.00) of **2e**	399 (84 %) of **6e**
6	481 (3.00) of **2f**	393 (61 %) of **6f**
7	198 (3.00) of **2g**	337 (74 %) of **6g**

Diethyl 5,5''-bis(4-methoxyphenyl)-[3,2':5',3''-terthiophene]-2,2''-dicarboxylate (6a)

According to the GP 327 mg (74 %) of **6a** were obtained as orange solid; mp 145 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37 (t, J = 7.1 Hz, 6 H), 3.85 (s, 6 H), 4.35 (q, J = 7.1 Hz, 4 H), 6.95 (d, J = 8.9 Hz, 4 H), 7.39 (s, 2 H), 7.60 (d, J = 8.8 Hz, 4 H), 7.62 (s, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.3 (2 CH_3), 55.3 (2 CH_3), 61.1 (2 CH_2), 114.5 (CH), 124.0 (CH), 125.7 (C_{quat}), 126.0 (CH), 127.5 (C_{quat}), 129.2 (C_{quat}), 137.5 (C_{quat}), 140.5 (C_{quat}), 148.2 (C_{quat}), 160.4 (C_{quat}), 162.0 (C_{quat}). MALDI MS *m/z* (%): 604 ([M], 85), 559 ([M] – C_2H_5O, 100). IR (KBr): $\tilde{\nu}$ [cm^{-1}] 2959 (w), 2930 (w), 2862 (w), 1699 (s), 1605 (m), 1541 (w), 1504 (m), 1464 (m), 1427 (m), 1416 (m), 1292 (w), 1236 (s), 1177 (s), 1101 (s), 1074 (s), 1032 (s), 866 (w), 808 (s), 758 (m), 704 (w), 658 (w). UV/vis (CH_2Cl_2): λ_{max} (ε) 340 nm (54800). Emission (CH_2Cl_2): λ_{max} (Stokes shift) 443 nm (6800 cm^{-1}). Quantum yield (CH_2Cl_2): Φ_f = 0.08. Anal. calcd. for $C_{32}H_{28}O_6S_3$ (604.8): C 63.55, H 4.67; Found: C 63.36, H 4.82.

Diethyl 3,2'-5',3''-terthiophene-5,5''-bis(*p*-tolyl)-2,2''-dicarboxylate (6b)

According to the GP 452 mg (81 %) of **6b** were obtained as yellow solid; mp 134 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.40 (t, J = 7.1 Hz, 6H), 2.41 (s, 6H), 4.37 (q, J = 7.1 Hz, 4H), 7.25 (d, J = 7.9 Hz, 4H), 7.48 (s, 2H), 7.58 (d, J = 8.1 Hz, 4H), 7.65 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.5 (2 CH_3), 21.4 (2 CH_3), 61.3 (2 CH_2), 124.7 (2 C_{quat}), 126.2 (4 CH), 126.7 (2 CH), 129.3 (2 CH), 129.9 (4 CH) , 130.3 (2 C_{quat}), 137.6 (2 C_{quat}), 139.3 (2 C_{quat}), 140.5 (2 C_{quat}), 148.5 (2 C_{quat}), 162.1 (2 C_{quat}). MALDI MS: *m/z* (%) = 572 ([M], 75), 527 ([M] - C_2H_5O, 100). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3021 (w), 2984 (w), 2905 (w), 2866 (w), 1699 (m), 1609 (w), 1545 (w), 1504 (m), 1466

(w), 1427 (m), 1387 (w), 1348 (w), 1273 (w), 1231 (s), 1184 (m), 1157 (w), 1105 (s), 1078 (m), 1043 (w), 1016 (m), 962 (w), 941 (w), 876 (w), 806 (s), 785 (m), 692 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) = 328 nm (51500). Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 442 nm (7900 cm^{-1}). Quantum yield (CH_2Cl_2): Φ_f = 0.09. Anal. calcd. for $C_{32}H_{28}O_4S_3$ (572.8): C 67.10, H 4.93; Found: C 66.99, H 5.01.

Diethyl [2,2':4',2'':5'',3''':5''',2''''-quinquethiophene]-2''',5'-dicarboxylate (6c)

According to the GP 312 mg (76 %) of **6c** were obtained as yellow solid; mp 141 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37 (t, J = 7.1 Hz, 6 H), 4.35 (q, J = 7.1 Hz, 4 H), 7.07 (dd, J = 5.0 Hz, J = 3.7 Hz, 2 H), 7.33 (m, 4 H), 7.35 (s, 2 H), 7.61 (s, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.3 (2 CH_3), 61.2 (2 CH_2), 124.2 (2 C_{quat}), 125.5 (2 CH), 126.4 (2 CH), 127.1 (2 CH), 128.2 (2 CH), 129.3 (2 CH), 135.8 (2 C_{quat}), 137.2 (2 C_{quat}), 140.2 (2 C_{quat}), 141.3 (2 C_{quat}), 161.7(2 C_{quat}). MALDI MS *m/z* (%): 556 ([M], 88), 511 ([M] – C_2H_5O, 100). IR (KBr): $\tilde{\nu}$ [cm^{-1}] 2977 (w), 1710 (s), 1701 (s), 1655 (w), 1638 (w), 1551 (w), 1509 (w), 1474 (w), 1434 (m), 1387 (w), 1232 (s), 1104 (m), 1076 (m), 1019 (w), 805 (m), 758 (m), 733 (m), 690 (m). UV/vis (CH_2Cl_2): λ_{max} (ε) = 344 nm (63800). Emission (CH_2Cl_2): λ_{max} (Stokes shift) 445 nm (6600 cm^{-1}). Emission (film): λ_{max} (Stokes shift) 481 nm (8300 cm^{-1}). Emission (solid): λ_{max} (Stokes shift) 512 nm (9500 cm^{-1}). Quantum yield (CH_2Cl_2): Φ_f = 0.11. Anal. calcd. for $C_{26}H_{20}O_4S_5$ (556.8): C 56.09, H 3.62; Found: C 56.17, H 3.76.

