

Hybrid Conjugated Organic Oligomers Consisting of Oligodiacetylene and Thiophene Units: Synthesis and Optical Properties

Gregor S. Pilzak, Kitty van Gruijthuijsen, Reindert H. van Doorn, Barend van Lagen, Ernst J. R. Sudhölter, and Han Zuilhof^{*[a]}

Abstract: Novel and highly soluble hybrid conjugated organic oligomers consisting of oligodiacetylene and thiophene units have been synthesized in high purity through iterative and divergent approaches based on a sequence of Sonogashira reactions. The series of thiophene-containing oligodiacetylenes (ThODAs) and homocoupled ThODAs (HThODAs) show-both in solution and in the solid state-a strong optical absorption, which is progressively red shifted with increasing chain length. The linear correlation of the absorption maximum (λ^{A}_{max}) with the inverse of conjugation length (CL=number of double and triple bonds) shows that the effective conjugation length of this system is extended up to at least CL = 20. Furthermore, absorption measurements of dropcast thin films display not only a bathochromic shift of the absorption maxima but also a higher wavelength absorption, which is attributed to increased π - π interactions. The wavelength of the maximum fluorescence emission (λ^{E}_{max}) also increases with CL, and emission is maximal for

Keywords: fluorescence • hybrid materials • oligomerization • optical absorption • pi interactions • Stokes shift oligomers with CL=7-12 (fluorescence quantum yield $\Phi_{\rm F} = \sim 0.2$). Both longer and shorter oligomers display marginal emission. The calculated Stokes shifts of these planar materials are relatively large (0.4 eV) for all oligomers, and likely due to excitation to the S_2 state, thus suggesting that the presence of envne moieties dominates the ordering of the lowest excited states. The fluorescence lifetimes $(\tau_{\rm F})$ are short $(\tau_{\rm Fymax} = \ll 1 \text{ ns})$ and closely follow the tendency obtained for the fluorescence quantum yield. The anisotropy lifetimes show a near-linear increase with CL, in line with highly rigid oligomers.

Introduction

Structurally well-defined π -conjugated oligomers such as oligothiophenes, oligoarylvinylenes, and oligodiacetylenes have attracted considerable attention as promising nanoscale candidates for organic electronic devices.^[1-4] To study the evolution of the optoelectronic properties of these materials as a function of the chain length, a new series of monodisperse oligomers were designed as model compounds.^[5] Recently, we developed novel methods for the synthesis of oligodiacetylene-based materials that have allowed a detailed photo-

[a] G. S. Pilzak, K. van Gruijthuijsen, R. H. van Doorn, B. van Lagen, Prof. Dr. E. J. R. Sudhölter, Prof. Dr. H. Zuilhof Laboratory of Organic Chemistry Wageningen University Dreijenplein 8, 6703 HB Wageningen (The Netherlands) Fax: (+31)317-484914 E-mail: han.zuilhof@wur.nl

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200900893.

physical study that clarified the optical properties of poly-diacetylenes. $^{\left[6-8\right] }$

The development of new oligodiacetylene-based materials is often hampered by their low solubility and a laborious and troublesome synthesis of significantly elongated oligomers.^[9,10] Although extensive studies based on oligoenes,^[11,12] oligoarylenevinylenes,^[13,14] oligotriacetylenes,^[15-21] and oligothiophenes,^[22-28] are known, analogous studies centered around the diacetylene functionality as present in polydiacetylenes are rather scarce. This lack of study is a shortcoming given several of the unique properties of polydiacetylenes, such as nonlinear optical (NLO) properties and chromic properties, that arise due to its π -conjugated system.^[4,29-34] Furthermore, few examples of the structural modulation of such π -oligometric chains by incorporation of an aromatic moiety are reported.^[35-37] Such an approach provides a new and versatile way to explore and optimize the optoelectronic properties of conjugated oligomers. Moreover, the use of a bifunctional aromatic moiety as a central unit provides a new and rapid divergent synthetic approach to the preparation of long conjugated oligomers.

Chem. Eur. J. 2009, 15, 9085-9096

© 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



- 9085

As a result, we have set out to develop new synthetic routes toward thiophene-containing enyne-based oligomers and study their photophysical behavior in detail. Herein, we describe the synthesis of a novel series of highly soluble thiophene-containing oligodiacetylenes (ThODAs) and homocoupled ThODAs (HThODAs; Scheme 1).



Scheme 1. Series of novel ThODAs and HThODAs studied herein in which n = 1-3.

In our approach, the thiophene moiety is positioned either as a conjugation-extending end cap, a central anchor unit, or both. The linear ThODA series 1-n is end capped with a trimethylsilyl (TMS) moiety and a thiophene group, whereas the 2-n series has two thiophene end caps, in contrast to 3-n, which has been synthesized by us previously^[6] and is equipped with a TMS unit and *tert*-C(CH₃)₂OCH₃ end groups. The banana-shaped ThODAs are constructed in a new, divergent way. A central thiophene molecule is used to couple two oligodiacetylene building blocks, thus resulting in a rapid extension of the oligomeric chain conjugation. Series 4-*n* is equipped with two thiophene end caps, whereas the 5-*n* series has two $C(CH_3)_2OMe$ endgroups. The homocoupled ThODAs 6-n consist of two symmetric ThODA subunits. All these novel oligomers with oligodiacetylene subunits up to a trimer are synthesized in high purity $(\geq 99\%)$ and moderate-to-high yields (30-90%). These yields allow the isolation of significant amounts of all members of these series (including the longest ThODA 4-3 with 20 conjugated π - π bonds) and the systematic study of their optical properties. Therefore, we also report in detail an investigation of the optical properties by using both steady-state and picosecond time-resolved optical spectroscopic analysis.

Results and Discussion

Synthesis of ThODAs and HThODAs: The ThODA and HThODA series were prepared according to the synthetic route illustrated in Scheme 2. The synthesis of oligodiacetylene building block 1 has been reported by us previously.^[6] The 2-ethynyl-5-methylthiophene used to introduce a second thiophene end cap was synthesized from 2-carboxyl-5-methylthiophene through a short sequence including bromination of the carboxyl group and reduction of 2-(2,2-dibromovinyl)-5-methylthiophene. This thiophene end cap is introduced through a Sonogashira coupling of the iodoenyne 1 with the 2-ethynyl-5-methylthiophene and results in the formation of 1-1. Compound 1-1 was protodesilylated under alkaline conditions and subjected to a catalytic coupling with 2-iodo-5-methylthiophene in a reductive atmosphere to afford 2-1 bearing two thiophene end caps. The use of a 1:1 mixture of H₂/Ar and a large excess of iodothiophene provided suppression of the homocoupling of terminal acetylenes down to 15%. However, a negative side effect of this approach is slow poisoning of the catalyst by the thiophene moiety, which resulted in somewhat lower yields compared to the analogous reaction with oligodiacetylenes.^[6] Similar reaction conditions (10 equiv of 1 and a reductive atmosphere) were chosen for the catalytic elongation of the ThODA backbone. Iodoenyne 1 was recovered quantitatively after each step, which justified the use of this large excess. This chain extension is performed up to a trimer through a sequence of protodesilylation of 1-n followed by a Sonogashira coupling with 1. After each step, a second thiophene end cap is introduced to yield 2-n.

The synthesis of the banana-shaped **4**-*n* and **5**-*n* series was performed through a Sonogashira coupling of two **1**-*n* or **3**-*n* building blocks, respectively, and a central 2,5-di-iodothiophene moiety. To achieve completion of this transformation, an excess of the oligodiacetylene moiety is used, which unfortunately, results in slightly lower yields compared to the catalytic reaction of similar oligodiacetylenes due to an increased degree of homocoupling.

FULL PAPER



Scheme 2. Synthesis of the ThODA and HThODA series based on a sequence of Sonogashira couplings.i) $[Pd(Ph_3)_4]$, CuI, Et₂NH, THF, RT, H₂/Ar; ii) K₂CO₃ cat. H₂O, MeOH/THF.

Chem. Eur. J. 2009, 15, 9085-9096

© 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

www.chemeurj.org

- 9087

The synthesis of HThODAs 6-n is performed quantitatively by a mild catalytic reaction under ambient air conditions: two protodesilylated building blocks 1-n are coupled symmetrically to yield the corresponding HThODAs 6-n up to a homocoupled trimer with two thiophene end caps. The use of tetrakis(triphenylphosphine)palladium(0) in an oxygen atmosphere generates a Pd^{II} catalyst in situ, which is the active catalyst for the homocoupling of terminal acetylenes.^[8] To increase the rate of the reaction and to minimize the formation of the cross-coupled side product, the concentration of the tetrakis(triphenylphosphine)palladium catalyst and Cu^I cocatalyst is kept higher (>5 mol %) than when a crosscoupled Sonogashira product was targeted. Under these optimized conditions, the homocou-

pling of long ThODAs proceeded almost quantitatively (~90% yield of isolated products) within 3 h.



