Chirally organized oligo(thiophene)s: toward modeling interchain interactions within π -conjugated systems

David Cornelis, Thierry Verbiest, and Guy Koeckelberghs*

The research in conjugated polymers and oligomers is driven on one hand by the optimization of the intrinsic molecular features of the conjugated system itself and on the other hand by the fine-tuning of the intermolecular interactions between the conjugated segments.^[1] These intermolecular interactions play a crucial role in the properties of conjugated materials, not only in the neutral but also in the oxidized state. Several oligomeric model compounds, composed of stacked oligothiophenes, have recently been prepared to model the intermolecular π -dimerization upon oxidation.^[2] This π -dimer formation has even been used as the driving force for molecular actuators, composed of tweezer-like oligothiophenes with flexible molecular hinges.^[3] Finally, also chirality has been implemented in conjugated models, which created the possibility to visualize the induced conformational changes through chiroptical techniques.^[4]

The present approaches monitoring the strength of the intermolecular interactions and their dependence on external stimuli, such as oxidation, typically focus on the spectral changes of the oligomers induced by the interaction. However, such study is usually severely impeded by the fact that both the interaction and the external stimulus affect the electronic properties of the oligomer. Indeed, if oxidation is taken as an example, oxidation results in both the appearance of new, (bi)polaronic bands due to the altered electronic structure and (blue-)shifts, originating from π -dimerization, *i.e.* the interaction.^[2,3,5] Moreover, the magnitude and nature of the spectral changes do not only depend on the strength of the particular interaction (π -interaction, π -dimerization, ...), but also on the oligomer itself and the external stimulus (oxidation, deprotonation, ...). Therefore, the present studies remain typically focussed on a comparison of the spectral changes induced by the same external stimulus (*e.g.* oxidation) in an analogous series of oligomers.

In contrast, a more general protocol can be obtained if two oligomers are attached to a flexible hinge-molecule and if the

relative orientation of the two parts of this hinge are monitored, since in that case the spectral changes do not depend on the particular oligomer or external stimulus. Indeed, external stimuli, such as oxidation, can alter the interaction, and consequently, the distance between the two oligomers held together by the molecular tweezer. On its turn, this change is translated to an altered relative orientation and distance of the two parts of the flexible hinge (Figure 1). Finally, these changes can conveniently be monitored by, for instance, circular dichroism (CD) spectroscopy. As a consequence, this protocol is not limited to study differences in interactions within the same class of molecules, but it can in principle generally be used for comparing totally different molecules and interactions, provided that the same linking group (*e.g.* ethenylene group) and oligomers of similar bulkiness and rigidity are employed.

Figure 1: General protocol and the structure of MDC 1-4.

A survey of the molecules studied is shown in Figure 1. As flexible, chiral linker, a binaphthalene moiety (BN) was used. An overall X-type geometry of the oligomers was preferred, since this results in the strongest intermolecular interactions.^[6] All model

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Figure 2. UV-vis and CD spectra of **MDC 2** ($c = 1.47 \cdot 10^{-5}$ M) (a, b), **MDC 3** ($c = 3.94 \cdot 10^{-5}$ M) (c, d) and **MDC 4** ($c = 3.13 \cdot 10^{-5}$ M) (e, f) in dichloromethane during gradual oxidation with $\text{Et}_3\text{OSbCl}_6$. In the region $280 \text{ nm} < \lambda < 320 \text{ nm}$, indicated as , the CD signals originate from the BN hinge; $\lambda > 380 \text{ nm}$, shown in , the UV-vis and CD spectra arise from the oligomer. See Supporting Information for more detailed spectra.

compounds were prepared by a Wittig-Horner reaction of (*S*)-1,1'-binaphthalene-2,2'-dialdehyde with different phosphonated (oligo)thiophenes in a *trans*-selective configuration, as evidenced by $^1\text{H-NMR}$ spectroscopy.^[7] In order to verify whether the conformation as shown in Figure 1 is indeed possible, some Hyperchem simulations were performed on **MDC 2**. These calculations reveal that the proposed sandwich-like conformation is energetically favored.^[7]

The CD spectrum of a chiral BN is composed of a bisignate couplet(s), which intensity (and sign) depend on the dihedral angle (θ), the strength of the transition dipole moment and the orientation of these transition dipole moments with respect to the naphthalene axis.^[8] More in particular, the high-energy lobe of the CD signal in a typical (*S*)-BN geometry evolves from a small positive to a strong negative effect, with a zero-crossing $\sim 110^\circ$ and a moderate signal $\sim 90^\circ$ - the typical angle of most BN molecules.^[8] By further decreasing θ , the intensity again drops (Figure 5). It should be mentioned that the dihedral angle can vary between a broad range and even adopt small values, provided that an additional driving force, such as incorporation into a ring, is present.^[9] Consequently, probing this CD signal can be used to visualize changes in the dihedral angle of the BN core and, hence, interactions between the oligomers and even qualitatively compare them^[10], provided that following requirements are fulfilled:

(i) the tracked signal must solely originate from the BN couplet, *i.e.* it may not interfere with signals from the oligomer. A comparison of the UV-vis and CD spectra of **MDC 1** and the oligothiophene reveals that indeed overlapping occurs.^[7] However, $\lambda > 380 \text{ nm}$ - where **MDC 1** does not give any signal - the UV-vis and CD spectra are exclusively governed by the oligomer. On the other hand, for $280 \text{ nm} < \lambda < 320 \text{ nm}$ - where the shape of the CD spectra of **MDC 1** and **MDC 2** coincide and the chromophores hardly absorb - the Cotton effects solely arise from the BN hinge molecule. Therefore, $\Delta\epsilon$ at the minimum of the lobe near 310 nm, denoted as $\Delta\epsilon_{\text{BN}}$, can be monitored as 'tell-tale' signal.

(ii) the CD signal must not be affected by variations in the strength or orientation of the monitored transition dipole moment. Although

substituents can indeed influence the orientation, this effect is only important for quantitative studies and can therefore be neglected.^[8] Concerning the influence of changes in ϵ , one might speculate that oxidation affects ϵ and, in this way, the CD response, as it changes the electronic properties of the oligothiophene and introduces additives. Therefore, **MDC 3** was oxidized by gradual addition of Meerwein salts ($\text{Et}_3\text{OSbCl}_6$). This oxidant was chosen, since it has shown to result in an one-electron oxidation of oligothiophenes without any other side-reaction.^[3,11] The UV-vis spectra (Figure 2a) show that oxidation of the oligothiophene indeed occurs, but, importantly, the Cotton effect near 320 nm is not affected. Therefore, possible changes of $\Delta\epsilon_{\text{BN}}$ of **MDC 2** and **MDC 4** upon oxidation cannot be due to an altered orientation or strength of the transition dipole moment of the monitored BN transition, but must originate from a different dihedral angle.

Next, **MDC 4**, in which an electronpoor oligothiazole and the pentathiophene are stacked, is subjected to oxidation. Due to the electron poverty of oligothiazole, only oxidation of the oligothiophene is possible, which is again visualized by the UV-vis spectra. Importantly, $\Delta\epsilon_{\text{BN}}$ decreases upon oxidation, revealing a decline in dihedral angle and hence, a change in the interaction between the conjugated pentamers.^[12] Note that **MDC 4** shows a clear bisignate Cotton effect near 400 nm, which originates from chiral exciton coupling between the two oligomers and which is therefore absent in **MDC 3**, being equipped with only one oligomer. In this way, the BN moiety transfers its chirality to the oligothiophenes. Finally, **MDC 2**, which is composed of two oxidizable pentathiophenes, is oxidized. From the UV-vis spectra, it can be concluded that oxidation indeed occurs and that at higher degrees of oxidation, additional, blue-shifted peaks (near 650 and 950 nm) arise, which can be attributed to π -dimerization.^[2,3,5] A second indication of interactions between the oxidized oligothiophenes is provided by cyclic and differential pulse voltammetry (Figure 3).^[13] The cyclic voltammogram of **MDC 2** shows two quasi-reversible oxidations. In the case of **MDC 4** one quasi-reversible oxidation is present together with an irreversible second oxidation at higher potential, which can be attributed to the

instability of an oxidized oligothiazole moiety. The first oxidation of **MDC 2** clearly occurs at a lower potential than the first oxidation of **MDC 4**, showing that the oxidized pentathiophene is more stabilized by a pentathiophene (**MDC 2**) than by an oligothiazole (**MDC 4**). This observation clearly demonstrates the interaction between the (oxidized) oligothiophenes.

Figure 3. Calibrated cyclic voltammograms (up) of **MDC 2** (—) and **MDC 4** (---) in dichloromethane with ferrocene as internal standard versus SCE (scan rate = 100 mV/s); Calibrated and normalized differential pulse voltammograms (down) under the same conditions, but with a pulse amplitude of 75 mV (50 ms) and a scan rate of 20 mV/s.