Diethyl 3,2'-5',3''-terthiophene-5,5''-bis(*m*-fluorophenyl)-2,2''-dicarboxylate (6d)

According to the GP 385 mg (68 %) of **6d** were obtained as yellow solid; mp 144 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.39 (t, J = 7.1 Hz, 6H), 4.37 (q, J = 7.1 Hz, 4H), 7.04 – 7.11 (m, 2H), 7.33 – 7.47 (m, 6H), 7.50 (s, 2H), 7.63 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.4 (2 CH_3), 61.5 (2 CH_2), 113.3 (d, ^2J = 23.0 Hz, 2 CH_2), 116.0 (d, ^2J = 21.2 Hz, 2 CH), 122.0 (d, ^4J = 2.8 Hz, 2 CH), 125.9 (2 CH), 127.7 (2 CH), 129.5 (2 CH), 130.9 (d, ^3J = 8.2 Hz, 2 CH), 135.1 (d, ^3J = 8.2 Hz, 2 C_{quat}), 137.5 (2 C_{quat}), 140.4 (2 C_{quat}), 146.7 (2 C_{quat}), 161.9 (2 C_{quat}), 162.3 (d, ^1J = 247.1 Hz, 2 C_{quat}). MALDI MS: *m/z* (%) = 580 ([M], 85), 535 ([M] - C_2H_5O, 100). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2988 (w), 2940 (w), 2901 (w), 2874 (w), 1717 (m), 1611 (w), 1586 (m), 1557 (w), 1533 (w), 1483 (w), 1468 (w), 1445 (m), 1431 (m), 1389 (w), 1354 (w), 1244 (s), 1188 (w), 1175 (m), 1160 (m), 1109 (m), 1076 (m), 1049 (w), 1016 (m), 997 (w), 964 (w), 845 (m), 831 (m), 804 (m), 772 (m), 756 (m), 706 (w), 677 (m). UV/vis (CH_2Cl_2): λ_{max} (ε) = 305 nm (42300). Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 444 nm (10300 cm^{-1}). Quantum yield (CH_2Cl_2): Φ_f = 0.07. Anal. calcd. for $C_{30}H_{22}F_2O_4S_3$ (580.7): C 62.05, H 3.82; Found: C 61.89, H 3.91.

Diethyl 5,5''-bis(4-chlorophenyl)-[3,2':5',3''-terthiophene]-2,2''-dicarboxylate (6e)

According to the GP 399 mg (84 %) of **6e** were obtained as orange solid; decomposition at 130 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.38 (t, J = 7.1 Hz, 6 H), 4.35 (q, J = 7.1 Hz, 4 H), 7.40 (d, J = 8.6 Hz, 4 H), 7.46 (s, 2 H), 7.59 (d, J = 8.6 Hz, 4 H), 7.63 (s, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.3 (CH_3), 61.3 (CH_2), 125.4 (C_{quat}), 127.2 (CH), 127.3 (CH), 129.3 (CH), 129.3 (CH), 131.4 (C_{quat}), 135.0 (C_{quat}), 137.3 (C_{quat}), 140.3 (C_{quat}), 146.7 (C_{quat}), 161.7 (C_{quat}). MALDI MS *m/z* (%): 614 ([^{37}Cl-^{35}Cl-M], 100), 569 ([^{37}Cl-^{35}Cl-M] – C_2H_5O, 90). IR (KBr): $\tilde{\nu}$ [cm^{-1}] 2982 (w), 1715 (s), 1682 (m), 1555 (w), 1489 (m), 1468 (w), 1429 (m), 1269 (m), 1240 (s), 1182 (m), 1094 (s), 1076 (s), 1013 (m), 893 (w), 816 (s), 797 (m), 756 (m) 692 (w). UV/vis (CH_2Cl_2): λ_{max} (ε) 307 nm (43300). Emission (CH_2Cl_2): λ_{max} (Stokes shift) 445 nm (10100 cm^{-1}). Quantum yield (CH_2Cl_2): Φ_f = 0.10. Anal. calcd. for $C_{30}H_{22}Cl_2O_4S_3$ (613.6): C 58.72, H 3.61; Found: C 58.53, H 3.55.

Diethyl 3,2'-5',3''-terthiophene-5,5''-bis(*p*-(methoxycarbonyl)phenyl)-2,2''-dicarboxylate (6f)

According to the GP 393 mg (61 %) of **6f** were obtained as orange solid; decomposition at 173 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.38 (t, ^3J = 7.1 Hz, 6H), 3.94 (s, 6H), 4.36 (q, J = 7.1 Hz, 4H), 7.58 (s, 2H), 7.64 (s, 2H), 7.73 (d, J = 8.2 Hz, 4H), 8.09 (d, J = 8.2 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.4 (2 CH_3), 52.4 (2 CH_3), 61.6 (2 CH_2), 126.1 (4 CH), 126.4 (2 C_{quat}), 128.20 (2 CH), 129.5 (2 CH), 130.4 (2 C_{quat}), 130.6 (4 CH), 137.1 (2 C_{quat}), 137.4 (2 C_{quat}), 140.5 (2 C_{quat}), 146.6 (2 C_{quat}), 161.8 (2 C_{quat}), 166.6 (2 C_{quat}). MALDI MS: *m/z* (%) = 660 ([M], 75), 615 ([M] - C_2H_5O, 100). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2982 (w), 2955 (w), 2359 (w), 2330 (w), 1717 (m), 1701 (m), 1605 (w), 1503 (w), 1447 (w), 1425 (w), 1410 (w), 1366 (w), 1315 (w), 1279 (m), 1233 (m), 1184 (m), 1101 (s), 1082 (m), 1067 (m), 1045 (m), 1016 (m), 961 (w), 934 (w), 883 (w), 847 (m), 824 (m), 768 (s), 735 (w), 692 (m), 656 (w). UV/vis (CH_2Cl_2): λ_{max} (ε) = 321 nm (55500). Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 449 nm (8900 cm^{-1}). Quantum yield (CH_2Cl_2): Φ_f = 0.10. Anal. calcd. for $C_{34}H_{28}O_8S_3$ (660.8): C 61.80, H 4.27; Found: C 61.60, H 4.22.

Diethyl 3,2'-5',3''-terthiophene-5,5''-bis(cyclopropyl)-2,2''-dicarboxylate (6g)

According to the GP 337 mg (74 %) of **6g** were obtained as yellow solid, mp 47 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.79 – 0.84 (m, 4H), 1.07 – 1.11 (m, 4H), 1.33 (t, J = 7.1 Hz, 6H), 2.08 (ddd, J = 13.3, 8.4, 5.0 Hz, 2H), 4.29 (q, J = 7.1 Hz, 4H), 6.96 (s, 2H), 7.53 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 10.9 (2 CH_2), 11.8 (2 CH_3), 14.4 (2 CH), 61.0 (4 CH_2), 122.4 (2 C_{quat}), 127.1 (2 CH), 129.1 (2 CH), 137.6 (2 C_{quat}), 139.9 (2 C_{quat}), 154.1 (2 C_{quat}), 162.0 (2 C_{quat}). MALDI MS: *m/z* (%) = 472 ([M], 75), 427 ([M] - C_2H_5O, 100). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3082 (w), 2980 (w), 2936 (w), 2903 (w), 2870 (w), 1703 (m), 1549 (w), 1524 (w), 1477 (w), 1452 (m), 1435 (w), 1371 (m), 1229 (s), 1198 (m), 1186 (m), 1171 (m), 1094 (s), 1069 (m), 1022 (m), 962 (w), 937 (w), 941 (w), 874 (m), 829 (m), 808 (m), 760 (m), 719 (w), 694 (w), 665 (w), 640 (w). UV/vis (CH_2Cl_2): λ_{max} (ε) = 359 nm (21500). Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 440 nm (5100 cm^{-1}). Quantum yield (CH_2Cl_2): Φ_f = 0.08. Anal. calcd. for $C_{24}H_{24}O_4S_3$ (472.6): C 60.99, H 5.12; Found: C 60.18, H 5.26.