Figure 1. Electronic absorption spectra of the oligomers measured in *n*-hexane (the **3**-*n* series has been reported previously^[6]). $\varepsilon = \text{extinction coefficient}$.

Steady-state optical absorption

in solution: The high solubility

of the synthesized ThODAs and HThODAs that result from the asymmetric laterally attached alkyl side chains and polar end caps, allowed us to study their optical properties in solution. The ground-state optical absorption of all series was measured both in solution and as a dropcast thin film (see Figure 1 for the absorption of these series in *n*-hexane). Additionally, Table 1 shows an overview of the optical absorption characteristics of these oligomers measured in solutions of *n*-hexane, toluene, and methanol.

The steady-state absorption spectra recorded in all solvents show the expected red shift of the maximum absorption peak (λ^{A}_{max}) with an increase in the conjugation length (CL=number of double and triple bonds). A similar dependence is observed for the extinction coefficient (ε_{max}) determined in *n*-hexane. The evolution of the maximum absorption peak shows that the bathochromic shift ($\Delta\lambda^{A}_{max}$) decreases slightly with an increasing CL for all solvents, in line with observed trends for oligodiacetylenes,^[6] homocoupled oligodiacetylenes,^[8] and oligothiophenes^[3] and as expected from simple 'particle-in-a-box' considerations.

Changing the solvent induces a small shift of the maximum absorption peak as well. The bathochromic shift ranges from $\Delta \lambda^{A}_{max} = 0.03 \text{ eV}$ for **4-3** up to $\Delta \lambda^{A}_{max} = 0.10 \text{ eV}$

Table 1. Absorption data of the studied oligomers in n-hexane, toluene, and methanol.

Oligomer (CL) ^[a]	λ^	_{max} [nm] ([eV])		$\varepsilon_{\rm max} [\times 10^3 {\rm mol}^{-1}]$
	<i>n</i> -hexane	toluene	methanol	<i>n</i> -hexane
1-1 (5)	327 (3.79)	332 (3.73)	327 (3.79)	20.0
1-2 (7)	360 (3.44)	365 (3.40)	360 (3.44)	23.1
1-3 (9)	386 (3.21)	393 (3.16)	386 (3.21)	49.4
2-1 (7)	355 (3.49)	360 (3.44)	355 (3.49)	25.4
2-2 (9)	380 (3.26)	386 (3.21)	380 (3.26)	32.4
2-3 (11)	396 (3.13)	403 (3.08)	395 (3.14)	57.8
4-1 (12)	403 (3.08)	410 (3.02)	402 (3.08)	61.4
4-2 (16)	419 (2.96)	426 (2.91)	417 (2.97)	71.4
4-3 (20)	429 (2.89)	433 (2.86)	[b]	100.4
5-1 (8)	373 (3.32)	378 (3.28)	372 (3.33)	34.9
5-2 (12)	407 (3.05)	412 (3.01)	404 (3.07)	54.4
5-3 (16)	421 (2.95)	427 (2.90)	418 (2.97)	94.2
6-1 (10)	377 (3.29)	385 (3.22)	382 (3.25)	50.4
6-2 (14)	412 (3.01)	419 (2.96)	410 (3.02)	81.9
6-3 (18)	426 (2.91)	434 (2.86)	[b]	153.1

[a] Conjugation length is the total number of the conjugated double and triple bonds. [b] Not obtained due to low solubility in methanol.

for **1–2** upon changing the solvent from *n*-hexane (refractive index = 1.375; $E_{\rm T}(30) = 31.0 \text{ kcalmol}^{-1})^{[38]}$ to toluene (refractive index = 1.50; $E_{\rm T}(30) = 33.9 \text{ kcalmol}^{-1})^{.[38]}$ This observa-

tion shows the stabilizing effect of an aromatic solvent on the excited state of these molecules. This red shift in the maximum absorption resembles those values determined previously for oligodiacetylenes^[6] and homocoupled oligodiacetylenes^[8] and is analogous to data reported for shorter diacetylene-based oligomers.^[7,10,39-41] The shortest ThODA series **1-n** displays similar absorption maxmia in both hexane and methanol. The shift of the maximum absorption peak going from *n*-hexane to methanol (refractive index = 1.33; $E_{\rm T}(30) = 55.4 \,\rm kcal \,mol^{-1})^{[38]}$ for the other oligomers under study is marginal. We observed a small blue shift in the maximum absorption ($\Delta \lambda^{\rm A}_{\rm max} = \sim 0.2 \,\rm eV$), which is caused by destabilization of the excited state of these oligomers by a smaller solvent refractive index.^[38,42,43]

Plots of the maximum absorption, expressed in energy units versus 1/CL for the oligomers under study are depicted in Figure 2 together with reported linear fits for oligodiace-



Figure 2. Energy of maximum absorption versus 1/CL of the ThODAs and HThODAs in *n*-hexane at micromolar concentrations $(2 \times 10^{-6} \text{ M})$ and room temperature, together with linear fits of the corresponding data reported for oligodiacetylenes,^[6] homocoupled oligodiacetylenes,^[8] and oligothiophenes,^[3]

tylenes,^[6] homocoupled oligodiacetylenes,^[8] and oligothiophenes for comparison.^[3] For each of the five current series, a linear correlation was observed, with $r^2 \ge 0.99$, although the curves will of course flatten eventually upon further increase of CL (decrease of 1/CL).^[5]

The optical absorption maxima for ThODAs and HThO-DAs are almost parallel to those of the diacetylene-based series. The extrapolated value of the absorption for the polymers (1/CL \rightarrow 0) is nearly identical for all the thiophene-containing series (between $\lambda^{A}_{max} = 2.61$ and 2.41 eV) and is basically identical to values derived from oligodiacetylenes and homocoupled oligodiacetylenes ($\lambda^{A}_{max} = 2.55$ and 2.56 eV, respectively). However, the values reported for the oligothiophenes are slightly lower ($\lambda^{A}_{max} = 2.23 \text{ eV}$).^[3] This outcome is revealing in terms of the nature of the excited singlet states to which the oligomers are excited upon photon absorption. Both oligothiophenes (nonplanar)^[44] and oligodiacetylenes (C_{2h} symmetry)^[41,45] have two low-lying, planar excited singlet states (S_1 and S_2 ; Figure 3), but these are accessed with different ease.



Figure 3. Schematic depiction of the electronic transitions in the oligo-thiophenes $^{[46,47]}$ and oligodiacetylenes $^{[45]}$ upon one-photon excitation.

From the A_g ground state in planar conjugated oligomers, such as oligodiacetylenes, only the transition to the excited singlet state B_u is allowed; excitation to the second 2A_g singlet state is symmetry forbidden.^[41,48] Because of these symmetry reasons, for the diacetylene-based oligomers only the transition to the S₂ state is allowed.^[6-8,41,48] For the oligothiophenes, electronic excitation is to the S_1 state.^[3,46] As a result, mixing the thiophene moieties into an oligodiacetylene-based framework can qualitatively be expected to lead to higher excitation energies when compared to pure oligothiophenes, as is indeed observed. The absorption maxima of the thiophene-containing compounds generally resemble those of diacetylene-based oligomers with a similar CL (see Figures 4, 6 and below). Whereas for all the ThODA series, the presence of thiophene moieties causes a marginal blue shift of the absorption, λ^{A}_{max} of the HThODA series matches almost exactly the values reported for the rod-like homocoupled oligodiacetylenes with identical CL. Obviously, in these materials, the thiophene moiety, which is positioned at the end of the homocoupled oligodiacetylene structure, results in an extension of the conjugation that is similar to chain prolongation with one oligodiacetylene unit. In comparison with, for example, series 4-n, which also features terminal thiophene moieties, it is seen that the excited-state character is significantly affected by the central unit (thiophene or diacetylene) within the molecule.

The linear relation of the energy of the maximum absorption with 1/CL up to CL=20 indicates that the elongation of the conjugation length in the thiophene-containing oligodiacetylenes is preserved for all the compounds in the present study. The conjugation in ThODA and HThODA oligomeric chains is therefore not significantly decreased by kinks or torsions in the backbone.^[6-8] The effective conjugation length (ECL) for these oligomers is therefore at least 20 and most likely >20 conjugated double and triple bonds.

Steady-state optical absorption in thin films: The optical absorption in the solid state of the members of the ThODA and HThODA series that are solids at room temperature was investigated by using dropcast thin films. The absorption spectrum was recorded 12 hours after the start of the solvent evaporation from the quartz plate containing the solid mate-



Figure 4. Normalized absorption spectra of 4-n and 6-n in solution (l) versus thin solid film (s).

rial prepared through dropcasting. (Unfortunately, the shorter oligomers such as the **1**-*n* and **2**-*n* series and **5**-*1* and **5**-*2* are liquids, thus hampering such studies.) The absorption plots of the dropcast thin films of **4**-*n* and **6**-*n* compared to solution plots are shown in Figure 4 (the plot of **5**-*3* is similar and is given in the Supporting Information). The solidstate absorption data of the studied solid oligomers are summarized in Table 2.