Oxidation also affects the CD spectra. Moreover, the clear absence of an isosbestic point is in agreement with two subsequent one-electron oxidations (one on each pentathiophene), the latter being accompanied by π -dimerization. This is in contrast with the single-step oxidation of **MDC 4**, in which such isosbestic point can be observed. Finally, the comparison of the magnitude of the change of $\Delta\epsilon_{BN}$ of **MDC 2** and **MDC 4** reveals that the interaction between oxidized pentathiophenes – although both being electron-poor and charged – is much stronger^[12] than the interaction between oxidized

pentathiophene and electron-poor but neutral oligothiazole, which clearly reflects the strength of the π -dimerization.

As already mentioned, the magnitude of $\Delta\epsilon_{BN}$ directly depends on the interaction between the two moieties (if present) connected to the naphthalenes. Therefore, probing $\Delta\epsilon_{BN}$ cannot only be used to monitor changes in interactions upon oxidation, but it can already reveal differences in π -interactions in different neutral oligothiophenes. Indeed, $\Delta\epsilon_{BN}$ of **MDC 1**, in which no interactions between oligomers are present, is $\sim 60 \text{ M}^{-1}\text{cm}^{-1}$,^[7] while, in contrast, $\Delta\epsilon_{BN}$ of **MDC 2** and **MDC 4** are $\sim 100 \text{ M}^{-1}\text{cm}^{-1}$, pointing at a smaller θ and thus reflecting the π -interactions between the oligomers in the latter compounds. Second, since the model does not rely on the chiroptical properties of the oligomers, it is not restricted to study π -interactions and their differences induced by oxidation, but it can more generally be used to probe any interaction between moieties connected to the binaphthalene core via the same ethynylene linker. In order to test this hypothesis, **MDC 5-6** (Figure 4) are prepared, in which deprotonation instead of oxidation allows for the manipulation of the interactions between the oligomers.

Figure 4. Structure of **MDC 5-6**.

In order to confirm that the deprotonation does not wrongly affect $\Delta\epsilon_{BN}$, KOtBu is first gradually added to **MDC 5**. The red-shift (from 400 to 440 nm, Figure 5) confirms the deprotonation of the oligomer, but leaving $\Delta\epsilon_{BN}$ unchanged. This again demonstrates

Figure 5. UV-vis and CD spectra of **MDC 5** ($c = 2.41 \cdot 10^{-5} \text{ M}$) (a, b) and **MDC 6** ($c = 2.41 \cdot 10^{-5} \text{ M}$) (c, d) in THF:BuOH (1:1) during gradual deprotonation with KOtBu and **MDC 6** ($c = 2.41 \cdot 10^{-5} \text{ M}$) (e, f) in THF:MeOH (8:2) during gradual deprotonation with KOH. In the region $280 \text{ nm} < \lambda < 320 \text{ nm}$, indicated as , the UV-vis and CD signals originate from the BN hinge; $\lambda > 380 \text{ nm}$, shown in , the UV-vis and CD spectra arise from the oligomer. See Supporting Information for more detailed spectra.

that nor changing the nature of the chromophore, nor the introduction of ions, influence $\Delta\epsilon_{\text{BN}}$. Aggregation can also be ruled out as **MDC 6** dissolves in *t*BuOH.^[7] Moreover, also the fact that the CD spectra of **MDC 3** and **MDC 5** are very similar in both shape and magnitude, again supports the fact that they are essentially due to the chiral BN, irrespective of the presence and nature of the oligomer. Next, **MDC 6** is subjected to deprotonation, which can be visualized in both the UV-vis and CD spectra. Interestingly, after deprotonation the original, neutral situation can be restored by the addition of HCl.^[7] Furthermore, a more detailed inspection of the spectra reveals that the deprotonation is a two-step process – the second deprotonation only occurring at large quantities of KO*t*Bu (these spectra are shown in grey, Figure 5). The necessity to use large quantities of the base for the second deprotonation suggests that the deprotonation of the first oligomer significantly decreases the acidity of the second one. This is confirmed by the fact that if the less basic KOH is employed, the second deprotonation does not occur, even at a very large excess. If the CD spectra are considered, it is striking that $\Delta\epsilon_{\text{BN}}$ again amounts $\sim 100 \text{ M}^{-1}\text{cm}^{-1}$ (**MDC 6**). The first deprotonation results in a relative small drop of $\Delta\epsilon_{\text{BN}}$; the second deprotonation further increases the interactions between the oligomers, as is reflected by the smaller $\Delta\epsilon_{\text{BN}}$ and, hence, θ .^[12]

As already mentioned, the universality of the approach allows to qualitatively compare interactions between a set of two oligomers, as this is reflected by the magnitude of $\Delta\epsilon_{\text{BN}}$. Such comparison (Figure 6) shows that in the absence of any interactions (**MDC 1**) $\Delta\epsilon_{\text{BN}} \sim 60 \text{ M}^{-1}\text{cm}^{-1}$, corresponding to a typical $\theta \sim 90^\circ$.^[8] π -interactions (**MDC 2**, **MDC 4** and **MDC 6**) decrease θ . The fact that similar values are found ($\Delta\epsilon_{\text{BN}} \sim 100 \text{ M}^{-1}\text{cm}^{-1}$) can be attributed to the fact that the interaction is in all cases the same and/or the $\Delta\epsilon_{\text{BN}} - \theta$ relationship reaches a plateau. Both oxidation and deprotonation increases the interactions between the oligomers (θ further decreases), but the (multiple) oxidation to a larger extent than (multiple) deprotonation.

Figure 6. Comparison of the dihedral angle (θ) in the model compounds before and after the external stimulus. The evolution of $\Delta\epsilon_{\text{BN}}$ in function of θ was calculated using classical physics, assuming standard binaphthalene geometries, Gaussian absorption bands ($\sigma = 1.5 \cdot 10^{14} \text{ s}^{-1}$), a transition dipole strength of 50 D^2 located along the naphthalene long axis.^[14]

In conclusion, a protocol which allows to monitor (changes in) interactions between two oligomers is reported. It consists of the attachment of two oligomers to a chiral, flexible binaphthalene core and monitoring $\Delta\epsilon_{\text{BN}}$. Since this property is independent on the nature of the oligothiophene or external stimulus performed, it can be generally used to monitor and compare interactions between two π -conjugated oligomers.

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Keywords: Binaphthalenes • Chiral • Conjugated polymers • Interchain Interactions • Oligothiophenes

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- [12] If θ is such that a maximal CD intensity is obtained, any variation of θ , and, hence, of the interaction between the oligomers (decrease or increase), results in a decline of the CD intensity. Applied on the experiments performed, the drop of the CD intensity upon applying the external stimulus can in principle both point at an increase or a decrease of θ , provided that was started from a maximal CD intensity. However, the nature of the interaction (delocalization of charges, π -dimerization) and the vast amount of literature on these subjects, rules out the possibility that the interaction weakens.
- [13] The first and second oxidation, resulting in **MDC 2**** and **MDC 2*** respectively, occur at a lower potential than oxidation of the parent, uncoupled pentathiophene, which can be attributed to charge delocalization of the radical cation by the second pentathiophene and π -dimerization. These results will be published elsewhere.
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A model is proposed to compare the strength of the interaction between two conjugated oligomers. It consists of probing changes in the angle between the parts of a binaphthalene hinge, invoked by the interaction between the oligomers. This allows to compare the strength of the interaction between any set of oligomers or to monitor changes in the interactions upon oxidation or deprotonation.

Chirally organized oligo(thiophene)s: toward modeling interchain interactions within π -conjugated systems

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Experimental Section

Reagents and instrumentations

All reagents were purchased from Aldrich Chemical Co., Acros Organics, Merck, Fluka, Alkemi and were used as received. Tetrahydrofuran (THF) was dried over a Na/K alloy. Diisopropylamine, dimethylformamide (DMF), dichloromethane and hexane were freshly distilled and further dried on molecular sieve (4Å).

^1H and ^{13}C nuclear magnetic resonance (NMR) measurements were carried out with a Bruker Avance 300 MHz and a Bruker Avance 400 MHz. UV-vis and CD spectra were recorded with a Varian Cary 400 and a JASCO 62 DS apparatus respectively. The DSC measurements were performed on a Perkin-Elmer DSC 7 apparatus at the 2nd heating (heating rate = 40 °C/min). Cyclic and differential pulse voltammetry were performed on a Princeton Applied Research PARSTAT 2273, equipped with a standard three-electrode configuration. A Ag/AgCl (3M NaCl) electrode served as a reference electrode and a Pt wire and disk as the counter- and working electrode. The measurements were done in homogeneous solutions of $\pm 10^{-4}$ M binaphthalene derivative, 10^{-4} M ferrocene (internal standard) and 0.1 M Bu_4NBF_4 (supporting electrolyte) in dry dichloromethane under an argon atmosphere. The cyclic and differential pulse voltammograms were calibrated toward the Fe(II/III) couple at 0.60 V versus a standard calomel electrode.^[1] (S)-**1**^[2], **2**^[3], **3**^[4], **5**^[5] and **12**^[6] were synthesized according to the literature procedures.