General Procedure (GP) for the pseudo-five-component Sonogashira alkynylation - Fiesselmann cyclocondensation of 2,5-diethynylthiophene (7) with acid chloride 1 to give oligothiophenes 8

The TMS protected thiophene-2,5-dialkyne[18] (277 mg, 1.00 mmol), KOH (27 µL of a 0.5 m aqueous KOH solution) and dry MeOH (5.4 mL) were successively placed in a reaction vessel under nitrogen and exclusion of light at room temperature and stirred for 30 min. After the addition of 5.4 mL of water the solution was extracted three times with 50 mL *n*-hexane. The combined organic layers were dried with anhydrous $MgSO_4$ and the volatile components were removed under reduced pressure. In the meantime $Pd(PPh_3)_4$ (92 mg, 0.08 mmol), CuI (30 mg, 0.16 mmol), and dry THF (2 mL) were successively placed in another reaction vessel under nitrogen at room

temp and stirred for 5 min. After the addition of the acid chloride **1** (3.00 mmol) and triethylamine (223 mg, 2.20 mmol) the previously deprotected 2,5-diethynylthiophene (**7**) was dissolved in 8 mL of THF and added dropwise over 15 min (for experimental details see Table 3). The reaction mixture was stirred for another 4 h at room temp. Then, ethanol (2 mL), ethyl 2-mercapto acetate (**3**) (300 mg, 2.50 mmol), and DBU (533 mg, 3.50 mmol) were successively added and the solution was stirred for 20 h at 70 °C. For workup, the volatile components were removed under reduced pressure. The crude product was extracted three times with a mixture of CH_2Cl_2 and aqueous 1M HCl. The combined organic layers were dried with anhydrous $MgSO_4$, absorbed on celite®, and purified by automated column chromatography on fine silica gel (n-hexane/THF, gradient: 20 % to 35 %, 15 column volumes, 100 g) to give the compounds **8** as yellow to orange solids. Further purification can easily be achieved by recrystallization from ethanol.

Table 3 Experimental details for the synthesis of the oligothiophenes **8**.

entry	acid chloride **1** [mg] (mmol)	oligothiophene **8** [mg] (yield)
1	440 (3.00) of **1a**	411 (74 %) of **8a**
2	464 (3.00) of **1b**	269 (47 %) of **8b**
3	314 (3.00) of **1c**	398 (84 %) of **8c**
4	476 (3.00) of **1d**	322 (57 %) of **8d**
5	590 (3.00) of **1e**	526 (83 %) of **8e**
6	362 (3.00) of **1f**	307 (61 %) of **8f**

Diethyl 2,2'-5',2''-terthiophene-4,4''-bis(*p*-^{t}butylphenyl)-5,5''-dicarboxylate (8a)

According to the GP 411 mg (74 %) of **8a** were obtained as orange solid; mp 185 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 (t, J = 7.1 Hz, 6H), 1.37 (s, 18H), 4.26 (q, J = 7.1 Hz, 4H), 7.17 (s, 2H), 7.24 (s, 2H), 7.44 (s, 8H). ^{13}C NMR (125 MHz, $CDCl^3$): δ = 14.3 (2 CH_3), 31.5 (6 CH_3), 34.8 (2 C_{quat}), 61.2 (2 CH_2), 125.0 (4 CH), 125.5 (2 C_{quat}), 126.2 (2 CH), 128.2 (2 CH), 129.0 (4 CH), 132.5 (2 C_{quat}), 136.8 (2 C_{quat}), 140.5 (2 C_{quat}), 149.5 (2 C_{quat}), 151.3 (2 C_{quat}), 161.9 (2 C_{quat}). MALDI MS: *m/z* (%) = 657 ([M], 100). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3063 (w), 2955 (m), 2922 (m), 2853 (m), 2687 (w), 1709 (m), 1614 (w), 1510 (w), 1466 (m), 1433 (m), 1362 (m), 1256 (s), 1221 (m), 1202 (m), 1190 (m), 1126 (m), 1101 (m), 1074 (m), 1049 (m), 1022 (m), 970 (w), 905 (m), 870 (w), 822 (m), 783 (s), 760 (m), 746 (m), 729 (w), 706 (w), 689 (w), 671 (w), 631 (w). UV/vis (CH_2Cl_2): λ_{max} (ε) = 398 nm (30900). Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 449 nm (2900 cm^{-1}), 472 nm. Anal. calcd. for $C_{38}H_{40}O_4S_3$ (656.9): C 69.48, H 6.14; Found: C 69.87, H 6.60.

Diethyl 2,2'-5',2''-terthiophene-4,4''-bis(*p*-tolyl)-5,5''-dicarboxylate (8b)

According to the GP 269 mg (47 %) of **8b** were obtained as orange solid; mp 149 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.28 (t, J = 7.1 Hz, 6H), 2.41 (s, 6H), 4.25 (q, J = 7.1 Hz, 4H), 7.15 (s, 2H), 7.24 (s, 2H), 7.23 (d, J = 9.4 Hz, 4H), 7.39 (d, J = 8.0 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.3 (2 CH_3), 21.5 (2 CH_3), 61.2 (2 CH_2), 125.5 (2 C_{quat}), 126.2 (2 CH), 128.1 (2 CH), 128.7 (4 CH), 129.2 (4 CH), 132.5 (2 C_{quat}), 136.8 (2 C_{quat}), 138.2 (2 C_{quat}), 140.5 (2 C_{quat}), 149.6 (2 C_{quat}), 161.9 (2 C_{quat}). MALDI MS: *m/z* (%) = 572 ([M], 100). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3078 (w), 3024 (w), 2980 (w), 2918 (w), 2857 (w), 2718 (w), 1715 (m), 1682 (m), 1616 (w), 1545 (w), 1512 (w), 1468 (w), 1433 (m), 1366 (m), 1260 (s), 1225 (m), 1188 (m), 1155 (w), 1107 (m), 1072 (m), 1022 (m), 935 (w), 903 (w), 866 (w), 833 (m), 799 (m), 781 (m), 758 (m), 718 (w), 667 (m), 631 (w). UV/vis (CH_2Cl_2): λ_{max} (ε) = 396 nm (42200). Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 449 nm (3000 cm^{-1}), 472 nm. Anal. calcd. for $C_{32}H_{28}O_4S_3$ (572.8): C 67.10, H 4.93; Found: C 67.06, H 5.04.