The solid-state absorption of ThODAs and HThODAs is characterized by three features: 1) a red-shifted maximum absorption relative to the absorption maxima in solution; 2) a clearly visible red-shifted shoulder, and 3) an additional

Table 2. Solid-state absorption data of the 4-n, 5-3, and 6-n series.

Oligomer (CL)	λ_{\max} [nm] ([eV])	λ _{max} (right shoulder) [nm] ([eV])
4-1 (12)	421 (2.95)	466 (2.66)
4-2 (16)	441 (2.81)	484 (2.56)
4-3 (20)	455 (2.73)	498 (2.49)
5-3 (16)	444 (2.79)	492 (2.52)
6-1 (12)	408 (3.04)	446 (2.78)
6-2 (14)	437 (2.84)	479 (2.59)
6-3 (18)	455 (2.73)	496 (2.50)

higher-wavelength absorption from $\lambda = 550$ nm upwards. The liquid-to-solid red shift of the absorption maxima of the **4-n** series and **5-3** is approximately $\Delta \lambda^{A}_{max} = 0.15 \text{ eV}$ and is slightly larger compared to the reported shift ($\Delta \lambda^{A}_{max} = -0.10 \text{ eV}$) for the oligodiacetylene **3-n** series.^[6] The HThO-DAs show an even larger liquid-to-solid red shift that ranges from $\Delta \lambda^{A}_{max} = 0.17$ to 0.25 eV for **6-3** and **6-1** compared to $\Delta \lambda^{A}_{max} = 0.07 \text{ eV}$ observed for homocoupled oligodiacetylenes.^[8] The available data are used for a correlation between the reciprocal value of CL and the absorption maxima for both liquids and solids and are compared to the reported values for oligodiacetylenes.^[6] and homocoupled oligodiacetylenes.^[8] as dropcast films (Figure 5).



Figure 5. The absorption maximum (λ^{A}_{max}) of **4-n**, **5-3** (top), and **6-n** (bottom) in *n*-hexane $(2 \times 10^{-6} \text{ M})$ (l) and dropcast films (s) with additional electronic transitions (λ_{max}) compared to reports of dropcast films of oligodiacetylenes^[6] and homocoupled oligodiacetylenes^[8] as a function of 1/CL.

The trends for the **4**-*n* series and **5**-*3* are similar to that observed for (homocoupled) oligodiacetylenes, thus pointing to a dominant effect of the ODA moieties in determining this liquid-to-solid effect. For the **6**-*n* series, it may tentatively be concluded that extension to an infinite polymer would yield a further decrease in the excitation energy in comparison to the analogous homocoupled oligodiacetylenes (i.e., from $\lambda^{A}_{max} = 2.5$ to 2.3 eV). Furthermore, we observe an additional electronic transition that appears at lower energy

FULL PAPER

 $(\lambda^{A}_{max} = \sim 0.26 \text{ eV})$ below the main absorption maxima, followed by a significant absorption increase in the range $\lambda =$ 550-800 nm. This red-shifted shoulder positioned at a higher wavelength region is already present for shorter oligomers in solution, such as ThODAs 1-n, 2-1, 2-2, and 5-1 (Figure 1), but is absent in solutions of longer hybrid oligomers. We interpret this outcome to mean that for short ThODAs without a central thiophene unit, the flat oligomeric geometry (C_{2h} -like) is dominant, as reported for rod-like oligodiacetylene chains.^[41,45] For longer oligomers, entropic reasons might also allow other geometries to play a role (e.g., with slight rotations around the C-C bonds), and the resulting peak broadening may make the lowest-energy transition invisible as a separate shoulder. In the solid state, interchain interactions may force planarity, and thus bring back the shoulder. Moreover, the significantly increased long-wavelength absorption (above $\lambda = 550 \text{ nm}$ for longest studied oligomers) is caused by the intermolecular stacking of π orbitals in the solid state, which is absent in diluted solution. Due to steric repulsion from the alkyl side chains, these oligomers do not show aggregation even in concentrated solution up to 5 mм.

Steady-state fluorescence in solution: Emission spectra measured for homogeneous millimolar solutions of the ThODA and HThODA series were recorded in *n*-hexane, methanol, and toluene. Table 3 summarizes the characteristic features

Table 3. Emission data of the studied oligomers in n-hexane.

Oligomer	λ^{E}_{max} [nm]	Quantum yield	Stokes shift
(CL)	([eV])	$(\Phi_{\mathrm{F}})^{\mathrm{[a,b]}}$	[eV]
1-1 (5)	370 (3.35)	0.003	0.422
1-2 (7)	407 (3.05)	0.170	0.446
1-3 (9)	441 (2.81)	0.005	0.426
2-1 (7)	397 (3.12)	0.110	0.370
2-2 (9)	431 (2.88)	0.140	0.386
2-3 (11)	452 (2.74)	0.002	0.388
4-1 (12)	457 (2.71)	0.100	0.364
4-2 (16)	478 (2.59)	0.003	0.365
4-3 (20)	490 (2.53)	0.002	0.360
5-1 (8)	415 (2.99)	0.210	0.336
5-2 (12)	461 (2.69)	0.006	0.357
5-3 (16)	480 (2.58)	0.002	0.362
6-1 (10)	438 (2.83)	0.067	0.458
6-2 (14)	468 (2.65)	0.001	[c]
6-3 (18)	482 (2.57)	0.001	[c]

[a] Quantum yield is determined by comparison with tryptophan: $\Phi_{\rm F} = 0.13$.^[49] [b] Experimental error = ± 0.002 . [c] Not determined due to an absence of a visible 0–0 transition.

of the steady-state fluorescence of these oligomers measured in *n*-hexane (similar features were observed in methanol and toluene and are given in the Supporting Information). These marked features are 1) a clear red shift of the emission maxima (λ^{E}_{max}) with increasing CL and 2) a sharp maximum of the fluorescence quantum yield ($\Phi_{F,max}$) for the oligomers where CL \leq 12 and 3, which arises from a resolved 0– 0 transition (Figure 6). This last feature differs from the emission of diacetylene-based oligomers,^[6,8] in which no distinguishable shoulder at the high-energy side of the fluorescence band was visible for these oligomers with $CL \ge 6$. For the linear ThODAs series **1-n** and **2-n**, the maximum fluorescence quantum yield is observed for dimers **1-2** and **2-2**, whereas the monomers display this maximum in the linear



Figure 6. Fluorescence spectra of ThODAs and HThODA measured in *n*-hexane (because of the marginal emission all the spectra, except **1-2**, **2-1**, **2-2**, **4-1**, **5-1**, and **6-1** are multiplied by a factor of five).

HThODAs **6-***n* and the banana-shaped **4-***n* and **5-***n* ThODAs series. Upon further chain elongation, the fluorescence quantum yield becomes marginal, likely as a result of highly efficient internal conversion.^[45]

Changing the solvent from *n*-hexane to toluene induces a red shift of emission maxima. This red shift is rather small for ThODAs in toluene (between $\Delta \lambda^{E}_{max} = 0.05$ and 0.07 eV), but becomes slightly larger for the HThODA series ($\Delta \lambda^{E}_{max}$ ranging from 0.07 eV up to 0.13 eV). Increasing the polarity even more by changing the solvent to methanol results, only for the 1-n series, in a relatively large red shift of λ^{E}_{max} ($\Delta \lambda^{E}_{max}$ ranging from 0.08 to 0.17 eV. For all other studied oligomers, this shift is smaller (${\bigtriangleup \lambda^{\rm E}}_{\rm max} \leq \, 0.04$ eV for 2-*n*, 4-*n*, and 5-*n*) or similar ($\triangle \lambda^{E}_{max} \ge 0.08$ eV for 1**n**) compared to the red shift in π -electron-rich toluene. In line with this pattern, the emission maxima for ThODAs and HThODAs are highest in toluene, except for the 1-n series. For oligomers, such as 1-n and 3-n with two different endgroups, the solvent polarity plays an important role. For oligomers without a (significant) dipole, the possibilities for increased $\pi - \pi$ interactions with the solvent (as in toluene) are obviously more important.