Synthesis of MDC 1

Scheme 1: Synthesis of **MDC 1**.

II.1 Preparation of **MDC 1**

A suspension of NaH (425 μmol , 10.2 mg), (S)-**1** (170 μmol , 52.7 mg) and **2** (425 μmol , 167 mg) in dry THF (7 mL) was purged with argon and vigorously stirred for 24 h at reflux temperature. The mixture was poured into a HCl solution (1 M) and extracted with dichloromethane. The combined organic layers were washed with a saturated NaCl solution and dried over MgSO_4 . The solvents were removed under reduced pressure and the crude compound was twice purified by column chromatography (silicagel, eluent: hexane:dichloromethane (50:50 v/v) and hexane:ethylacetate (95:5 v/v)). A pale white oil was isolated.

Yield: 50.0 mg (37 %).

¹ H-NMR (CD ₂ Cl ₂ ; 400 MHz)	δ(ppm)	#H(mp)	H _?
8,05	4H(s)	H _{a,b}
	7,95	2H(d, J=8,6Hz)	H _c
	7,45	2H(t, J=8,6Hz)	H _e
	7,22	2H(t, J=8,6Hz)	H _d
	7,04	2H(d, J=16,1Hz)	H _h
	7,03	2H(d, J=8,6Hz)	H _f
	6,57	2H(s)	H _g
	6,53	2H(d, J=16,1Hz)	H _i

¹³C-NMR (CD₂Cl₂; 400 MHz): δ = 139.4, 134.8, 133.9, 133.7, 133.6, 129.7, 129.0, 128.4, 127.7, 127.1, 126.9, 126.6, 123.1, 121.8, 111.9, 110.6.

MS (EI): m/z = 786 (M⁺) (calc. 786.22).

Elemental analysis calcd (%) for $C_{32}H_{18}Br_4S_2$: C 48.88, H 2.31, S 8.16; found: C 49.01, H 2.49, S 8.16.

Synthesis of MDC 2 and MDC 3

Conditions: i) Pd_2dba_3 , $AsPh_3$, THF; ii) NaH, THF.

Scheme2: Synthesis of **MDC 2** and **MDC 3**.

Preparation of 4

A solution of **3** (4.16 mmol, 1.72 g), **2** (1.89 mmol, 743 mg), Pd_2dba_3 (189 μ mol, 173 mg) and $AsPh_3$ (1.51 mmol, 464 mg) in THF (5 mL) was purged with argon and refluxed for 20 h. The mixture was poured into water and the product was extracted with diethylether. The combined organic layers were washed with a saturated NaCl solution and dried over $MgSO_4$. The solvents were removed under reduced pressure. The crude compound was further purified by column chromatography (silicagel, eluent: hexane:ethylacetate (95:5 v/v)) and isolated as an orange solid.

Yield: 1.22 g (88 %).

m.p.: 61.8-62.4 $^{\circ}C$ (determined by optical microscopy).

¹ H-NMR (CD ₂ Cl ₂ ; 300 MHz)	δ(ppm)	#H(mp)	H ₇
	7,23	1H(d, J=3,8Hz)	H _{c/d/f/g}
	7,18	1H(s)	H _e
	7,08	1H(d, J=3,8Hz)	H _{c/d/f/g}
	7,07	1H(d, J=3,8Hz)	H _{c/d/f/g}
	6,95-7,04	3H(m)	H _{c/d/f/g,b,h}
	6,71	2H(d, J=3,8Hz)	H _{a,i}
	4,07	4H(qu)	H _q
	3,28	2H(d, J=21,0Hz)	H _p
	2,80	4H(t)	H _{j,j'}
	1,68	4H(qu)	H _{k,k'}
	1,20-1,50	12H(m)	H _{l,l'-n,n'}
	1,28	6H(t)	H _r
	0,90	6H(t)	H _{o,o'}

¹³C-NMR (CD₂Cl₂; 300 MHz): δ = 146.4, 146.3, 138.9, 137.5, 135.7, 134.9, 134.5, 134.4, 133.1, 132.0, 131.8, 129.1, 128.9, 128.0, 127.2, 127.1, 125.3, 124.8, 123.9, 123.8, 62.6, 31.9, 30.4, 29.1, 27.9, 22.9, 16.6, 14.2.

MS(EI): m/z = 730 (M⁺) (calc. 731.11).

Elemental analysis calcd (%) for C₃₇H₄₇O₃PS₅: C 60.79, H 6.48, S 21.93; found: C 61.01, H 6.68, S 21,69.

Preparation of MDC 3

A suspension of NaH (134 μ mol, 3.20 mg), **4** (134 μ mol, 97.8 mg) and (*S*)-**1** (134 μ mol, 41.5 mg) in dry THF (4 mL) was purged with argon and vigorously stirred for 20 h at room temperature. The mixture was poured into a HCl solution (1 M) and extracted with dichloromethane. The combined organic layers were washed with a saturated NaCl solution and dried over MgSO₄. The solvents were removed under reduced pressure and the crude compound was further purified by column chromatography (silicagel, eluent: hexane:dichloromethane (50:50 v/v)). An orange solid was isolated.

Yield: 81.4 mg (68 %).

No melting point or glass transition detected by optical microscopy or DSC below 250 °C.

¹ H-NMR (CD ₂ Cl ₂ ; 400 MHz)	δ (ppm)	#H(mp)	H ₂
<p>—R = —CHO</p> <p>—R' = </p> <p>—R'' = </p> <p>—R''' = </p>	9,63	1H(s)	CHO
	8,18	1H(d, J=8,6Hz)	H _a
	8,12	1H(d, J=8,6Hz)	H _b
	8,05	1H(d, J=8,6Hz)	H _h
	8,03	1H(d, J=8,6Hz)	H _c
	8,00	1H(d, J=8,6Hz)	H _g
	7,95	1H(d, J=8,6Hz)	H _i
	7,62	1H(t, J=8,6Hz)	H _d
	7,46	1H(t, J=8,6Hz)	H _k
	7,37	1H(d, J=16,1Hz)	H _v
	7,35	1H(t, J=8,6Hz)	H _e
	7,33	1H(d, J=8,6Hz)	H _f
	7,25	1H(t, J=8,6Hz)	H _j
	7,07	1H(d, J=3,8Hz)	H _{n/o/p/r/s/t}
	7,05	1H(d, J=3,8Hz)	H _{n/o/p/r/s/t}
	7,00	1H(d, J=8,6Hz)	H _l
	6,97	1H(d, J=3,8Hz)	H _{n/o/p/r/s/t}
	6,96	1H(d, J=3,8Hz)	H _{n/o/p/r/s/t}
	6,94	1H(d, J=3,8Hz)	H _{n/o/p/r/s/t}
	6,91	1H(d, J=3,8Hz)	H _{n/o/p/r/s/t}
	6,74	1H(d, J=3,8Hz)	H _{m/u}
	6,70	1H(d, J=3,8Hz)	H _{m/u}
	6,64	1H(s)	H _q
	6,55	1H(d, J=16,1Hz)	H _w
	2,82	2H(t)	H _{x/x'}
	2,79	2H(t)	H _{x/x'}
	1,69	4H(m)	H _{y,y'}
	1,30-1,50	12H(m)	H _{z0,z0'-z2,z2'}
	0,90	6H(t)	H _{z3,z3'}

^{13}C -NMR (CD_2Cl_2 ; 400 MHz): δ = 192.3, 146.6, 146.5, 143.4, 139.4, 137.7, 136.7, 136.5, 135.7, 135.5, 134.5, 134.4, 134.3, 133.2, 133.1, 133.0, 132.3, 131.3, 129.5, 129.5, 129.4, 128.8, 128.7, 128.4, 128.0, 127.7, 127.4, 126.8, 126.6, 125.3, 125.2, 125.1, 124.4, 124.1, 123.9, 123.8, 123.3, 122.5, 122.3, 31.9, 30.4, 29.1, 22.9, 14.2.

MS (APCI): m/z = 887 (M^+) (calc. 887.35).

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D. Camelia MDC1

401A01156 #23-26 RT: 0.56-0.64 AV: 4 NL: 3.54E4
T: + c sid=60.00 Full ms [150.00-2000.00]

Elemental analysis calcd (%) for $\text{C}_{55}\text{H}_{50}\text{OS}_5$: C 74.45, H 5.68, S 18.07; found: C 74.22, H 5.88, S 18.37.

Preparation of MDC 2

The procedure described for the preparation of **MDC 3** was followed, starting from a suspension of NaH (330 μmol , 8.00 mg), **4** (320 μmol , 236 mg) and (*S*)-**1** (161 μmol , 50.0 mg) in dry THF (3 mL). The crude compound was purified by column chromatography (silicagel, eluent: hexane:dichloromethane (70:30 v/v)) and isolated as an orange solid.

Yield: 100 mg (42 %).

m.p.: 116.4 °C; Tg: 157 °C (determined by DSC).