Diethyl 2,3'-5',2''-5'',2'''-4''',2''''-quinquethiophene-2',5'''-dicarboxylate (8c)

According to the GP 398 mg (84 %) of **8c** were obtained as orange solid; mp 174 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.36 (t, J = 7.1 Hz, 6H), 4.33 (q, J = 7.1 Hz, 4H), 7.10 (dd, J = 5.1 Hz, J = 3.7 Hz, 2 H), 7.24 (s, 2 H), 7.30 (s, 2 H), 7.40 (dd, J = 5.1 Hz, J = 1.0 Hz, 2 H), 7.61 (dd, J = 3.7 Hz, J = 1.0 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.4 (2 CH_3), 61.5 (2 CH_2), 124.9 (2 C_{quat}), 126.4 (2 CH), 126.9 (2 CH), 127.3 (2 CH), 127.8 (2 CH), 129.3 (2 CH), 135.9 (2 C_{quat}), 136.5 (2 C_{quat}), 140.4 (2 C_{quat}), 140.8 (2 C_{quat}), 161.7 (2 C_{quat}). MALDI MS: *m/z* (%) = 556 ([M], 100). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3092 (w), 2984 (w), 2928 (w), 2907 (w), 1709 (s), 1676 (s), 1547 (w), 1479 (w), 1462 (w), 1443 (s), 1422 (s), 1373 (m), 1310 (w), 1340 (w), 1273 (s), 1248 (s), 1233 (s), 1175 (w), 1125 (w), 1107 (s), 1078 (S), 1067 (m), 1043 (m), 1022 (w), 1011 (w), 856 (w), 818 (m), 799 (s), 756 (m), 683 (s), 658 (w). UV/vis (CH_2Cl_2): λ_{max} (ε) = 397 nm (35300). Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 450 nm (3000 cm^{-1}), 472 nm. Anal. calcd. for $C_{26}H_{20}O_4S_5$ (556.8): C 56.09 H 3.62; Found: C 55.89 H 3.91.

Diethyl 2,2'-5',2''-terthiophene-4,4''-bis(*p*-fluorophenyl)-5,5''-dicarboxylate (8d)

According to the GP 322 mg (57 %) of **8d** were obtained as yellow solid; mp 193 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 (t, J = 7.1 Hz, 6H), 4.25 (q, J = 7.1 Hz, 4H), 7.13 (s, 2H), 7.08 – 7.12 (m, 4H), 7.25 (s, 2H), 7.43 – 7.50 (m, 4H) ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.3 (2 CH_3), 61.3 (2 CH_2), 114.9 (d, 4 CH), 126.0 (2 C_{quat}), 126.3 (2 CH), 127.9 (2 CH), 131.1 (d, 4 CH), 131.4 (d, 2 C_{quat}), 136.7 (2 C_{quat}), 140.7 (2 C_{quat}), 148.3 (2 C_{quat}), 161.8 (2 C_{quat}), 163.8 (2 C_{quat}). MALDI MS: *m/z* (%) = 580 ([M], 100). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3071 (w), 3001 (w), 2980 (w), 2934 (w), 2874 (w), 2361 (w), 2330 (w), 1713 (m), 1678 (m), 1601 (w), 1528 (w), 1499 (m), 1476 (w), 1435 (m), 1425 (m), 1377 (m), 1327 (w), 1287 (m), 1263 (s), 1234 (m), 1223 (m), 1188 (w), 1159 (m), 1123 (m), 1096 (m), 1076 (m), 1020 (m), 957 (w), 934 (w), 822 (m), 799 (m), 787 (m), 758 (m). UV/vis (CH_2Cl_2): λ_{max} (ε) = 395 nm (30800). Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 449 nm (3000 cm^{-1}), 470 nm. Anal. calcd. for $C_{30}H_{22}F_2O_4S_3$ (580.7): C 62.05, H 3.82; Found: C 61.91, H 4.08.

Diethyl 2,2'-5',2''-terthiophene-4,4''-bis(^{t}butyl)-5,5''-dicarboxylate (8e)

According to the GP 526 mg (83 %) of **8e** were obtained as yellow solid; decomposition at 126 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.38 (t, J = 7.1, 6 H), 1.49 (s, 18 H), 4.32 (q, J = 7.1, 4 H), 7.17 (d, J = 1.8, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.4 (2 CH_3), 30.3 (6 CH_3), 35.2 (2 C_{quat}), 61.3 (2 CH_2), 125.7 (2 C_{quat}), 125.8 (2 CH), 126.1 (2 CH), 136.8 (2 C_{quat}), 139.4 (2 C_{quat}), 159.5 (2 C_{quat}), 162.0 (2 C_{quat}). MALDI MS: *m/z* (%) = 504 ([M], 100). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2959 (w), 2947 (w), 2907 (w), 2870 (w), 1699 (m), 1526 (w), 1460 (w), 1447 (w), 1412 (m), 1391 (m), 1362 (m), 1248 (m), 1391 (m), 1362 (m), 1248 (m), 1231 (s), 1206 (m), 1159 (m), 1115 (w), 1067 (s), 1013 (m), 941 (m), 858 (w), 835 (m), 785 (m), 762 (m), 675 (m).

UV/vis (CH_2Cl_2): λ_{max} (ε) = 395 nm (42000). Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 451 nm (3100 cm^{-1}), 473 nm. Anal. calcd. for $C_{26}H_{20}O_4S_5$ (556.8): C 61.87, H 6.39; Found: C 61.91, H 6.39.