The emission quantum yield is highly dependent on CL. We observe a sharp maximum for the fluorescence quantum yield $(\Phi_{\rm F})$ in all solvents for relatively short ThODAs, that is, the fluorescence quantum yield in *n*-hexane is highest for **1-2** ($\Phi_{\rm F}$ =0.17, CL=7), **2-2** ($\Phi_{\rm F}$ =0.14, CL=9), and similar to an oligodiacetylene trimer ($\Phi_{\rm F}=0.16$, CL=7).^[6] For the longer series 4-n, 5-n, and 6-n, the maximum fluorescence quantum yield is recorded for the monomers 4-1 ($\Phi_{\rm F}$ =0.10, CL=12), **5-1** ($\Phi_{\rm F}$ =0.21, CL=8), and **6-1** ($\Phi_{\rm F}$ =0.07, CL= 10). These values are-for 5-1-five times larger than the marginal emission reported for oligodiacetylenes with such CL values^[6] or for homocoupled oligodiacetylenes ($\Phi_{\rm Emax}$ = 0.041, reported for the monomer with $CL = 6^{[8]}$). This phenomenon shows that incorporation of the thiophene moiety into an oligodiacetylene framework increases the fluorescence quantum yield, which is further increased in toluene. This behavior clearly indicates that an aromatic solvent stabilizes the intramolecular charge transfer in the excited state of the hybrid oligomers, which results not only in a fluorescence emission at longer wavelengths but effects also an increased efficiency thereof.

From the absorption and emission data, the Stokes shifts in *n*-hexane were obtained (Table 3; see the Supporting Information for similar data in toluene and methanol). These values are rather large (0.30-0.45 eV) and similar to those of oligodiacetylenes^[41] but slightly smaller than reported for oligothiophenes (~0.6 eV).^[50,51] For oligothiophenes, the large Stokes shift is attributed to significant differences in geometry of the nonplanar ground state and the planar excited state.^[44,51,52] In contrast, the S₂ excitation in oligodiacetylenes causes this large shift, which is followed by rapid internal conversion to the S₁ state and fluorescence from there (Figure 3).^[45] For the studied hybrid systems, the planarity was investigated by DFT calculations (B3LYP/6-311G(d,p)) on **2-1** (Figure 7). The resulting geometry dis-



Figure 7. Planar geometry of the ThODA oligomer 2-1 (front and side view; optimized at the B3LYP/6-311G(d,p) level of theory).

plays the planarity of this species, which implies that – in contrast to oligothiophenes – the observed large Stokes shift of the these hybrid materials is likely not due to large geometrical changes, such as rotations, upon excitation, but to excitation to a higher excited state, in line with Figure 3 (right). In other words, the order of the B_u and $2A_g$ states seems fixed by the presence of the enyne moieties, even in molecules, such as **2-1**, with two thiophene moieties and only one enyne unit.

Fluorescence lifetimes and anisotropy: Picosecond time-resolved single-photon counting at five different excitation wavelengths ($\lambda = 295$, 360, 380, 400, and 410 nm) was used to determine the fluorescence lifetimes ($\tau_{\rm F}$) of the studied oligomer series. The observed lifetimes for the ThODA and HThODA series measured in *n*-hexane are shown in Table 4 and fall typically in the range $\tau_{\rm F} = 100-900$ ps. The decay curves of the compounds with lifetimes of $\tau_{\rm F} > 200$ ps could all be fitted with one exponent. The compounds with marginal fluorescence displayed more complex decay kinetics, thus requiring a sum of two or three exponentials. In that

Table 4. Fluorescence lifetimes $(\tau_{\rm F})$, relative amplitudes (A), average lifetimes $(\tau_{\rm avg})$, and rotation correlation times $(\tau_{\rm R})$ of the ThODA and HThODA series in *n*-hexane.

Oligomer	$ au_1$	τ 2	τ 2	τ	τ
(CL)	$(A_1) [ps]$	(A_2) [ps]	(A_2) [ps]	avg [ps]	_R ^[b] [ps]
1-1 (5)	10 (66) ^[c]	41 (29)	150 (5)	26	50
1-2 (7)	781 (100)				119
1-3 (9)	13 (9) ^[c]	204 (91)		187	200
2-1 (7)	200 (100)				205
2-2 (9)	839 (100)				250
2-3 (11)	7 (49) ^[c]	94 (51)		51	321
4-1 (12)	551 (100)				218
4-2 (16)	6 (49) ^[c]	300 (21)	793 (30)	304	643
4-3 (20)	3 (91) ^[c]	514 (9)		49	910
5-1 (8)	304 (100)				380
5-2 (12)	20 (92)	678 (8)		73	
5-3 (16)	13 (100)				731
6-1 (10)	280 (100)				151
6-2 (14)	6 (72) ^[c]	84 (16)	742 (12)	107	441

[a] Calculated by using Equation (1). [b] Experimental error = \leq 50 ps. [c] Values not accurate because the instrument response time was approximately 400 ps.

9092

FULL PAPER

case, the average fluorescence lifetime $(\tau_{F,avg})$ was calculated according to Equation (1):

$$\tau_{\rm F,AVG} = \frac{A_1}{A_1 + A_2 + A_3} \tau_1 + \frac{A_2}{A_1 + A_2 + A_3} \tau_2 + \frac{A_3}{A_1 + A_2 + A_3} \tau_3$$
(1)

where A_1 , A_2 , and A_3 are the contributions of the decays obtained from the curve fitting. The evolution of fluorescence lifetime with increasing oligomeric chain length closely follows the trend shown for the fluorescence quantum yield (Table 3).

We determined the rotation correlation times (τ_R) for ThODAs and HThODAs in *n*-hexane (Table 4).^[49] Because the longer oligomers display marginal emission, the experimental error for these measurements was relatively high. The anisotropy lifetimes show an increase with the CL, thus indicating an increased rotation time around the perpendicular axis for the longer oligomers. This behavior is illustrated in Figure 8, in which a linear dependence of the rotation



Figure 8. Anisotropy lifetimes versus the CL of the ThODA and HThODA series.

correlation time and CL of the oligomers is depicted. This outcome is as expected for conjugated oligomers with a linear increase in the distance between the terminal atoms going from one member of the series to the next, thus showing the rigidity of even the longest oligomers in the present study.

Conclusion

Novel series of highly soluble oligodiacetylenes with thiophene moieties as an end cap and/or a central unit were synthesized in high purity. These oligomers display photophysical properties in between those of oligodiacetylenes and homocoupled oligodiacetylenes on the one hand and oligothiophenes on the other. Whereas the presence of the thiophene units affects the energy of the excited states and the relaxation thereof, the nature of the lowest-excited state of these hybrid materials (A_g or B_u) is determined by the presence of

envne moieties and for all the studied compounds a 2A_g state. These oligomers show a clear linear increase in absorption maxima for the π - π * transition with the conjugation length both in solution and the dropcast solid-state film. Optical absorption studies of the drop-cast films display a second red-shifted absorption maximum and higherwavelength absorption, which are attributed to molecular planarization and aggregation, respectively. A more efficient π-electron delocalization along the oligodiacetylene backbone is obtained upon introduction of electron-rich-thiophene moieties, which result in a red-shifted maximum emission compared to the oligodiacetylenes. This modulation also results in a significant increase of the quantum yield of emission up to a factor of 5, in comparison to oligodiacetylenes and homocoupled oligodiacetylenes of the same conjugation length.

Experimental Section

Solvents and reagents: For all dry reactions performed under a steady stream of argon (or a reductive atmosphere of argon/hydrogen (1:1)), the equipment was dried in an oven at 150 °C for several hours and allowed to cool in an atmosphere of dry nitrogen or argon. Pure, dry, and degassed ether and THF were obtained by distillation of the commercial material over sodium particles. CH_2Cl_2 was distilled and dried over calcium hydride or sodium hydride. Dry DMF was purchased from Sigma–Aldrich and stored under argon. All the other specified chemicals were commercially purchased (Aldrich, Fluka, or Riedel-de Haën) and used without further purification.

General workup and purification procedure: Reaction monitoring and reagent visualization was performed on silica gel or reversed-phase silica gel plates with UV light (λ =254 and 366 nm) combined with GCMS. Usually the reaction mixture was diluted with water and extracted threefold with an organic solvent (petroleum ether 40/60, hexane, or ethyl acetate). The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate prior to filtration, and the solvent was removed by evaporation under reduced pressure. Flash chromatography was performed on commercially available silica gel (pore diameter: 0.035–0.070 nm) and with mixtures of freshly distilled petroleum ether 40/60 and ethyl acetate. Final purification was performed on Shimadzu preparative HPLC using a C18 column ($250 \times 22 \text{ mm}$; 5 μ ; Alltech Alltima) with HPLC-grade water, acetonitrile, and ethyl acetate mixture.

NMR spectroscopic and mass-spectrometric analysis: ¹H and ¹³C NMR spectra were determined on a Bruker CXP 300 NMR spectrometer in a solution of CDCl₃, unless indicated otherwise. Chemical shifts are reported in ppm downfield relative to tetramethylsilane (TMS; $\delta = 0$ ppm for ¹H NMR) or the solvent peak (CDCl₃; $\delta = 77.00$ ppm for ¹³C NMR) as an internal standard. HRMS was performed on Finnigan Mat95 mass spectrometer.