¹ H-NMR (CD ₂ Cl ₂ ; 400 MHz)	δ(ppm)	#H(mp)	H _?
8,03	2H(d, J=8,8Hz)	H _b
	7,99	2H(d, J=8,8Hz)	H _a
	7,95	2H(d, J=8,6Hz)	H _c
	7,44	2H(t, J=8,6Hz)	H _e
	7,31	2H(d, J=16,1Hz)	H _p
	7,24	2H(t, J=8,6Hz)	H _d
	7,11	2H(d, J=8,6Hz)	H _f
	6,93	2H(d, J=3,8Hz)	H _{h/i/j/l/m/n}
	6,91	2H(d, J=3,8Hz)	H _{h/i/j/l/m/n}
	6,90	2H(d, J=3,8Hz)	H _{h/i/j/l/m/n}
	6,89	2H(d, J=3,8Hz)	H _{h/i/j/l/m/n}
	6,86	2H(d, J=3,8Hz)	H _{h/i/j/l/m/n}
	6,84	2H(d, J=3,8Hz)	H _{h/i/j/l/m/n}
	6,72	2H(s)	H _k
	6,66	2H(d, J=3,8Hz)	H _{g/o}
	6,65	2H(d, J=16,1Hz)	H _q
	6,63	2H(d, J=3,8Hz)	H _{g/o}
	2,77	8H(m)	H _{r,r'}
	1,67	8H(m)	H _{s,s'}
	1,20-1,50	24H(m)	H _{t,t'-v,v'}
	0,90	12H(t)	H _{w,w'}

¹³C-NMR (CD₂Cl₂; 400 MHz): δ = 146.4, 146.3, 139.0, 137.6, 136.9, 135.6, 135.0, 134.7, 134.5, 134.4, 133.8, 133.5, 133.4, 131.9, 129.7, 129.0, 128.4, 127.9, 127.1, 126.9, 126.3, 125.2, 125.0, 124.0, 123.9, 123.9, 123.8, 123.7, 123.6, 122.4, 31.9, 30.4, 29.1, 22.9, 14.2.

MS (APCI): m/z = 1463 (M⁺) (calc. 1464.34).

401A0078 #65-69 RT: 1,63-1,74 AV: 5 NL: 7,43E4
T: + c ms [150,00-2000,00]

Elemental analysis calcd (%) for $C_{88}H_{86}S_{10}$: C 72.18, H 5.92, S 21.90; found: C 71.93, H 6.23, S 21.99.

Synthesis of MDC 4

Conditions: *i*) 1) LDA, THF, 2) C₆H₁₃Br; *ii*) 1) *n*-BuLi, THF, 2) Me₃SnCl; *iii*) Pd(PPh₃)₄, DMF; *iv*) NaH, THF.

Scheme 2: Synthesis of MDC 4.

Preparation of 6

A solution of diisopropylamine (1.20 mmol, 121 mg) in dry THF (3 mL) was purged with argon and cooled to -20 °C. *n*-BuLi (1.00 mmol, 400 µL, 2.5 M in hexane) was slowly added under an argon atmosphere and the mixture was further stirred at room temperature for 30 min. After cooling the reaction at -78 °C, a solution of **5** (1.00 mmol, 168 mg) in dry THF was added under vigorously stirring at -78 °C for 50 min. Subsequently, 1-bromohexane (1.00 mmol, 165 mg) was added and the reaction was allowed to reach room temperature. After 3 h of stirring at room temperature, the reaction mixture was poured into a saturated NH₄Cl solution and the product was extracted with diethylether. The combined organic layers were dried over MgSO₄ and the solvents were removed under reduced pressure. The crude compound was further purified by column chromatography (silicagel, eluent: hexane:ethylacetate (80:20 v/v)) and isolated as a white solid.

Yield: 129 mg (51 %).

m.p.: 74.8-75.4 °C (determined by optical microscopy).

¹ H-NMR (CDCl ₃ ; 300 MHz)	δ(ppm)	#H(mp)	H ₇
7,86	1H(d, J=3,7Hz)	H _b
	7,56	1H(s)	H _c
	7,39	1H(d, J=3,7Hz)	H _a
	2,87	2H(t)	H _d
	1,70	2H(qu)	H _e
	1,20-1,50	6H(m)	H _{f-h}
	0,89	3H(t)	H _i

¹³C-NMR (CDCl₃; 300 MHz): δ = 162.2, 159.7, 143.8, 142.7, 140.8, 120.5, 31.5, 28.7, 27.2, 22.6, 14.1.

MS (EI): m/z = 252 (M⁺) (calc. 252.42).

Elemental analysis calcd (%) for C₁₂H₁₆N₂S₂: C 57.10, H 6.39, N 11.10; found: C 57.34, H 6.22, N 11.39.

Synthesis of 7

A solution of **6** (4.44 mmol, 1.12 g) in dry THF (15 mL) was purged with argon and cooled to -78 °C. *n*-BuLi (4.44 mmol, 1.78 mL, 2.5 M in hexane) was slowly added under vigorously stirring for 30 min. Subsequently, a solution of Me₃SnCl (4.89 mmol, 974 mg) in dry THF (5 mL) was added and the reaction was allowed to reach room temperature. After 2 h of stirring at room temperature, the solvent

was removed under reduced pressure and the product was redissolved in dry hexane. LiCl was filtered off and, after removal of the solvent, white crystals were isolated.

Yield: 1.75 g (95 %).

m.p.: 52.0-53.0 °C (determined by optical microscopy).

¹ H-NMR (CDCl ₃ ; 300 MHz)	δ(ppm)	#H(mp)	H ₇
7,76	1H(s)	H _b
	7,53	1H(s)	H _c
	2,85	2H(t)	H _d
	1,69	2H(qu)	H _e
	1,20-1,50	6H(m)	H _{f-h}
	0,88	3H(t)	H _i
	0,43	9H(s)	H _a

¹³C-NMR (CDCl₃; 300 MHz): δ = 166.7, 159.8, 149.9, 142.2, 140.9, 132.0, 31.6, 28.7, 27.2, 22.6, 14.2, -8.0.

MS (EI): m/z = 415 (M⁺) (calc. 415.22).

Elemental analysis calcd (%) for C₁₅H₂₄N₂S₂Sn: C 43.39, H 5.83, N 6.75; found: C 43.08, H 6.01, N 6.60.

Synthesis of 8

A solution of **2** (315 μ mol, 124 mg), **7** (788 μ mol, 327 mg) and Pd(PPh₃)₄ (16.0 μ mol, 18.2 mg) in dry DMF (4 mL) was purged with argon and heated at 80 °C for 24 h. After reaction, DMF was removed under reduced pressure and the product was extracted with chloroform. The combined organic layers were washed with a saturated KCl solution and dried over MgSO₄. The solvents were removed and the crude compound was further purified by column chromatography (silicagel, eluent: dichloromethane:ethylacetate (50:50 v/v)). A yellow solid was isolated.

Yield: 200 mg (86 %).

m.p.: 147.0-148.0 °C (determined by optical microscopy).

¹ H-NMR (CDCl ₃ ; 300 MHz)	δ (ppm)	#H(mp)	H ₇
	8,03	1H(s)	H _{b/d}
	7,91	1H(s)	H _{b/d}
	7,58	1H(s)	H _{a/e}
	7,57	1H(s)	H _{a/e}
	7,34	1H(s)	H _c
	4,11	4H(qu)	H _m
	3,30	2H(d, J=21,9Hz)	H _l
	2,89	2H(t)	H _{f/f'}
	2,88	2H(t)	H _{f/f'}
	1,72	4H(m)	H _{g,g'}
	1,20-1,50	12H(m)	H _{h,h'-j,j'}
	1,27	6H(t)	H _n
	0,90	6H(m)	H _{k,k'}

¹H-NMR (CDCl₃; 300 MHz): δ = 8.03 (s, 1H), 7.91 (s, 1H), 7.58 (s, 1H), 7.57 (s, 1H), 7.34 (s, 1H), 4.11 (qu, 4H), 3.30 (d, J = 21.9 Hz, 2H), 2.89 (t, 2H), 2.88 (t, 2H), 1.72 (m, 4H), 1.5-1.1 (m, 18H), 0.90 (t, 6H).

¹³C-NMR (CDCl₃; 400 MHz): δ = 162.3, 160.9, 159.2, 143.3, 143.2, 142.7, 141.2, 141.1, 140.1, 133.0, 131.0, 130.9, 130.8, 129.5, 129.2, 129.1, 62.6, 31.6, 28.8, 27.9, 27.3, 22.7, 16.6, 14.2.

MS (EI): m/z = 734 (M⁺) (calc. 735.07).

Elemental analysis calcd (%) for $C_{33}H_{43}N_4O_3PS_5$: C 53.92, H 5.90, N 7.62; found: C 54.26, H 6.27, N 7.39.