Diethyl 2,2'-5',2''-terthiophene-4,4''-bis(cyclopropyl)-5,5''-dicarboxylate (8f)

According to the GP 307 mg (61 %) of **8f** were obtained as yellow solid; mp 142 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.60-0.90 (m, 4 H), 1.00-1.10 (m, 4 H), 1.38 (t, ^3J = 7.1 Hz, 6 H), 2.90-3.10 (m, 2 H), 4.35 (q, ^3J = 7.1 Hz, 4 H), 6.59 (s, 2 H), 7.13 (s, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 10.5 (4 CH_2), 10.9 (2 CH), 14.5 (2 CH_3), 61.0 (2 CH_2), 121.4 (2 CH), 125.0 (2 C_{quat}), 125.9 (2 CH), 136.7 (2 C_{quat}), 140.9 (2 C_{quat}), 154.2 (2 C_{quat}), 162.9 (2 C_{quat}). MALDI MS: *m/z* (%) = 472 ([M], 100). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3063 (w), 2990 (w), 2938 (w), 2903 (w), 1697 (m), 1670 (m), 1547 (m), 1524 (w), 1476 (w), 1443 (m), 1383 (m), 1364 (w), 1342 (m), 1281 (m), 1227 (s), 1186 (m), 1113 (w), 1084 (s), 1051 (m), 1016 (m), 974 (m), 862 (m), 802 (s), 760 (m), 689 (w), 654 (m). UV/vis (CH_2Cl_2): λ_{max} (ε) = 395 nm (41300). Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 446 nm (2900 cm^{-1}), 470 nm. Anal. calcd. for $C_{24}H_{24}O_4S_3$ (472.6): C 60.99, H 5.12; Found: C 60.75, H 5.03.

General Procedure (GP) for the pseudo-five-component Sonogashira alkynylation - Fiesselmann cyclocondensation of terephthaloyl dichloride (9) with alkyne 2 to give oligothiophenes 10

$Pd(PPh_3)_4$ (92 mg, 0.08 mmol) and CuI (30 mg, 0.16 mmol) were successively placed in the reaction vessel under nitrogen at room temp. After the addition of terephthaloyl dichloride (**9**) (203 mg, 1.00 mmol), the alkyne **2** (3.00 mmol) and triethylamine (5 mL) the reaction mixture was stirred at 90 °C for 1 h (for experimental details see Table 4). Then, ethanol (2 mL), THF (2 mL), ethyl 2-mercapto acetate (**3**) (300 mg, 2.50 mmol), and DBU (533 mg, 3.50 mmol) were successively added at 0 °C and the solution was stirred for 20 h and allowed to come to room temp. For workup, the volatile components were removed under reduced pressure. The crude product was extracted three times with a mixture of CH_2Cl_2 and aqueous 1M HCl. The combined organic layers were dried with anhydrous $MgSO_4$, absorbed on celite®, and purified by automated column chromatography on fine silica gel (*n*-hexane/THF, gradient: 20 % to 35 %, 15 column volumes, 100 g) to give the compounds **10** as yellow to orange solids. Further purification can easily be achieved by recrystallization from ethanol.

Table 4 Experimental details for the synthesis of the oligothiophenes **10**.

entry	alkyne **2** [mg] (mmol)	oligothiophene **10** [mg] (yield)
1	232 (3.00) of **2b**	269 (49 %) of **10a**
2	324 (3.00) of **2c**	208 (38%) of **10b**

Diethyl 3,3'-(1,4-phenylene)bis(5,5'-*p*-tolylthiophene-2,2'-carboxylate) (10a)

According to the GP 269 mg (49 %) of **10a** were obtained as white solid; decomposition at 228 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.30 (t, *J* = 7.1 Hz, 6H), 2.40 (s, 6H), 4.28 (q, *J* = 7.1 Hz, 4H), 7.21 – 7.26 (m, 4H), 7.32 (s, 2H), 7.52 – 7.61 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.3 (2 CH_3), 21.4 (2 CH_3), 61.1 (2 CH_2), 125.6 (2 C_{quat}), 126.1 (4 CH), 127.1 (2 CH), 128.8 (4 CH), 129.9 (4 CH), 130.6 (2 C_{quat}), 135.6 (2 C_{quat}), 139.1 (2 C_{quat}), 148.7 (2 C_{quat}), 149.1 (2 C_{quat}), 162.2 (2 C_{quat}). MALDI MS: *m/z* (%) = 566 ([M], 100). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2963 (w), 2901 (w), 2857 (w), 2361 (w), 1800 (w), 1715 (m), 1607 (w), 1551 (w), 1495 (w), 1443 (m), 1350 (w), 1246 (m), 1231 (m), 1207 (m), 1184 (m), 1128 (m), 1103 (m), 1080 (m), 1043 (m), 1018 (m), 962 (w), 895 (w), 827 (w), 812 (s), 795 (m), 760 (m), 692 (w). UV/vis (CH_2Cl_2): λ_{max} (ε) = 318 nm (42000). Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 396 nm (6200 cm^{-1}). Anal. calcd. for $C_{34}H_{30}O_4S_2$ (566.7): C 72.06, H 5.34; Found: C 70.25, H 5.14.

Diethyl 3,3'-(1,4-phenylene)bis(5,5'-(2-thienyl)-2,2'-carboxylate) (10b)

According to the GP 208 mg (38 %) of **10b** were obtained as white solid; decomposition at 199 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.30 (t, *J* = 7.1 Hz, 6 H), 4.27 (q, *J* = 7.1 Hz, 4 H), 7.10 – 7.05 (m, 2 H), 7.21 (s, 2 H), 7.32 (d, *J* = 4.4 Hz, 4 H), 7.55 (s, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.3 (2 CH_3), 61.2 (2 CH_2), 125.3 (2 C_{quat}), 125.4 (2 CH), 126.3 (2 CH), 127.8 (2 CH), 128.3 (2 CH), 128.9 (4 CH), 135.4 (2 C_{quat}), 136.3 (2 C_{quat}), 141.6 (2 C_{quat}), 149.0 (2 C_{quat}), 162.0 (2 C_{quat}). MALDI MS: *m/z* (%) = 550 ([M], 100). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3387 (w), 3111 (w), 3073 (w), 2974 (w), 2928 (w), 2853 (w), 1715 (m), 1557 (w), 1497 (w), 1449 (m), 1423 (m), 1368 (m), 1260 (s), 1227 (m), 1198 (m), 1155 (w), 1126 (m), 1105 (m), 1074 (s), 1049 (m), 1020 (m), 910 (w), 847 (m), 808 (m), 758 (m), 685 (s), 658 (m). UV/vis (CH_2Cl_2): λ_{max} (ε) = 328 nm (43200). Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 408 nm (6000 cm^{-1}). Anal. calcd. for $C_{34}H_{30}O_4S_2$ (566.7): C 61.06, H 4.03; Found: C 61.26, H 4.28.