Steady-state absorption and fluorescence: Absorption spectra of the oligodiacetylenes in *n*-hexane (spectrophotometric grade; Riedel-de Haën) and 1,2-dichloroethane (DCE; spectrophotometric grade; Sigma–Aldrich) were recorded on a Cary 100 UV/Vis spectrophotometer (scan range (λ) = 200–800 nm, scan rate = 300 nm min⁻¹, date interval = 0.5 nm) and steady-state fluorescence using a FLS920P Spectrometer (slit excitation = 2 nm, slit emission = 2 nm, step = 1.0, dwell = 0.2 s). The absorption spectra of oligodiacetylenes in film through dropcasting were recorded on a Cary 50 UV/Vis spectrophotometer (scan range (λ) = 200–850 nm, scan rate = 300 nm min⁻¹, data interval = 0.5 nm).

Determination of fluorescence quantum yield in solution: To evaluate the fluorescence quantum yield (Φ_F) of solutions of oligodiacetylenes in

n-hexane, toluene, and methanol, the areas of the corrected emission spectra were compared to a spectrum of a reference molecule. A diluted solution of tryptophan in water was used, and a value of $\Phi_{\rm R} = 0.13$ was obtained at 25°C measured at $\lambda = 280$ nm.^[49] The relevant fluorescence quantum yields of the oligodiacetylenes were determined from the relationship given in Equation (2):

$$\Phi_{\rm F} = \Phi_R \frac{I}{I_R} \frac{OD_R}{OD} \frac{n^2}{n_R^2} \frac{Rc_{\lambda exc,R}}{Rc_{\lambda exc}}$$
(2)

where *I* and $I_{\rm R}$ are the integrated emission intensities of solutions of oligodiacetylene and tryptophan, respectively, OD is the optical density of the respective solutions, and *n* is the refractive index. The ratio of $Rc_{\lambda exc}$ is a correction factor for the lamp spectrum due to the different excitation wavelength used for the determination of the OD and *I* values of the studied compound and solution of tryptophan.

Time-resolved fluorescence measurements: The fluorescence lifetime and anisotropy were recorded using a FLS920P spectrometer (Edinburgh Instruments) for time-correlated photon counting (TCSP; time setup=5 or 10 ns, channels=4096, counts=10000 for **1-1–1-4**, 1000 for **1-5–1-7**). Pulsed diode lasers (λ =372 nm, FWHM=54 ps; λ =444 nm, FWHM=63 ps) and pulsed LEDs (λ =283 nm, FWHM=<500 ps; λ =304 nm, FWHM=<350 ps; PicoQuant) were used as the light source. The anisotropy measurements were performed by using vertical and horizontal polarizations. All other conditions and setup parameters were reported earlier by Van Hoek and co-workers.^[53–55]

General method for the protodesilylation of the (Th)ODA series prior to the catalytic chain-elongation process (Scheme 2): A solution of oligodiacetylene (1 equiv) in THF/MeOH (1:1, 5 mLmm⁻¹) was stirred in roundbottomed flask. Water (3 drops mmol⁻¹) and K₂CO₃ (2 equiv) were added to the solution and stirred for 3 h. After the workup, following the general procedure given above, the terminal (Th)ODA was submitted to the catalytic chain-elongation step.

Catalytic Sonogashira coupling of terminal (Th)ODAs 1-*n* or 3-*n*^[6] with iododiacetylene (1): A mixture of ((*E*)-4-iodo-3-propyloct-3-en-1-ynyl)trimethylsilane (1; 10 equiv), [Pd(PPh₃)₄] (5 mol %), CuI (2 mol %), and dry, degassed diethylamine (2 mL mm⁻¹) and THF (5 mL mm⁻¹) were placed anaerobically in a dried, brown two-necked round-bottomed flask equipped with a magnetic stirrer, an argon/hydrogen in- and outlet, and a pressure-equalized dropping funnel containing terminal acetylene (1 equiv). The terminal (Th)ODA 1-*n* or 3-*n* was added slowly over 6 h to the stirred mixture under a constant flow of argon/hydrogen (1:1). The reaction mixture was further stirred overnight at 25 °C, concentrated, and filtrated over a short column of silica gel (5% Et₃N in petroleum ether 40/60). The residue was prepurified on reperative HPLC to give pure (99%) elongated (Th)ODA 1-*n* or 3-*n*,^[6] while iododiacetylene (1) was recovered quantitatively.

Catalytic Sonogashira coupling of protodesilylated members of ThODA series 1-*n* with 2-iodo-5-methylthiophene: A mixture of 2-iodo-5-methylthiophene (3 equiv), $[Pd(PPh_3)_4]$ (5 mol%), CuI (2 mol%), and dry, degassed diethyl amine (2 mLmm⁻¹) and THF (5 mLmm⁻¹) was placed anaerobically in a dried, brown two-necked round-bottomed flask equipped with a magnetic stirrer, an argon/hydrogen in- and outlet, and a pressure-equalized dropping funnel containing the terminal acetylene (1 equiv). The terminal ThODA 1-*n* was added slowly over 6 h to the stirred mixture under a constant flow of argon/hydrogen (1:1). The reaction mixture was further stirred overnight at 25 °C, concentrated, and filtrated over a short column of silica gel (petroleum ether 40/60). The residue was prepurified on reversed-phase silica gel (MeCN/EtOAc) and finally purified on preparative HPLC to give pure (99%) elongated ThODA 2-*n*.

Catalytic Sonogashira coupling of protodesilylated members of ThODA series 1-*n* or 3-*n* with 2,5-diiodothiophene: A mixture of 2,5-diiodothiophene (3 equiv), $[Pd(PPh_3)_4]$ (5 mol%), CuI (2 mol%), and dry, degassed diethyl amine (2 mLmm⁻¹) and THF (5 mLmm⁻¹) was placed anaerobically in a dried, brown two-necked round-bottomed flask equipped with a magnetic stirrer, an argon/hydrogen in- and outlet, and a pressure-

equalized dropping funnel containing the terminal acetylene (1 equiv). The terminal ThODA **1-n** or **3-n**^[6] was added slowly over 6 h to the stirred mixture under a constant flow of argon/hydrogen (1:1). The reaction mixture was further stirred overnight at 25 °C, concentrated, and filtrated over a short column of silica gel (5% ethyl acetate in petroleum ether 40/60). The residue was prepurified on reversed-phase silica gel (MeCN/EtOAc) and finally purified on preparative HPLC to give pure (99%) elongated ThODA **4-n** or **5-n**, respectively.

Catalytic homocoupling of protodesilylated members of ThODA series 3-*n* under Sonogashira conditions: A mixture of terminal acetylene $3-n_1^{[6]}$ [Pd(PPh₃)₄] (7 mol%), CuI (8 mol%), distilled diethyl amine (2 mLmm⁻¹), and THF (5 mLmm⁻¹) was placed in a round-bottomed flask equipped with a magnetic stirrer. The reaction mixture was stirred for 3 h at 25 °C under ambient atmosphere, concentrated, and filtrated over a short column of silica gel (5% ethyl acetate in petroleum ether 40/60). The residue was prepurified on reversed-phase silica gel (MeCN/ EtOAc) and finally purified on preparative HPLC to give pure (99.5%) HThODA 6-*n*.

2-Ethynyl-5-methylthiophene: 2-Thiophenecarbaldehyde (40 mmol 4.48 g) was added in portions to a stirred and cooled (0°C) solution of PPh₃ (100 mmol, 26.2 g) and CBr₄ (50 mmol, 16.6 g) in anhydrous dichloromethane (200 mL) in an argon atmosphere. After completion of the reaction (monitored by GCMS and TLC analysis), the crude reaction mixture was extracted as usual (see the general procedure) and purified by column chromatography on silica gel (petroleum ether 40/60). 2-(2,2-Dibromovinyl)-5-methylthiophene was obtained as light-brown solid (38.3 mmol, 10.8 g, 94%). A solution of nBuLi (4.27 mmol, 2.51 mL, $1.7 \,\mathrm{m}$ in hexanes) was added dropwise to a stirred and cooled ($-78 \,^{\circ}\mathrm{C}$) solution of 2-(2,2-dibromovinyl)-5-methylthiophene (2.13 mmol, 0.6 g) in anhydrous diethyl ether (30 mL) in an argon atmosphere. After stirring for 30 min, the reaction mixture was allowed to warm to room temperature. After completion (monitored by GCMS and TLC analysis), the reaction mixture was extracted as usual (see the general procedure) to yield 2-ethynyl-5-methylthiophene as a pale-brown liquid (1.87 mmol, 0.22 g, 88 %). ¹H NMR: δ = 2.48 (s, 3H), 3.30 (s, 1H), 6.64 (dq, 1H, *J* = 3 and 6 Hz), 7.10 ppm (d, 1H, *J* = 6 Hz); ¹³C NMR: δ = 15.32, 22.62, 80.37, 119.52, 125.15, 133.33, 142.36 ppm; HRMS: m/z: calcd: 122.0191; found: 122.0195.