Synthesis of MDC 4

The procedure described for the preparation of **MDC 3** was followed, starting from a suspension of NaH (110 μ mol, 2.60 mg), **MDC 3** (91.7 μ mol, 81.4 mg) and **8** (110 μ mol, 80.9 mg) in dry THF (4 mL). The crude compound was purified by column chromatography (silicagel, eluent: dichloromethane) and isolated as a yellow-orange solid.

Yield: 126 mg (94 %).

m.p.: 111.2 $^{\circ}$ C (determined by DSC).

¹ H-NMR (CD ₂ Cl ₂ ; 400 MHz)	δ(ppm)	#H(mp)	H ₂
7,90-8,10	6H(m)	H _{a,b,c,g,h,i}
	7,71	2H(s)	H _{y,z1}
	7,53	1H(s)	H _{x/z2}
	7,48	1H(s)	H _{x/z2}
	7,47	1H(t, J=8,6Hz)	H _k
	7,44	1H(t, J=8,6Hz)	H _e
	7,32	1H(d, J=16,1Hz)	H _v
	7,18-7,28	3H(m)	H _{d,j,z3}
	7,12	1H(d, J=8,6Hz)	H _f
	7,08	1H(d, J=8,6Hz)	H _l
	6,85-6,97	7H(m)	H _{n,o,p,r,s,t,z}
	6,73	1H(s)	H _q
	6,71	1H(d, J=16,1Hz)	H _{z4}
	6,66	1H(d, J=3,8Hz)	H _{m/u}
	6,64	1H(d, J=16,1Hz)	H _w
	6,62	1H(d, J=3,8Hz)	H _{m/u}
	2,86	2H(t)	H _{z5''/z5'''}
	2,84	2H(t)	H _{z5''/z5'''}
	2,78	2H(t)	H _{z5/z5'}
	2,75	2H(t)	H _{z5/z5'}
	1,67	8H(m)	H _{z6-z6'''}
	1,30-1,50	24H(m)	H _{(z7-z7''')-(z9-z9''')}
	0,90	12H(m)	H _{z10-z10'''}

¹³C-NMR (CD₂Cl₂; 400 MHz): δ = 162.1, 160.9, 159.2, 146.3, 146.2, 143.4, 142.5, 141.3, 140.3, 139.1, 138.8, 137.5, 136.8, 135.5, 135.1, 134.9, 134.7, 134.5, 134.4, 134.2, 133.8, 133.7, 133.5, 133.4, 133.0, 132.8, 131.9, 131.4, 131.3, 129.7, 129.1, 128.6, 128.5, 127.7, 127.2, 127.0, 126.5, 126.3, 125.2, 124.9, 124.1, 124.0, 123.8, 123.7, 123.6, 123.5, 122.7, 122.4, 31.8, 30.4, 29.1, 27.5, 22.9, 14.2.

MS (APCI): m/z = 1468 (M⁺) (calc. 1468.30).

401A01157_090710101936 #84-92 RT: 2,08-2,28 AV: 9 NL: 1,44E4
T: + c sid=60,00 Full ms [150,00-2000,00]

Elemental analysis calcd (%) for $C_{84}H_{82}N_4S_{10}$: C 68.72, H 5.63, N 3.82; found: C 68.87, H 5.88, N 3.60.

Synthesis of 10

Conditions: *i*) NaH, THF.

Scheme 3: Synthesis of **10**.

Preparation of 10

The procedure described for the preparation of **MDC 3** was followed, starting from a suspension of NaH (205 μ mol, 5.00 mg), **9** (205 μ mol, 18.0 mg) and **4** (205 μ mol, 150 mg) in dry THF (4 mL). The crude compound was purified by trituration in cold methanol and isolated as an orange solid.

Yield: 107 mg (79 %).

m.p.: 136.0-137.0 °C (determined by optical microscopy).

¹ H-NMR (CDCl ₃ ; 400 MHz)	δ (ppm)	#H(mp)	H _?
7,23	1H(s)	H _e
	7,06	2H(d, J=3,8Hz)	H _{d,f}
	7,02	1H(d, J=3,8Hz)	H _{g/c}
	7,00	2H(d, J=3,8Hz)	H _{b/h,g/c}
	6,99	1H(d, J=3,8Hz)	H _{b/h}
	6,69	2H(d, J=3,8Hz)	H _{a,i}
	6,62	1H(d, J=16,1Hz)	H _j
	6,22	1H(d, J=16,1Hz)	H _k
	2,80	4H(t)	H _{m,m'}
	1,69	4H(qu)	H _{n,n'}
	1,3-1,5	12H(m)	H _{o,o'-q,q'}
	1,15	9H(s)	H _l
	0,90	6H(t)	H _{r,r'}

¹³C-NMR (CDCl₃; 400 MHz): δ = 146.1, 144.6, 138.8, 137.6, 137.4, 135.6, 135.5, 134.8, 134.4, 130.2, 127.1, 125.0, 124.7, 123.9, 123.8, 123.7, 123.3, 118.8, 31.8, 31.7, 30.4, 29.9, 29.0, 22.7, 14.1.

MS (APCI): m/z = 663 (M⁺) (calc. 663.14).

401A01158 #113-117 RT: 2,81-2,91 AV: 5 NL: 7,41E4
T: + c sid=60,00 Full ms [150,00-2000,00]

Elemental analysis calcd (%) for $C_{38}H_{46}S_5$: C 68.83, H 6.99 S 24.18 ; found: C 68.49, H 7.09, S 23.98.

Synthesis of MDC 5 and MDC 6

Conditions: *i*) Pd(PPh₃)₄, THF; *ii*) 1) *n*-BuLi, THF, 2) Me₃SnCl; *iii*) Pd₂dba₃, AsPh₃, THF; *iv*) NaH, THF; *v*) KOH, THF:MeOH (3:1).

Scheme 4: Synthesis of **MDC 5** and **MDC 6**.

Synthesis of **13**

A solution of **11** (11.1 mmol, 1.81 g), **12** (10.1 mmol, 3.74 g) and Pd(PPh₃)₄ (252 μmol, 291 mg) in dry THF (20 mL) was purged with argon and refluxed for 24 h. The solvent was removed under reduced pressure and the crude compound was further purified by column chromatography (silicagel, eluent: hexane). A white solid was isolated.

Yield: 1.85 g (63 %).

m.p.: 33.2-33.8 °C (determined by optical microscopy).

¹ H-NMR (CDCl ₃ ; 300 MHz)	δ(ppm)	#H(mp)	H _?
7,47	2H(d, J=8,7Hz)	H _b
	7,20	1H(d, J=4,9Hz)	H _e
	7,19	1H(d, J=3,8Hz)	H _c
	7,04	1H(dd, J=4,9Hz, J=3,8Hz)	H _d
	6,84	2H(d, J=8,7Hz)	H _a
	0,99	9H(s)	H _g
	0,21	6H(s)	H _f

¹³C-NMR (CDCl₃; 300 MHz): δ = 155.4, 144.5, 128.0, 127.2, 123.9, 122.2, 120.6, 25.8, 18.4, -4.3.

MS (EI): m/z = 290 (M⁺) (calc. 290.52).

Elemental analysis calcd (%) for C₁₆H₂₂OSSi: C 66.15, H 7.63, S 11.03; found: C 66.16, H 7.98, S 10.69.

Synthesis of 14

The procedure described for the preparation of **7** was followed, starting from a solution of **13** (3.76 mmol, 1.09 g) in dry THF (8 mL), *n*-BuLi (3.94 mmol, 1.58 mL, 2.5 M in hexane) and Me₃SnCl (4.13 mmol, 823 mg).

Yield: 1.53 g (90 %).

m.p.: 27.5-28.2 °C (determined by optical microscopy).

¹ H-NMR (CDCl ₃ ; 300 MHz)	δ(ppm)	#H(mp)	H ₂
7,51	2H(d, J=8,6Hz)	H _b
	7,33	1H(d, J=3,3Hz)	H _c
	7,16	1H(d, J=3,3Hz)	H _d
	6,87	2H(d, J=8,6Hz)	H _a
	1,03	9H(s)	H _g
	0,42	9H(s)	H _e
	0,25	6H(s)	H _f

¹³C-NMR (CDCl₃; 300 MHz): δ = 155.3, 150.3, 136.5, 136.3, 128.2, 127.3, 123.6, 120.5, 25.8, 18.4, -4.2, -8.1.

MS (EI): m/z = 453 (M⁺) (calc. 453.32).

Elemental analysis calcd (%) for C₁₉H₃₀OSSiSn: C 50.34, H 6.67, S 7.07; found: C 50.09, H 6.38 S 7.19.

Synthesis of 15

The procedure described for the preparation of **4** was followed, starting from a solution of **14** (3.39 mmol, 1.53 g), **2** (1.53 mmol, 604 mg), Pd₂dba₃ (76.9 μmol, 70.4 mg) and AsPh₃ (615 μmol, 189 mg) in THF (5 mL). The crude compound was purified by column chromatography (silicagel, eluent: hexane:ethylacetate (50:50 v/v)) and isolated as an orange solid.

Yield: 1.11 g (89 %).