General Procedure (GP) for the pseudo-five-component Sonogashira alkynylation - Fiesselmann cyclocondensation of 1,4-diethynyl benzene (11) with acid chloride 1 to give oligothiophenes 12

$Pd(PPh_3)_4$ (92 mg, 0.08 mmol), CuI (30 mg, 0.16 mmol), and dry THF (10 mL) were successively placed in the reaction vessel under nitrogen at room temp and stirred for 5 min. After the addition of 1,4-diethynyl benzene (**9**) (126 mg, 1.00 mmol), the respective acid chloride **1** (3.00 mmol) and triethylamine (223 mg, 2.20 mmol) the reaction mixture was stirred at 80 °C for 4 h (for experimental details see Table 5). Then, ethanol (2 mL), ethyl 2-mercapto acetate (**3**) (300 mg, 2.50 mmol), and DBU (533 mg, 3.50 mmol) were successively added and the solution was stirred for another 20 h at 80 °C. For workup, the volatile components were removed under reduced pressure. The crude product was extracted three times with a mixture of CH_2Cl_2 and aqueous 1M HCl. The combined organic layers were dried with anhydrous $MgSO_4$, absorbed on celite®, and purified by automated column chromatography on fine silica gel (*n*-hexane/THF, gradient: 20 % to 45 %, 15 column volumes, 100 g) to give the compounds **12** as yellow to orange solids. Further purification can easily be achieved by recrystallization from ethanol.

Table 5 Experimental details for the synthesis of the oligothiophenes **12**.

entry	acid chloride **1** [mg] (mmol)	oligothiophene **12** [mg] (yield)
1	464 (3.00) of **1b**	227 (40 %) of **12a**
2	440 (3.00) of **1c**	421 (79%) of **12b**

Diethyl 2,2'-(1,4-phenylene)bis(4,4'-*p*-tolylthiophene-5,5'-carboxylate) (12a)

According to the GP 227 mg (40 %) of **12a** were obtained as orange solid; decomposition at 198 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.29 (t, J = 7.1 Hz, 6H), 2.41 (s, 6H) , 4.27 (q, J = 7.1 Hz, 4H) , 7.24 (d, J = 7.8 Hz, 4H) , 7.33 (s, 2H), 7.41 (d, J = 8.0 Hz, 4H), 7.70 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.3 (2 CH_3), 21.5 (2 CH_3), 61.1 (2 CH_2), 126.2 (2 C_{quat}), 126.8 (4 CH), 127.9 (2 CH), 128.7 (4 CH), 129.2 (4 CH), 132.9 (2 C_{quat}), 133.7 (2 C_{quat}), 138.1 (2 C_{quat}), 147.2 (2 C_{quat}), 149.7 (2 C_{quat}), 162.1 (2 C_{quat}). MALDI MS: *m/z* (%) = 567 ([M], 100). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3341 (w), 2980 (w), 2907 (w), 2864 (w), 2722 (w), 2357 (w), 2320 (w), 1678 (s), 1614 (w), 1497 (m), 1435 (m), 1412 (m), 1371 (m), 1352 (m), 1269 (s), 1242 (m), 1211 (m), 1184 (w), 1155 (w), 1132 (w), 1111 (w), 1072 (s), 1011 (m), 964 (m), 949 (w), 876 (m), 837 (s), 829 (m), 810 (s), 785 (m), 760 (m), 723 (w), 703 (m), 677 (w), 602 (w). UV/vis (CH_2Cl_2): λ_{max} (ε) = 361 nm (43000). Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 404 nm (2900 cm^{-1}), 425 nm. Anal. calcd. for $C_{34}H_{30}O_4S_2$ (566.7): C 72.06, H 5.34; Found: C 71.88, H 5.26.

Diethyl 2,2'-(1,4-phenylene)bis(4,4'-(2-thienyl)-5,5'-carboxylate) (12b)

According to the GP 421 mg (79 %) of **12b** were obtained as orange solid; decomposition at 181 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37 (t, J = 7.1 Hz, 6 H), 4.34 (q, J = 7.1 Hz, 4 H), 7.40 (dd, J = 5.1, 1.1 Hz, 2 H), 7.11 (dd, J = 5.1, 3.7 Hz, 2 H), 7.47 (s, 2 H), 7.62 (dd, J = 3.6, 1.1 Hz, 2 H), 7.70 (s, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.4 (2 CH_3), 61.4 (2 CH_2), 125.7 (2 C_{quat}), 126.7 (2 CH), 126.8 (4 CH), 127.3 (2 CH), 127.7 (2 CH), 129.2 (2 CH), 133.5 (2 C_{quat}), 136.3 (2 C_{quat}), 140.9 (2 C_{quat}), 147.0 (2 C_{quat}), 161.9 (2 C_{quat}). MALDI MS: *m/z* (%) = 550 ([M], 100). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3109 (w), 2976 (w), 2934 (w), 2851 (w), 2667 (w), 1715 (m), 1555 (w), 1504 (w), 1449 (m), 1425 (m), 1410 (m), 1279 (w), 1242 (s), 1188 (m), 1157 (w), 1130 (w), 1103 (m), 1078 (m), 1045 (m), 1020 (m), 962 (w), 854 (m), 824 (s), 795 (m), 758 (m), 694 (s), 660 (m), 625 (w). UV/vis (CH_2Cl_2): λ_{max} (ε) = 347 nm (37300). Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 408 nm (4300 cm^{-1}), 428 nm. Anal. calcd. for $C_{28}H_{22}O_4S_4$ (550.7): C 61.06, H 4.03; Found: C 61.06, H 4.26.

General Procedure (GP) for the bromination to give oligothiophenes 13 and 14

A Schlenk vessel was charged with oligothiophene **4a**[12] or **6c** (1.00 equiv) and N-bromosuccinimide (3.00 equiv). Then acetic acid (3.35 mL per 1.00 mmol oligothiophene **4a** or **6c**) and chloroform (3.35 mL per 1.00 mmol oligothiophene **4a** or **6c**) were added and the resulting solution was stirred for 12 h at room temp under exclusion of light (for experimental details see Table 6). When the reaction mixture became too viscous, additional solvent was added in the same ratio. For workup, the reaction mixture was extracted three times with a mixture of CH_2Cl_2 and saturated aqueous $NaHCO_3$. The combined organic layers were dried with anhydrous $MgSO_4$ and the solvent was removed at reduced pressure. Oligothiophene **13** was further purified by recrystallization from ethanol. Oligothiophene **14** was absorbed on celite®, and purified by automated column chromatography on fine silica gel (*n*-hexane/THF, gradient: 20 % to 30 % in 10 column volumes, 100 g). Further purification can easily be achieved by recrystallization from hexane/THF 1/1.