(*E*)-{3-Butyl-4-[2-(5-methylthiophen-2-yl)ethynyl]hept-3-en-1-ynyl]trimethylsilane (1-1): Colorless oil (0.57 mmol, 0.197 g, 95%) obtained from 1. ¹H NMR: $\delta = 0.22$ (s, 9H), 0.97 (t, 3H, J = 7.2 Hz), 0.98 (t, 3H, J =7.4 Hz), 1.38 (sextet, 2H J = 7.3 Hz), 1.53–1.69 (m, 4H), 2.42 (t, 2H, J =7.4 Hz), 2.45–2.55 (m, 5H), 6.66 (m, 1H,), 7.00 ppm (d, 1H, J = 3.5 Hz); ¹³C NMR: $\delta = 0.0$, 13.6, 13.9, 15.4, 21.7, 22.1, 30.5, 34.5, 36.8, 92.2, 92.3, 103.6, 104.7, 121.2, 125.4, 128.9, 130.8, 131.6, 142.2 ppm; HRMS: m/z: calcd: 342.1838; found: 342.1840.

{(3E,7E)-4,7-Dibutyl-8-[2-(5-methylthiophen-2-yl)ethynyl]-3-propylundeca-3,7-dien-1,5-diynyl}trimethylsilane (1-2): Pale-yellow oil (0.22 mmol, 0.106 g, 88%) obtained from **1–1**; ¹H NMR: δ =0.23 (s, 9H), 0.96 (t, 6H, *J*=7.4 Hz), 0.99 (t, 6H, *J*=7.9 Hz), 1.31–1.48 (m, 4H), 1.52–1.74 (m, 8H), 2.42 (t, 2H, *J*=7.4 Hz), 2.45–2.58 (m, 9H), 6.67 (m, 1H), 7.01 (d, 1H, *J*=3.6 Hz); ¹³C NMR: δ =0.0, 13.6, 13.9, 14.0, 15.4, 21.7, 21.8, 22.1, 22.3, 22.4, 30.5, 30.8, 32.0, 34.8, 34.8, 37.0, 37.2, 92.2, 92.7, 98.5, 99.0, 103.8, 104.9, 121.3, 125.2, 125.5, 128.8, 129.2, 131.3, 131.6, 131.9, 142.2; HRMS: *m/z*: calcd: 490.3090; found: 490.3089.

 Trimethyl-{(3E,7E,11E-3,8,11-tributyl-12-[2-(5-methylthiophen-2-yl)

 ethynyl]-4,7-dipropylpentadeca-3,7,11-trien-1,5,9-triynyl}silane

 (1-3):

Pale-yellow oil (0.06 mmol, 0.036 g, 85%) obtained from **1-2**. ¹H NMR: δ =0.23 (s, 9 H), 0.91–1.02 (m, 18 H), 1.32–1.48 (m, 6H), 1.52–1.71 (m, 12 H), 2.37–2.58 (m, 15 H), 6.67 (m, 1 H, *J*=3.6 Hz), 7.01 ppm (d, 1 H, *J*=3.6 Hz); ¹³C NMR: δ =0.4, 13.6, 13.9, 14.0, 14.0, 15.4, 21.7, 21.8, 21.9, 22.1, 22.3, 22.3, 30.5, 30.8, 34.7, 34.8, 35.1, 37.0, 37.2, 37.3, 92.3, 92.8, 98.7, 99.1, 99.1, 103.8, 104.9, 121.3, 125.5, 128.8, 129.2, 129.3, 129.7, 131.3, 131.6, 142.2 ppm; HRMS: *m/z*: calcd: 638.4342; found: 638.4337.

(*E*)-2-Methyl-5-{4-[2-(5-methylthiophen-2-yl)ethynyl]-3-propyloct-3-en-1ynyl}thiophene (2-*I*): Yellow oil (0.74 mmol, 0.217 g, 68%) obtained from 1-*I*. ¹H NMR: δ =0.96 (t, 3H, *J*=6.9 Hz), 0.98 (t, 3H, *J*=6.9 Hz), 1.45 (sextet, 2H, *J*=7.3 Hz), 1.56–1.77 (m, 4H), 2.50 (s, 6H), 1.47–2.60 (m, 4H), 6.67 (m, 2H), 6.98 (d, 1H, J=3.5 Hz), 6.99 ppm (d, 1H, J=3.5 Hz); ¹³C NMR: δ =13.7, 14.0, 15.4, 21.9, 22.2, 30.7, 34.6, 36.9, 92.1, 92.6, 92.7, 121.3, 125.5, 128.8, 129.3, 131.6, 142.2 ppm; HRMS: *m*/*z*: calcd: 366.1476; found: 366.1474.

2-{(3*E***,7***E***)-4,7-Dibutyl-8-[2-(5-methylthiophen-2-yl)ethynyl]-3-propylundeca-3,7-dien-1,5-diynyl}-5-methylthiophene (2-2)**: Yellow oil (0.07 mmol, 0.034 g, 53%) obtained from **1-2**. ¹H NMR: δ =0.92–1.04 (m, 12H), 1.43 (sextet, 4H, *J*=7.2 Hz), 1.54–1.74 (m, 8H), 2.46–2.58 (m, 14H), 6.67 (m, 2H), 7.00 (d, 1H, *J*=3.5 Hz), 7.01 ppm (d, 1H, *J*=3.5 Hz); ¹³C NMR: δ =13.7, 14.0, 14.0, 15.4, 21.9, 21.9, 22.2, 22.3, 22.6, 30.8, 30.9, 34.8, 34.9, 37.0, 37.2, 92.3, 92.3, 92.8, 98.9, 99.0, 121.3, 125.5, 128.8, 129.2, 129.3, 129.7, 131.6, 142.2 ppm; HRMS: *m/z*: calcd: 514.2727; found: 514.2727.

2,5-Bis{(E)-3-butyl-4-[2-(5-methylthiophen-2-yl)ethynyl]hept-3-en-1-

ynyl}thiophene (4-*I***)**: Yellow solid (0.26 mmol, 0.164 g, 40%) obtained from **1-***I*. ¹H NMR: δ =1.01 (t, 6H, *J*=7.2 Hz), 1.04 (t, 6H, *J*=7.2 Hz), 1.45 (sextet, 4H, *J*=7.3 Hz), 1.59–1.77 (m, 8H), 2.51 (s, 6H), 2.52–2.62 (m, 8H), 6.69 (m, 2H), 7.04 (d, 1H, *J*=3.5 Hz), 7.05 (d, 1H, *J*=3.5 Hz), 7.08 ppm (s, 2H); ¹³C NMR: δ =13.7, 14.0, 15.5, 21.9, 22.1, 22.2, 22.5, 29.7, 30.8, 30.9, 31.7, 34.8, 36.8, 91.6, 92.8, 92.9, 94.8, 121.1, 125.0, 125.6, 128.3, 130.6, 131.4, 132.0, 142.5 ppm; HRMS: *m/z*: calcd: 620.2605; found: 620.2599.

$2,5\text{-}Bis\{(3E,7E)\text{-}4,7\text{-}dibutyl\text{-}8\text{-}[2\text{-}(5\text{-}methylthiophen\text{-}2\text{-}yl)ethynyl]\text{-}3\text{-}pro\text{-}ideleften and a standard stan$

pylundeca-3,7-dien-1,5-diynyl}thiophene (4-2): Yellow-brown solid (0.02 mmol, 0.019 g, 30%) obtained from 1-2. ¹H NMR: δ =0.98 (t, 6H, J=7.3 Hz), 0.99 (t, 6H, J=6.9 Hz), 1.00 (t, 6H, J=7.3 Hz), 1.02 (t, 6H, J=6.9 Hz), 1.34–1.48 (m, 8H), 1.54–1.74 (m, 16H), 2.46–2.59 (m, 22H), 6.67 (m, 2H), 7.02 (d, 2H, J=3.5 Hz), 7.06 ppm (s, 2H); ¹³C NMR: δ = 13.7, 14.0, 15.4, 21.9, 22.0, 22.2, 22.3, 29.7, 30.8, 30.9, 34.9, 35.0, 36.9, 37.2, 91.5, 92.5, 92.8, 94.9, 98.8, 99.6, 121.2, 125.0, 125.5, 128.2, 129.1, 129.6, 131.0, 131.4, 131.7, 142.3 ppm; HRMS: m/z: calcd: 916.5109; found: 916.5116.