No melting point detected by optical microscopy or DSC below 250 °C; only a T_g at 140.6 °C could be determined by DSC.

¹ H-NMR (CD ₂ Cl ₂ ; 400 MHz)	δ(ppm)	#H(mp)	H _?
$\text{---R} = \text{---Si}(\text{CH}_3)_m(\text{CH}_2)_n$ $\text{---R}' = \text{---Si}(\text{CH}_3)_{m'}(\text{CH}_2)_{n'}$	7,51	2H(d, J=8,6Hz)	H _{b/h}
	7,50	2H(d, J=8,6Hz)	H _{b/h}
	7,29	1H(d, J=3,8Hz)	H _{d/f}
	7,22	1H(s)	H _e
	7,21	1H(d, J=3,8Hz)	H _{c/g}
	7,14	2H(s)	H _{c,d/f,g}
	6,89	2H(d, J=8,6Hz)	H _{a/i}
	6,88	2H(d, J=8,6Hz)	H _{a/i}
	4,08	4H(qu)	H _k
	3,32	2H(d, J=21,1Hz)	H _j
	1,29	6H(t)	H _l
	1,02	18H(s)	H _{n,n'}
	0,24	12H(s)	H _{m,m'}

¹³C-NMR (CD₂Cl₂; 400 MHz): δ = 156.1, 156.0, 145.3, 143.9, 136.0, 135.3, 133.4, 132.2, 132.1, 128.8, 128.7, 128.3, 127.6, 127.5, 127.2, 127.1, 127.0, 125.1, 123.2, 120.9, 62.7, 27.9, 25.8, 18.5, 16.6, -4.4.

MS (ESI): m/z = 1644 (2M⁺ + Na), 811 (M⁺) (calc. 811.27).

401S01146 #24-30 RT: 0,59-0,74 AV: 7 NL: 8,61E5
T: + c ms [150,00-2000,00]

Elemental analysis calcd (%) for $C_{41}H_{55}O_5PS_3Si_2$: C 60.70, H 6.83, S 11.86; found: C 60.37, H 7.11, S 11.55.

Synthesis of **16**

A suspension of NaH (365 μ mol, 8.80 mg), **15** (365 μ mol, 297 mg) and (*S*)-**1** (174 μ mol, 54.0 mg) in dry THF (4 mL) was purged with argon and heated to reflux for 4 h. The reaction mixture was poured into a HCl solution (0,001 M) and the product was extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$ and the solvents were removed under reduced pressure. The crude compound was further purified by column chromatography (silicagel, eluent: hexane:ethylacetate (80:20 v/v)) and isolated as an orange solid.

Yield: 91.1 mg (54 %).

No melting point or glass transition detected by optical microscopy or DSC below 250 $^{\circ}C$.

¹ H-NMR (CD ₂ Cl ₂ ; 400 MHz)	δ(ppm)	#H(mp)	H _?
9,65	1H(s)	CHO
	8,19	1H(d, J=8,6Hz)	H _a
	8,13	1H(d, J=8,6Hz)	H _b
	7,99-8,09	3H(m)	H _{c,g,h}
	7,95	1H(d, J=8,6Hz)	H _i
	7,62	1H(t, J=8,6Hz)	H _d
	7,53	2H(d, J=8,6Hz)	H _{n/t}
	7,38-7,50	4H(m)	H _{k,n/t,v}
	7,32-7,37	2H(m)	H _{f,e}
	7,26	1H(t, J=8,6Hz)	H _j
	7,20	1H(d, J=3,8Hz)	H _{p/r}
	7,06	1H(d, J=3,8Hz)	H _{p/r}
	7,05	1H(d, J=3,8Hz)	H _{o/s}
	7,00	1H(d, J=8,6Hz)	H _l
	6,97	1H(d, J=3,8Hz)	H _{o/s}
	6,91	2H(d, J=8,6Hz)	H _{m/u}
	6,87	2H(d, J=8,6Hz)	H _{m/u}
	6,69	1H(s)	H _q
	6,58	1H(d, J=15,8Hz)	H _w
	1,02	9H(s)	H _{y/y'}
	1,01	9H(s)	H _{y/y'}
	0,26	6H(s)	H _{x/x'}
	0,24	6H(s)	H _{x/x'}

¹³C-NMR (CD₂Cl₂; 400 MHz): δ = 192.3, 156.2, 156.1, 145.7, 144.1, 143.4, 136.7, 136.4, 135.9, 135.6, 134.9, 134.4, 133.6, 133.2, 133.1, 133.0, 132.6, 131.2, 129.5, 129.4, 129.3, 128.8, 128.5, 128.4, 128.3, 127.7, 127.5, 127.4, 127.3, 127.1, 126.8, 126.5, 125.4, 124.6, 123.2, 123.1, 122.5, 122.1, 121.0, 120.9, 25.8, 18.4, -4.4.

MS (ESI): m/z = 1957 (2M⁺ + Na), 967 (M⁺) (calc. 967.51).

401S01145 #36-43 RT: 0,90-1,07 AV: 8 NL: 2,08E4
T: + c ms [150,00-2000,00]

Elemental analysis calcd (%) for C₅₉H₅₈O₃S₃Si₂: C 73.25, H 6.04, S 9.94; found: C 73.20, H 6.40, S 9.65.

Synthesis of MDC 5

A solution of **16** (60.5 μmol, 58.5 mg) in THF:MeOH (3:1) (5 mL) was purged with argon and a solution of KOH (363 mol, 20.3 mg) in THF:MeOH (3:1) (2 mL) was added. The reaction mixture was stirred for 30 min at room temperature. A HCl solution (5 mL, 3 M) was added and the product was extracted with diethylether. The combined organic layers were dried over MgSO₄ and the solvents were removed under reduced pressure. The crude compound was further purified by trituration in pentane.

Yield: 42.5 mg (95 %).

No melting point or glass transition detected by optical microscopy or DSC below 250 °C.

¹ H-NMR (Aceton-d ₆ ; 400 MHz)	δ(ppm)	#H(mp)	H _?
<p>—R = —CHO</p> <p>—R' = </p>	9,66	1H(s)	CHO
	8,24	1H(d, J=8,6Hz)	H _a
	8,11-8,21	4H(m)	H _{b,c,g,h}
	8,05	1H(d, J=8,6Hz)	H _i
	7,68	1H(t, J=8,6Hz)	H _d
	7,58	2H(d, J=8,6Hz)	H _{n/t}
	7,52	1H(t, J=8,6Hz)	H _k
	7,48	2H(d, J=8,6Hz)	H _{n/t}
	7,44	1H(t, J=8,6Hz)	H _e
	7,44	1H(d, J=16,1Hz)	H _v
	7,34	1H(t, J=8,6Hz)	H _j
	7,33	1H(d, J=8,6Hz)	H _f
	7,31	1H(d, J=3,8Hz)	H _{p/r}
	7,17	1H(d, J=3,8Hz)	H _{p/r}
	7,09	1H(d, J=3,8Hz)	H _{o/s}
	7,05	1H(d, J=3,8Hz)	H _{o/s}
	7,00	1H(d, J=8,6Hz)	H _l
	6,94	2H(d, J=8,6Hz)	H _{m/u}
	6,91	2H(d, J=8,6Hz)	H _{m/u}
	6,86	1H(s)	H _q
	6,77	1H(d, J=16,1Hz)	H _w

¹³C-NMR (Aceton-d₆; 400 MHz): δ = 192.0, 146.6, 145.0, 143.7, 137.3, 136.9, 136.4, 136.1, 134.9, 134.6, 133.8, 133.7, 133.5, 133.2, 132.8, 131.6, 130.3, 130.1, 130.0, 129.6, 129.4, 129.2, 129.0, 128.5, 128.1, 128.0, 127.8, 127.2, 127.0, 126.3, 126.2, 126.1, 125.2, 124.2, 123.6, 123.4, 122.9, 122.6, 116.8, 116.7.

MS (APCI): m/z = 739 (M⁺) (calc. 738.95).

401A01149 #26-28 RT: 0,65-0,70 AV: 3 NL: 9,42E4
T: + c ms [150,00-2000,00]

Elemental analysis calcd (%) for $C_{47}H_{30}O_3S_3$: C 76.39, H 4.09, S 13.02; found: C 76.07, H 3.78, S 12.78.

Synthesis of **17**

The procedure described for the preparation of **16** was followed, starting from a suspension of NaH (384 μ mol, 9.20 mg), **15** (384 μ mol, 312 mg) and (*S*)-**1** (175 μ mol, 54.2 mg) in THF (4 mL). The crude compound was purified by column chromatography (silicagel, eluent: hexane:ethylacetate (80:20 v/v)) and isolated as an orange solid.

Yield: 42.3 mg (15 %).

No melting point detected by optical microscopy or DSC below 250 °C; only a T_g at 112.2 °C could be determined by DSC.