Table 6 Experimental details for the synthesis of the oligothiophenes **13** and **14**.

entry	oligothiophene [mg] (mmol)	NBS [mg] (mmol)	dibromo oligothiophene [mg] (yield)
1	4430 (13.80) of **4a**	7370 (41.40)	6060 (92 %) of **13**
2	278 (0.50) of **6c**	267 (1.50)	279 (78 %) of **14**

Diethyl 5,5''-dibromo-2,2'-4',2''-terthiophene-5'-carboxylate (13)

According to the GP 6060 mg (92 %) of **13** were obtained as white solid; mp 105 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.36 (t, J = 7.1 Hz, 3 H), 4.33 (q, J = 7.1 Hz, 2 H), 6.99-7.06 (m, 3 H), 7.15 (s, 1 H), 7.32 (d, J = 3.9 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.4 (CH_3), 61.6 (CH_2), 113.6 (C_{quat}), 114.4 (C_{quat}), 124.7 (C_{quat}), 125.8 (CH), 126.8 (CH), 129.5 (CH), 130.0 (CH), 131.2 (CH), 137.2 (C_{quat}), 137.4 (C_{quat}), 139.7 (C_{quat}), 140.5 (C_{quat}), 161.7 (C_{quat}). EI MS (70 eV): *m/z* (%) = 482 (9), 481 (11), 480 ([^{81}Br-^{81}Br-M]$^+$, 60), 479 (19), 478 ([^{81}Br-^{79}Br-M]$^+$, 100), 477 (11), 476 ([^{79}Br-^{79}Br-M]$^+$, 49), 452 (11), 450 (19), 448 (9), 435 ([^{81}Br-^{81}Br-M]$^+$ - C_2H_5O, 10), 433 ([^{81}Br-^{79}Br-M]$^+$ - C_2H_5O, 17), 431 ([^{79}Br-^{79}Br-M]$^+$ - C_2H_5O, 8), 408 (24), 407 (7), 406 (42), 404 (22), 400 (10), 399 (10), 398 (9), 397 (9), 371 (12), 369 (11), 354 (13), 353 (6), 352 (11), 343 (6), 341 (7), 327 (8), 326 (13), 325 (10), 324 (11), 281 (9), 279 (6), 246 (8), 245 (13), 244 (6), 233 (6), 201 (19), 188 (6), 186 (9), 138 (19), 123 (7), 122 (6), 101 (6), 100 (7), 93 (7), 69 (7). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3132 (w), 3094 (w), 2994 (w), 2913 (w), 2872 (w). 1707 (s), 1553 (m), 1510 (m), 1479 (m), 1454 (m), 1425 (m), 1366 (m), 1252 (s), 1233 (s), 1204 (m), 1179 (w), 1155 (w), 1103 (s), 1074 (m), 1053 (w), 1018 (m), 970 (m), 878 (m), 826 (m), 804 (s), 773 (s), 758 (m), 733 (w), 716 (w), 658 (m), 635 (w). UV/vis (CH_2Cl_2): λ_{max} (ε) = 319 nm (62600), 346 nm (71200). Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 423 nm (5300 cm^{-1}). Anal. calcd. for $C_{15}H_{10}Br_2O_2S_3$ (478.2): C 37.67, H 2.11; Found: C 37.70, H 2.27.

Diethyl 5,5''''-dibromo-2,2'-4',2''-5'',3'''-5''',2''''-quinquethiophene-5',2'''-dicarboxylate (14)

According to the GP 279 mg (78 %) of **14** were obtained as yellow solid; decomposition at 187 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37 (t, J = 7.1 Hz, 6 H), 4.34 (q, J = 7.1 Hz, 4 H), 7.03 (d, J = 3.9 Hz, 2 H), 7.06 (d, J = 3.9 Hz, 2 H), 7.27 (s, 2 H), 7.59 (s, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.4 (2 CH_3), 61.5 (2 CH_2), 113.5 (2 C_{quat}), 124.8 (2 C_{quat}) 125.7 (2 CH), 127.3 (2 CH), 129.6 (2 CH), 131.2 (2 CH), 137.2 (2 C_{quat}), 137.3 (2 C_{quat}), 140.3 (2x 2 C_{quat}), 161.7 (2 C_{quat}). MALDI MS: *m/z* (%) = 719 ([M], 5), 718 ([^{81}Br-^{81}Br-M], 20), 717 ([M], 40), 716 ([^{81}Br-^{79}Br-M], 85), 715 ([M], 60), 714 ([^{79}Br-^{79}Br-M], 100), 713 ([M], 30), 712 ([M], 40), 673 ([^{81}Br-^{81}Br-M] - C_2H_5O, 6), 672 ([M] - C_2H_5O, 8), 671 ([^{81}Br-^{79}Br-M] - C_2H_5O, 45), 670 ([M] - C_2H_5O, 20), 669 ([^{79}Br-^{79}Br-M] - C_2H_5O, 70), 668 ([M] - C_2H_5O, 5), 667 ([M] - C_2H_5O, 30), 663 ([M] - C_2H_5O, 15). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2980 (w), 2934 (w), 2909 (w), 2872 (w), 2357 (w), 1709 (m), 1674 (m), 1557 (m), 1508 (m), 1474 (m), 1447 (m), 1435 (m), 1423 (m), 1379 (m), 1366 (m), 1250 (s), 1231 (s), 1177 (m), 1103 (m), 1076 (m), 1042 (m), 1018 (m), 970 (m), 878 (m), 864 (m), 829 (m), 804 (m), 779 (s), 756 (m), 714 (w), 687 (w), 662 (m), 635 (m). UV/vis (CH_2Cl_2): λ_{max} (ε) = 349 nm (49300). Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 446 nm (6200 cm^{-1}). Anal. calcd. for $C_{26}H_{18}Br_2O_4S_5$ (714.6): C 43.70, H 2.54; Found: C 43.47, H 2,72.

General Procedure (GP) for the Sonogashira coupling of the brominated oligothiophene 13 and 14 with ethyl heptynoic acid to give oligothiophene substrates 15 and 16

A 25 mL Schlenk vessel was charged with $Pd(PPh_3)_4$ (58 mg, 0.08 mmol), CuI (19 mg, 0.10 mmol), PPh_3 (26 mg, 0.10 mmol) and 1.00 mmol of the brominated oligothiophene **13** or **14** (for experimental details see Table 8). Then THF (5 mL), NEt_3 (304 mg, 3.00 mmol) and ethyl heptynoate (463 mg, 3.00 mmol) was added and the resulting solution was stirred for 12 h at 60 °C. For the synthesis of compound **16** a five times higher amount of THF was used and the reaction was stirred for 24 h. For workup, the reaction mixture was absorbed on celite®, and purified by automated column chromatography on fine silica gel (*n*-hexane/THF, gradient: 25 % to 35 % in 10 column volumes, 100 g).