$2,5\text{-}Bis\{(3E,7E,11E)\text{-}3,8,11\text{-}tributyl\text{-}12\text{-}[2\text{-}(5\text{-}methylthiophen\text{-}2\text{-}yl)\text{e}thyndromyddiaethyldi$

yl]-4,7-dipropylpentadeca-3,7,11-trien-1,5,9-triynyl}thiophene (4-3): Orange/brown solid (0.02 mmol, 0.028 g, 30%) obtained from 1-3. ¹H NMR: δ =0.92–1.04 (m, 36H), 1.33–1.49 (m, 12H), 1.54–1.74 (m, 24H), 2.45–2.59 (m, 30H), 6.67 (d, 2H, *J*=3.7 Hz), 7.02 (d, 2H, *J*= 3.6 Hz), 7.06 ppm (s, 2H); ¹³C NMR: δ =13.7, 14.0, 14.0, 14.0, 15.4, 21.9, 22.0, 22.1, 22.3, 22.4, 30.8, 30.9, 30.9, 34.9, 35.0, 35.1, 36.9, 37.2, 37.3, 91.5, 92.4, 92.8, 95.0, 99.0, 99.1, 99.3, 99.8, 121.3, 125.0, 125.5, 128.2, 129.1, 129.3, 130.1, 131.0, 131.4, 131.7, 142.3 ppm; MALDI-TOF-MS: *m/z*: calcd: 1212.76; found: 1212.71.

2,5-Bis((E)-3-butyl-7-methoxy-7-methyl-4-propylocta-3-en-1,5-diynyl)-

thiophene (5-1): Pale-yellow oil (0.27 mmol, 0.157 g, 49%) obtained from **3-***I*.^[6] ¹H NMR: δ =0.94 (t, 6H, *J*=7.3 Hz), 0.95 (t, 6H, *J*=7.4 Hz), 1.37 (sextet, 4H, *J*=7.3 Hz), 1.52 (s, 12 H), 1.52–1.63 (m, 8H), 2.44 (t, 4H, *J*=7.2 Hz), 2.45 (t, 4H, *J*=7.2 Hz), 3.40 (s, 6H), 7.04 ppm (s, 2H); ¹³C NMR: δ =13.6, 14.0, 21.8, 22.1, 28.4, 30.6, 34.8, 36.7, 51.8, 71.2, 83.7, 90.7, 94.2, 100.8, 124.9, 128.5, 130.3, 131.4 ppm; HRMS: *m/z*: calcd: 572.3688; found: 572.3691.

2,5-Bis((3E,7E)-4,7-dibutyl-11-methoxy-11-methyl-3,8-dipropyldodeca-

3,7-dien-1,5,9-triynyl)thiophene (5-2): Yellow/orange oil (0.03 mmol, 0.262 g, 46%) obtained from **3-2**.^[6] ¹H NMR: δ =0.89–1.02 (m, 24H), 1.29–1.49 (m, 8H), 1.52 (s, 6H), 1.53–1.72 (m, 22H), 2.39–2.57 (m, 16H), 3.40 (s, 6H), 7.05 ppm (s, 2H); ¹³C NMR: δ =13.6, 13.6, 14.0, 14.0, 21.8, 21.9, 22.1, 22.2, 22.7, 28.4, 30.7, 30.7, 34.9, 35.0, 36.9, 37.1, 51.7, 71.2, 84.0, 91.4, 94.8, 98.1, 99.1, 100.5, 125.0, 128.2, 129.3, 129.3, 131.0, 131.4 ppm; HRMS: *m*/*z*: calcd: 868.6192; found: 868.6197.

2, 5-Bis((3E, 7E, 11E) - 3, 8, 11- tributyl - 15- methoxy- 15- methyl- 4, 7, 12- tripro-

pylhexadeca-3,7,11-trien-1,5,9,13-tetraynyl)thiophene (5-3): Yellow/ brown solid (0.02 mmol, 0.190 g, 66%) obtained from **3-3**.^[6] ¹H NMR: δ =0.90–1.00 (m, 36H), 1.30–1.49 (m, 12H), 1.52 (s, 12H), 1.53–1.70 (m, 24H), 2.41–2.56 (m, 24H), 3.40 (s, 6H), 7.06 ppm (s, 2H); ¹³C NMR: δ = 13.6, 13.6, 14.0, 14.0, 21.8, 21.9, 21.9, 22.1, 22.2, 22.3, 28.4, 30.7, 30.7, 30.8, 34.9, 35.0, 35.1, 36.9, 37.1, 37.3, 51.7, 71.2, 84.0, 91.5, 94.9, 98.4, 98.8, 99.7, 100.4, 125.0, 128.2, 129.0, 129.1, 129.4, 130.0, 131.0, 131.4 ppm; HRMS: *m/z*: calcd: 1164.8696; found: 1164.8670.

2-{(3E,9E)-4,9-Dibutyl-10-[2-(5-methylthiophen-2-yl)ethynyl]-3-propyltrideca-3,9-dien-1,5,7-triynyl}-5-methylthiophene (6-1): Yellow/brown solid (0.59 mmol, 0.320 g, 95%) obtained from **1-1**. ¹H NMR: δ = 0.97 (t, 6H, *J* = 7.3 Hz), 0.99 (t, 6H, *J* = 7.3 Hz), 1.41 (sextet, 4H, *J* = 7.4 Hz), 1.55–1.72 (m, 8H), 2.43–2.65 (m, 14H), 6.67 (d, 1H, *J* = 3.5 Hz), 6.68 (d, 1H, *J* = 3.5 Hz), 7.03 ppm (d, 2H, *J* = 3.7 Hz); ¹³C NMR: δ = 13.6, 13.9, 15.4, 21.8, 22.1, 30.7, 34.8, 36.8, 82.9, 84.4, 92.4, 94.2, 120.9, 125.6, 127.8, 132.0, 133.6, 142.7 ppm; HRMS: *m/z*: calcd: 538.2728; found: 538.2729.

2-Methyl-5-{(3*E*,7*E*,13*E*,17*E*)-4,7,14,17-tetrabutyl-18-[2-(5-methylthiophen-2-yl)ethynyl]-3,8,13-tripropylhenicosa-3,7,13,17-tetraen-1,5,9,11,15-

pentaynyl}thiophene (6-2): Dark-orange solid (0.28 mmol, 0.230 g, 90%) obtained from **1-2**. ¹H NMR: δ =0.80–1.03 (m, 24H), 1.40 (sextet, 8H, J=7.3 Hz), 1.55–1.72 (m, 16H), 2.43–2.65 (m, 22H), 6.67 (m, 2H), 7.02 ppm (d, 2H, J=3.7 Hz); ¹³C NMR: δ =13.6, 13.6, 13.9, 14.0, 15.4, 21.8, 21.9, 22.1, 22.3, 30.8, 30.8, 34.9, 35.2, 37.0, 37.2, 83.1, 84.7, 92.7, 92.7, 98.5, 100.9, 121.2, 125.5, 127.8, 129.0, 129.9, 131.7, 134.0, 142.4 ppm; HRMS: m/z: calcd: 834.5232; found: 834.5227.

2-{(3E,7E,11E,17E,21E,25E)-4,7,12,17,22,25-Hexabutyl-26-[2-(5-methyl-thiophen-2-yl)ethynyl]-3,8,11,18,21-pentapropylnonacosa-3,7,11,17,21,25-hexaen-1,5,9,13,15,19,23-heptaynyl}-5-methylthiophene (6-3): Orange/brown solid (0.10 mmol, 0.110 g, 89 %) obtained from **1-3**. ¹H NMR: δ = 0.88–1.03 (m, 36H), 1.33–1.44 (m, 12H), 1.50–1.70 (m, 24H), 2.43–2.65 (m, 30H), 6.67 (m, 2H), 7.01 ppm (d, 2H, J=3.7 Hz); ¹³C NMR: δ =13.6, 13,9, 14.0, 15.4, 21.8, 21.9, 22.1, 22.3, 22.3, 30.8, 30.8, 34.8, 35.1, 37.0, 37.2, 37.3, 83.1, 84.8, 92.4, 92.8, 98.8, 99.0, 99.5, 101.1, 121.2, 125.5, 127.8, 129.0, 129.2, 129.4, 130.4, 131.6, 134.0, 142.3 ppm; HRMS: *m/z*: calcd: 1130.7736; found: 1130.7749.

Acknowledgements

The authors thank the Dutch Technology Foundation STW for generous funding of this research (project no. WPC 5740), Dr. Jan Kroon (ECN) and Dr. Joost Smits (Shell) for helpful discussions, Dr. M. A. Posthumus for performing HRMS experiments, Dr. Jacob Baggerman for the quantum-chemical calculation of **2-1**, and Ing. E. J. Bakx for performing MALDI-TOF mass-spectrometric experiments.