¹ H-NMR (CD ₂ Cl ₂ ; 400 MHz)	δ(ppm)	#H(mp)	H _?
	8,04	2H(d, J= 8,6Hz)	H _b
	8,02	2H(d, J=8,6Hz)	H _a
	7,96	2H(d, J=8,6Hz)	H _c
	7,45	2H(t, J=8,6Hz)	H _e
	7,43	4H(d, J=8,6Hz)	H _{h/n}
	7,42	4H(d, J=8,6Hz)	H _{h/n}
	7,37	2H(d, J=16,1Hz)	H _p
	7,25	2H(t, J=8,6Hz)	H _d
	7,11	2H(d, J=8,6Hz)	H _f
	7,05	2H(d, J=3,8Hz)	H _{j/l}
	7,04	2H(d, J=3,8Hz)	H _{j/l}
	6,97	2H(d, J=3,8Hz)	H _{i/m}
	6,95	2H(d, J=3,8Hz)	H _{i/m}
	6,84	4H(d, J=8,6Hz)	H _{g/o}
	6,82	4H(d, J=8,6Hz)	H _{g/o}
	6,80	2H(s)	H _k
	6,68	2H(d, J=16,1Hz)	H _q
	0,99	18H(s)	H _{s/s'}
	0,98	18H(s)	H _{s/s'}
	0,22	12H(s)	H _{r/r'}
	0,21	12H(s)	H _{r/r'}

¹³C-NMR (CD₂Cl₂; 400 MHz): δ = 156.1, 156.0, 145.4, 144.0, 136.9, 135.8, 135.0, 134.5, 133.8, 133.7, 133.5, 132.2, 129.5, 128.9, 128.4, 128.3, 127.5, 127.2, 127.1, 126.9, 126.3, 125.3, 123.9, 123.6, 123.3, 123.1, 122.3, 120.9, 25.7, 18.4, -4.4.

MS (ESI): m/z = 1624 (M⁺) (calc. 1624.66).

401S01144 #56-59 RT: 1,39-1,47 AV: 4 NL: 8,90E4
T: + c ms [150,00-2000,00]

Elemental analysis calcd (%) for C₉₆H₁₀₂O₄S₆Si₄: C 70.97, H 6.33, S 11.84; found: C 70.80 , H 6.01, S 11.60.

Synthesis of MDC 6

The procedure described for the preparation of **MDC 5** was followed, starting from a solution of **17** (11.1 µmol, 18.1 mg) and KOH (13.3 mol, 7.50 mg) in THF:MeOH (3:1) (5 mL).

Yield: 12.8 mg (98 %).

No melting point detected by optical microscopy or DSC below 250 °C; only a T_g at 149.3 °C could be determined by DSC.

¹ H-NMR (Aceton- <i>d</i> ₆ ; 400 MHz)	δ(ppm)	#H(mp)	H _?
8,10	4H(s)	H _{a,b}
	8,01	2H(d, J=8,6Hz)	H _c
	7,46	2H(t, J=8,6Hz)	H _e
	7,44	4H(d, J=8,6Hz)	H _{h/n}
	7,40	4H(d, J=8,6Hz)	H _{h/n}
	7,39	2H(d, J=16,1Hz)	H _p
	7,28	2H(t, J=8,6Hz)	H _d
	7,10	2H(d, J=3,8Hz)	H _{j/l}
	7,08	2H(d, J=8,6Hz)	H _f
	7,07	2H(d, J=3,8Hz)	H _{j/l}
	6,94	2H(d, J=3,8Hz)	H _{i/m}
	6,92	2H(d, J=3,8Hz)	H _{i/m}
	6,87	8H(d, J=8,6Hz)	H _{g,o}
	6,82	2H(s)	H _k
	6,81	2H(d, J=16,1Hz)	H _q

¹³C-NMR (Aceton-*d*₆; 400 MHz): δ = 158.5, 158.4, 146.3, 144.9, 137.2, 136.4, 135.5, 135.0, 134.7, 134.4, 134.2, 133.4, 132.5, 130.2, 129.7, 129.2, 129.0, 127.9, 127.8, 127.7, 127.4, 127.0, 126.3, 126.1, 124.5, 124.4, 123.6, 123.5, 122.6, 116.8, 116.7.

MS (APCI): m/z = 1168 (M⁺) (calc. 1167.53).

401A01150 #102-113 RT: 2,52-2,79 AV: 12 NL: 3,41E3
T: + c Full ms [200,00-2000,00]

Elemental analysis calcd (%) for $C_{72}H_{46}O_4S_6$: C 74.07, H 3.97, S 16.48; found: C 74.27, H 4.11, S 16.32.

Synthesis of 20

Conditions: *i*) Pd₂dba₃, AsPh₃, THF; *ii*) KOH, THF:MeOH (3:1).

Scheme 5: Synthesis of **20**.

Synthesis of 19

The procedure described for the preparation of **4** was followed, starting from a solution of **14** (1.36 mmol, 617 mg), **18** (544 μmol, 193 mg), Pd₂dba₃ (27.2 μmol, 24.9 mg) and AsPh₃ (218 μmol, 66.6 mg) in THF (5 mL). The crude compound was purified by column chromatography (silicagel, eluent: hexane:dichloromethane (50:50 v/v)) and isolated as an orange solid.

Yield: 273 mg (65 %).

m.p.: 108.4 °C (determined by DSC).

¹ H-NMR (CDCl ₃ ; 400 MHz)	δ(ppm)	#H(mp)	H ₂
<p style="text-align: center;"> $\text{—R—} = \text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—}$ </p>	7,49	2H(d, J=8,6Hz)	H _{b/h}
	7,47	2H(d, J=8,6Hz)	H _{b/h}
	7,15	1H(d, J=3,8Hz)	H _{d/f}
	7,10	1H(d, J=3,8Hz)	H _{d/f}
	7,09	1H(d, J=3,8Hz)	H _{c/g}
	7,07	1H(d, J=3,8Hz)	H _{c/g}
	7,02	1H(s)	H _e
	6,86	2H(d, J=8,6Hz)	H _{a/i}
	6,85	2H(d, J=8,6Hz)	H _{a/i}
	2,78	2H(t)	H _j
	1,69	2H(qu)	H _k
	1,2-1,5	10H(m)	H _{l-p}
	1,01	18H(s)	H _{s,s'}
	0,89	3H(t)	H _q
	0,23	12H(s)	H _{r,r'}

¹³C-NMR (CDCl₃; 400 MHz): δ = 155.7, 144.2, 143.3, 140.3, 135.7, 135.2, 134.6, 129.8, 127.7, 127.6, 127.0, 126.9, 126.7, 126.4, 124.5, 122.9, 122.6, 120.7, 32.1, 30.7, 29.7, 29.6, 29.5, 29.4, 25.8, 22.8, 18.4, 14.3, -4.2.

MS (ESI): m/z = 773 (M⁺) (calc. 773.38).

401A01153 #19-22 RT: 0,46-0,54 AV: 4 NL: 7,57E5
T: + c Full ms [200,00-2000,00]

Elemental analysis calcd (%) for $C_{44}H_{60}O_2S_3Si_2$: C 68.34, H 7.82, S 12.44; found: C 68.11, H 7.76, S 12.33.

Synthesis of 20

The procedure described for the preparation of **MDC 5** was followed, starting from a solution of **19** (202 μ mol, 157 mg) and KOH (2.32 mmol, 131 mg) in a mixture of THF:MeOH (3:1) (5 mL).

Yield: 108 mg (98 %).

m.p.: 168.7 °C (determined by DSC).

¹ H-NMR (THF- <i>d</i> ₈ ; 400 MHz)	δ(ppm)	#H(mp)	H _?
8,40	2H(s)	OH
	7,41	2H(d, J=8,6Hz)	H _{b/h}
	7,40	2H(d, J=8,6Hz)	H _{b/h}
	7,12	1H(d, J=3,8Hz)	H _{d/f}
	7,08	2H(s)	H _{c,d/f,g}
	7,03	1H(s)	H _e
	7,02	1H(d, J=3,8Hz)	H _{c/g}
	6,72	4H(d, J=8,6Hz)	H _{a,i}
	2,75	2H(t)	H _j
	1,66	2H(qu)	H _k
	1,2-1,5	10H(m)	H _{l-p}
	0,83	3H(t)	H _q

¹³C-NMR (THF-*d*₈; 400 MHz): δ = 158.5, 145.4, 144.4, 140.6, 135.8, 135.5, 134.3, 130.2, 127.4, 127.3, 127.2, 126.7, 126.2, 125.0, 122.9, 122.5, 116.4, 32.7, 31.2, 30.3, 30.2, 30.0, 23.4, 14.3.

MS (APCI): m/z = 545 (M⁺) (calc. 544.82).

Elemental analysis calcd (%) for C₃₂H₃₂O₂S₃: C 70.55, H 5.92, S 17.65; found: C 70.63, H 6.11, S 17.59.