Table 8 Experimental details for the synthesis of the oligothiophenes **15** and **16**.

entry	dibromo oligothiophene [mg] (mmol)	oligothiophene [mg] (yield)
1	478 (1.00) of **13**	460 (96 %) of **15**
2	715 (1.00) of **14**	850 (99 %) of **16**

Diethyl 5,5''-bis(7-ethoxy-7-oxohept-1-ynyl)-2,2'-4',2''-terthiophene-5'-carboxylate (15)

According to the GP 460 mg (96 %) of **15** were obtained as yellow solid; mp 75 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.26 (t, J = 7.1 Hz, 6 H), 1.34 (t, J = 7.1 Hz, 3 H), 1.56 – 1.72 (m, 4 H), 1.72 – 1.79 (m, 4 H), 2.35 (t, J = 7.3 Hz, 4 H), 2.47 (m, 4 H), 4.14 (q, 3J = 7.1 Hz, 4 H), 4.31 (q, J = 7.1 Hz, 2 H), 7.03 (d, J = 3.8 Hz, 1 H), 7.07 (d, J = 3.9 Hz, 1 H), 7.11 (d, J = 3.8 Hz, 1 H), 7.20 (s, 1 H), 7.42 (d, J = 3.9 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.4 (3 CH_3), 19.7 (2 CH_2), 24.4 (2 CH_2), 28.0 (2 CH_2), 34.0 (2 CH_2), 60.5 (CH_2), 61.5 (2 CH_2), 95.3 (2 C_{quat}), 96.3 (2 C_{quat}), 125.2 (CH), 127.1 (CH), 129.1 (CH), 131.2 (CH), 132.2 (CH), 135.7 (2 C_{quat}), 136.1 (C_{quat}), 140.0 (2 C_{quat}), 140.9 (2 C_{quat}), 161.7 (C_{quat}), 173.5 (2 C_{quat}). EI MS (70 eV): *m/z* (%) = 626 (21), 625 ([M]$^+$, 39), 624 (100), 581 (9), 580 (18), 579 (49), 578 (15), 551 (11), 536 (8), 509 (10), 491 (9), 478 (10), 477 (21), 231 (13), 218 (9), 217 (9), 203 (10), 197 (8), 196 (10), 195 (8), 191 (8), 183 (9), 171 (12), 145 (9). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2976 (w), 2934 (w), 2903 (w), 2870 (w), 2220 (w), 1728 (w), 1705 (m), 1555 (w), 1506 (w), 1470 (w), 1447 (w), 1418 (w), 1368 (w), 1312 (w), 1252 (s), 1229 (s), 1177 (m), 1103 (s), 1071 (m), 1047 (w), 1020 (m), 945 (w), 876 (w), 829 (w), 810 (w), 787 (s), 756 (m), 735 (w), 662 (w). UV/vis (CH_2Cl_2): λ_{max} (ε) = 340 nm (33200), 363 nm (34000). Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 442 nm (4900 cm^{-1}). Anal. calcd. for $C_{33}H_{36}O_6S_3$ (624.8): C 63.43, H 5.81; Found: C 63.34, H 6.08.

Diethyl 5,5''''-bis(7-ethoxy-7-oxohept-1-ynyl)-2,2'-4',2''-5'',3'''-2''',2''''-quinquethiophene-5',2'''-dicarboxylate (16)

According to the GP 850 mg (99 %) of **16** were obtained as orange solid; mp 68 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.26 (t, J = 7.1 Hz, 6 H), 1.36 (t, J = 7.1 Hz, 6 H), 1.72 – 1.61 (m, 4 H), 1.87 – 1.73 (m, 4 H), 2.36 (t, J = 7.3 Hz, 4 H), 2.48 (t, J = 6.9 Hz, 4 H), 4.14 (q, J = 7.1 Hz, 4 H), 4.34 (q, J = 7.1 Hz, 4 H), 7.04 (d, J = 3.8 Hz, 2 H), 7.14 (d, J = 3.8 Hz, 2 H), 7.30 (s, 2 H), 7.58 (s, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.4 (2 CH_3), 14.4 (2 CH_3), 19.7 (2 CH_2), 24.4 (2 CH_2), 28.0 (2 CH_2), 34.0 (2 CH_2), 60.5 (2 CH_2), 61.5 (2 CH_2), 74.0 (2 C_{quat}), 96.2 (2 C_{quat}), 124.6 (2 C_{quat}), 125.2 (2 CH), 125.2 (2 CH), 127.3 (2 CH), 129.5 (2 CH), 132.2 (2 C_{quat}), 135.8 (2 C_{quat}), 137.3 (2 C_{quat}), 140.3 (2 C_{quat}), 140.8 (2 C_{quat}), 161.8 (2 C_{quat}), 173.5 (2 C_{quat}). EI MS (70 eV): *m/z* (%) = 862 (27), 861 ([M]$^+$, 36), 860 (77), 815 (15), 710 (30), 709 (40), 708 (100), 663 (14), 295 (17), 294 (23), 287 (14), 281 (14), 275 (15), 269 (17), 260 (17), 88 (15), 85 (15), 69 (14), 57 (17), 55 (27), 45 (13), 44 (31), 43 (23), 41 (23). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2976 (w), 2934 (w), 2905 (w), 2868 (w), 2837 (w), 1730 (s), 1707 (s), 1682 (m), 1557 (m), 1510 (m), 1478 (m), 1460 (m), 1427 (m), 1373 (m), 1352 (m), 1271 (m), 1252 (s), 1231 (s), 1175 (s), 1148 (m), 1105 (s), 1074 (m), 1022 (m), 937 (w), 864 (w), 801 (s), 756 (m), 650 (m). UV/vis (CH_2Cl_2): λ_{max} (ε) = 366 nm (65400). Emission (CH_2Cl_2): λ_{max} (Stokes shift) = 447 nm (5100 cm^{-1}). Anal. calcd. for $C_{44}H_{44}O_8S_5$ (861.1): C 61.37, H 5.15; Found: C 61.22, H 5.15.

Notes and references

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† Electronic Supplementary Information (ESI) available: Spectra (^{1}H NMR, ^{13}C NMR, UV/vis, fluorescence) of compounds **6**, **8**, **10** and **12-16**.

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