- [1] J. M. Tour, Chem. Rev. 1996, 96, 537-553.
- [2] J. Roncali, Chem. Soc. Rev. 2005, 34, 483-495.
- [3] D. Fichou in Handbook of Oligo- and Polythiophenes, Wiley-VCH, Weinheim, 1999, p. 366.
- [4] H. Zuilhof, H. M. Barentsen, M. van Dijk, E. J. R. Sudhölter, R. J. O. M. Hoofman, L. D. A. Siebbeles, M. P. de Haas, J. M. Warman in *Polydiacetylenes* (Ed.: H. S. Nalwa), Academic Press, San Francisco, **2001**, pp. 339–437.
- [5] J. Gierschner, J. Cornil, H.-J. Egelhaaf, Adv. Mater. 2007, 19, 173– 191.
- [6] G. S. Pilzak, B. van Lagen, C. C. J. Hendrikx, E. J. R. Sudhölter, H. Zuilhof, *Chem. Eur. J.* 2008, 14, 7939–7950.
- [7] G. S. Pilzak, B. van Lagen, E. J. R. Sudhölter, H. Zuilhof, *Tetrahedron Lett.* 2008, 49, 4949–4952.
- [8] G. S. Pilzak, J. Baggerman, B. van Lagen, E. J. R. Sudhölter, H. Zuilhof, *Chem. Eur. J.* 2009, 15, 2296–2304.
- [9] M. Polhuis, C. C. J. Hendrikx, H. Zuilhof, E. J. R. Sudhölter, *Tetrahedron Lett.* 2003, 44, 899–901.

CHEMISTRY

A EUROPEAN JOURNAL

- [10] R. Giesa, R. C. Schulz, Polym. Int. 1994, 33, 43-60.
- [11] M. R. Bryce, M. A. Coffin, P. J. Skabara, A. J. Moore, A. S. Batsanov, J. A. K. Howard, *Chem. Eur. J.* **2000**, *6*, 1955–1962.
- [12] C. Czekelius, J. Hafer, Z. J. Tonzetich, R. R. Schrock, R. L. Christensen, P. Mueller, J. Am. Chem. Soc. 2006, 128, 16664–16675.
- [13] J. Roncali, Chem. Soc. Rev. 2005, 34, 483-495.
- [14] R. Sander, V. Stuempflen, J. H. Wendorff, A. Greiner, *Macromolecules* 1996, 29, 7705–7708.
- [15] R. E. Martin, F. Diederich, Angew. Chem. 1999, 111, 1440–1469; Angew. Chem. Int. Ed. 1999, 38, 817–821.
- [16] R. E. Martin, U. Gubler, J. Cornil, M. Balakina, C. Boudon, C. Bosshard, J.-P. Gisselbrecht, F. Diederich, P. Gunter, M. Gross, J.-L. Bredas, *Chem. Eur. J.* 2000, *6*, 3622–3635.
- [17] J. F. Nierengarten, D. Guillon, B. Heinrich, J. F. Nicoud, Chem. Commun. 1997, 1233–1234.
- [18] Y. Zhao, R. R. Tykwinski, J. Am. Chem. Soc. 1999, 121, 458-459.
- [19] Y. Zhao, R. McDonald, R. R. Tykwinski, J. Org. Chem. 2002, 67, 2805–2812.
- [20] S. C. Ciulei, R. R. Tykwinski, Org. Lett. 2000, 2, 3607-3610.
- [21] Y. Zhao, S. C. Ciulei, R. R. Tykwinski, *Tetrahedron Lett.* 2001, 42, 7721–7723.
- [22] G. Zotti, G. Schiavon, A. Berlin, G. Pagani, Chem. Mater. 1993, 5, 430–436.
- [23] G. Zotti, G. Schiavon, A. Berlin, G. Pagani, Chem. Mater. 1993, 5, 620-624.
- [24] G. Zotti, G. Schiavon, A. Berlin, G. Pagani, Adv. Mater. 1993, 5, 551–554.
- [25] W. Ten Hoeve, H. Wynberg, E. E. Havinga, E. W. Meijer, J. Am. Chem. Soc. 1991, 113, 5887–5889.
- [26] S. S. Zade, M. Bendikov, J. Org. Chem. 2006, 71, 2972-2981.
- [27] D. Fichou, G. Horowitz, B. Xu, F. Garnier, Synth. Met. 1990, 39, 243–259.
- [28] U. Segelbacher, N. S. Sariciftci, A. Grupp, P. Baeuerle, M. Mehring, *Synth. Met.* **1993**, *57*, 4728–4733.
- [29] C. Sauteret, J. P. Hermann, R. Frey, F. Pradère, J. Ducuing, R. H. Baughman, R. R. Chance, *Phys. Rev. Lett.* **1976**, *36*, 956.
- [30] A. F. Garito, C. C. Teng, K. Y. Wong, O. Zammani'Khamiri, Mol. Cryst. Liq. Cryst. 1984, 106, 219–258.
- [31] K. J. Donovan, E. G. Wilson, Synth. Met. 1989, 28, 569-574.
- [32] S. Spagnoli, K. J. Donovan, K. Scott, M. Somerton, E. G. Wilson, *Chem. Phys.* **1999**, 250, 71–79.
- [33] S. Jo, H. Yoshikawa, A. Fujii, M. Takenaga, Synth. Met. 2005, 150, 223–226.
- [34] M. Schott, Synth. Met. 2003, 139, 739-742.

- [36] U. Gubler, S. Concilio, C. Bosshard, I. Biaggio, P. Gunter, R. E. Martin, M. J. Edelmann, J. A. Wytko, F. Diederich, *Appl. Phys. Lett.* 2002, 81, 2322–2324.
- [37] Y. Nakano, K. Ishizuka, K. Muraoka, H. Ohtani, Y. Takayama, F. Sato, Org. Lett. 2004, 6, 2373–2376.
- [38] D. V. Matyushov, R. Schmid, B. M. Ladanyi, J. Phys. Chem. B 1997, 101, 1035–1050.
- [39] F. Wudl, S. P. Bitler, J. Am. Chem. Soc. 1986, 108, 4685-4687.
- [40] Y. Takayama, C. Delas, K. Muraoka, F. Sato, Org. Lett. 2003, 5, 365–368.
- [41] C. C. J. Hendrikx, M. Polhuis, A. Pul-Hootsen, R. B. M. Koehorst, A. van Hoek, H. Zuilhof, E. J. R. Sudhölter, *Phys. Chem. Chem. Phys.* 2005, 7, 548–553.
- [42] N. S. Bayliss, E. G. McRae, J. Phys. Chem. 1954, 58, 1002-1006.
- [43] C. Reichardt, Solvents and Solvent Effects in Organic Chemistry, Wiley-VCH, Weinheim, 2003, p. 630.
- [44] H. Chosrovian, S. Rentsch, D. Grebner, D. U. Dahm, E. Birckner, H. Naarmann, Synth. Met. 1993, 60, 23–26.
- [45] G. M. Balkowski, M. Groeneveld, H. Zhang, H. C. C. J. ;, M. Polhuis, H. Zuilhof, W. J. Buma, J. Phys. Chem. A 2006, 110, 11435– 11439.
- [46] G. Lanzani, G. Cerullo, S. Stagira, S. De Silvestri, J. Photochem. Photobiol. A 2001, 144, 13–19.
- [47] S. Meng, J. Ma, Y. Jiang, J. Phys. Chem. B 2007, 111, 4128-4136.
- [48] B. E. Kohler, D. E. Schilke, J. Chem. Phys. 1987, 86, 5214-5215.
- [49] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Kluwer Academic, New York, 2006, p. 420–421.
- [50] P. Garcia, J. M. Pernaut, P. Hapiot, V. Wintgens, P. Valat, F. Garnier, D. Delabouglise, J. Phys. Chem. 1993, 97, 513–516.
- [51] P. F. van Hutten, R. E. Gill, J. K. Herrema, G. Hadziioannou, J. Phys. Chem. 1995, 99, 3218–3224.
- [52] J. Gierschner, H. G. Mack, H. J. Egelhaaf, S. Schweizer, B. Doser, D. Oelkrug, Synth. Met. 2003, 138, 311–315.
- [53] A. Van Hoek and A. J. W. G. Visser, Int. Sci. Technol. 1985, 14, 143– 154.
- [54] E. G. Novikov, A. van Hoek, A. J. W. G. Visser and J. W. Hofstraat, Opt. Commun. 1999, 166, 189–198.
- [55] A. V. Digris, V. V. Skakoun, E. G. Novikov, A. van Hoek, A. Claiborne and A. J. W. G. Visser, *Euro. Biophys. J.* **1999**, *28*, 526–531.

Received: April 3, 2009 Published online: July 27, 2009

9096 -