UV-vis and CD spectra

Comparison UV-vis and CD spectra of MDC 1, MDC 2 and 10

Figure S1. UV-vis and CD spectra of **MDC 1** ($c = 2.86 \cdot 10^{-5}$ M) (a), **MDC 2** ($c = 1.47 \cdot 10^{-5}$ M) (b) and **10** ($c = 2.96 \cdot 10^{-5}$ M) (c) in dichloromethane.

A comparison of the UV-vis spectra of **MDC 1** (Figure S1a) and **10** (Figure S1c), the model compounds for respectively the extended binaphthalene and the oligothiophene transitions, reveals that absorption at $\lambda > 380$ nm is solely due to the oligothiophene. Below 380 nm overlapping of both transitions occurs, but at $280 \text{ nm} < \lambda < 320 \text{ nm}$, the UV-vis spectra are almost solely due to the binaphthalene transition. The UV-vis spectrum of **MDC 2** (Figure S1b) is therefore a superposition of the spectra of **MDC 1** and **10** of doubled intensity (two oligothiophenes are present) without exciton coupling between the two oligothiophenes.

The CD spectrum of **MDC 1** shows a strong bisignate Cotton effect corresponding to the binaphthalene absorption near 340 nm. Consequently, the CD spectrum of **MDC 2** is a superposition of a bisignate Cotton effect arising from the oligothiophene around 400 nm and a bisignate Cotton effect originating from the binaphthalene transition. Overlapping occurs, but $\lambda > 380$ nm, a region where the binaphthalene transition is CD silent, the CD spectrum is solely governed by the oligothiophene and $280 \text{ nm} < \lambda < 320 \text{ nm}$, which is far from the $\pi\text{-}\pi^*$ transition of the chromophore, the CD spectrum solely originates from the binaphthalene transition. The latter conclusion is further supported by the fact that oxidation of **MDC 3** (Figure S3), which alters the nature of the oligothiophene transition, leaves the CD spectra unchanged.

UV/vis- and CD-spectrum of MDC 2

Figure S2. UV-vis (a) and CD (b) spectra of **MDC 2** (concentration = $1,98 \cdot 10^{-5} \text{ M}$) in dichloromethane from 180-600 nm.

Below 225 nm, the solvent strongly absorbs, which prevents recording the spectra starting from wavelengths < 225 nm.

UV-vis and CD spectra during oxidation

Figure S3. UV-vis (a) and CD (b) spectra of a mixture of **(S)-1** + **10** in dichloromethane (concentration = $1.48 \cdot 10^{-5}$ M, respectively $2.96 \cdot 10^{-5}$ M) during gradual oxidation with $\text{Et}_3\text{OSbCl}_6$. Mind that ϵ and $\Delta\epsilon$ are concentration dependent and that they are calculated relative to the concentration of **(S)-1**.

During oxidation with $\text{Et}_3\text{OSbCl}_6$, by-products (SbCl_3 , diethylether and ethyl chloride) are introduced in the solution, which can affect the dielectric constant of the solution and, in turn, ϵ and $\Delta\epsilon$. However, the CD spectra clearly reveal that the Cotton effect of the binaphthalene hinge is not affected by gradual oxidation of the oligothiophene (which is confirmed by the appearance of low energetic oxidation bands in the corresponding UV-vis spectra). This experiment safely excludes any possible change in $\Delta\epsilon_{\text{BN}}$ originating from the introduction of by-products from oxidation.

Figure S4. UV-vis (a) and CD (b) spectra of **MDC 3** in dichloromethane (concentration = $3.94 \cdot 10^{-5} \text{ M}$) during gradual oxidation with $\text{Et}_3\text{OSbCl}_6$.

During oxidation, the electronic transitions of the oligothiophene drastically change as visualized in the appearance of low energetic oxidation bands in the UV-vis spectra. However, these changes do not influence the Cotton effect of the binaphthalene hinge ($\Delta\epsilon_{\text{BN}}$) near 320 nm. This experiment rules out that changes in $\Delta\epsilon_{\text{BN}}$ are due to changes of the electronic properties of the attached oligothiophene from oxidation.

Figure S5. UV-vis (a) and CD (b) spectra of **MDC 2** in dichloromethane (concentration = $1.47 \cdot 10^{-5} \text{ M}$) during gradual oxidation with $\text{Et}_3\text{OSbCl}_6$.

During gradual oxidation with $\text{Et}_3\text{OSbCl}_6$, the appearance of low energetic oxidation bands from the oxidized oligothiophene can be observed in the UV-vis spectra. The corresponding CD spectra show no clear isosbestic point, which is in agreement with two subsequent one-electron oxidations; the latter being accompanied by the formation of π -dimers. This π -dimerisation is reflected in the UV-vis spectra by the additional, blue-shifted peaks (near 650 and 950 nm) of the oxidation bands at higher degrees of oxidation.

Figure S6. UV-vis (a) and CD (b) spectra of **MDC 4** in dichloromethane (concentration = $3.13 \cdot 10^{-5} \text{ M}$) during gradual oxidation with $\text{Et}_3\text{OSbCl}_6$.

Unlike the previous experiment with **MDC 2**, **MDC 4** shows no additional blue-shifts of the oxidation bands in the UV-vis spectra at higher degrees of oxidation. Also in contrast with **MDC 2**, the corresponding CD spectra now reveal a clear isosbestic point. Both facts support a one-electron oxidation of the neutral oligothiophene, while the oligothiazole remains unaffected by oxidation, and the absence of π -dimerization.

UV-vis and CD spectra during deprotonation

Figure S7. UV-vis spectra of **20** in THF:*t*BuOH (50:50) (concentration = $2.50 \cdot 10^{-5}$ M) during gradual deprotonation with KO*t*Bu.

During gradual deprotonation of **20**, the π - π^* transition of the oligomer undergoes a distinct bathochromic shift, accompanied with a clear isosbestic point as evidenced by the UV-vis spectra. This experiment is in agreement with a single deprotonation step of the oligomer, even at large excess of KO*t*Bu, indicating that the mono-anion significantly decreases the acidity of the second phenolic proton.

Figure S8. UV/vis (a) and CD (b) spectra of **MDC 5** in THF:tBuOH (50:50) (concentration = $2.41 \cdot 10^{-5}$ M) during gradual deprotonation with KOtBu.

During deprotonation, again a clear red-shift of the $\pi-\pi^*$ transition is visualized by the UV-vis spectra. However, the corresponding CD spectra safely rule out any influence of the deprotonated oligothiophene on the Cotton effect of the binaphthalene hinge ($\Delta\epsilon_{\text{BN}}$) near 320 nm.

Figure S9. UV-vis (a) and CD (b) spectra of **MDC 6** in THF:tBuOH (50:50) (concentration = $2.41 \cdot 10^{-5}$ M) during gradual deprotonation with KOtBu.

During gradual deprotonation with KOtBu, again a clear red shift of the $\pi-\pi^*$ transition of the oligomer can be observed in the UV-vis spectra. The corresponding CD spectra in turn reveal an isosbestic point at small quantities of KOtBu, corresponding to a single deprotonation step. However, at large quantities (i.e. the last three spectra) a significant deviation from the isosbestic point is observed, indicating a subsequent second deprotonation of the second oligomer.

Figure S10. UV-vis (a) and CD (b) spectra of **MDC 6** in THF:MeOH (80:20) (concentration = $2.41 \cdot 10^{-5}$ M) during gradual deprotonation with KOH.

Unlike the previous experiment with KO^tBu, a clear isosbestic point is now observed in the CD spectra during deprotonation with the less basic KOH, even at large excess. This is in agreement with a single deprotonation process. The second deprotonation on the second oligomer does not occur, which suggests that the deprotonation of the first oligomer significantly decreases the acidity of the second one; the latter deprotonation only occurring with the more basic KO^tBu.

Solvent-independent (chiroptical) properties of MDC 6

Figure S11. UV-vis and CD spectra of **MDC 6** (concentration = $2.50 \cdot 10^{-5}$ M) in (a) *t*-BuOH/THF (50/50), (b) MeOH/THF (20/80) and (c) H₂O/THF (50/50).

In order to exclude the possibility that the CD effects are affected by aggregation, the UV-vis and CD spectra were recorded in different solvent mixtures. Exactly the same spectra were obtained in all cases. Moreover, it should be mentioned that **MDC 6** is soluble in both THF, methanol and *t*-butanol. Aggregation in the conditions employed can therefore be ruled out.

Reversible deprotonation/protonation experiment

Figure S12. UV-vis (a) and CD (b) spectra of **MDC 6** in THF:tBuOH (50:50) (concentration = $2.50 \cdot 10^{-5}$ M) before deprotonation, after deprotonation with KOtBu and subsequent protonation with HCl.

From the UV-vis and the CD spectra it can be concluded that after deprotonation, the original, neutral situation can be restored by the addition of HCl. The stronger absorption at $\lambda < 350$ nm can be attributed to KOtBu/HOtBu.

Hyperchem simulation of MDC 2

Figure S13. Hyperchem simulation of **MDC 2**. The hexyl groups were omitted to facilitate the modelling. The optimization was done by molecular mechanics.

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