Synthesis of semiconducting polymers for organic electronics

Bachelor thesis

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Jonathan Groß

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This bachelor thesis was carried out in the time period 23 May 2016 to 19 August 2016 in the group of Prof. Dr. Paul Blom in the Max Planck Institue for Polymer Research of Mainz.

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Jonathan Groß

Betreuerin: M. Sc. Ann-Kathrin Schönbein

Erstgutachter: Dr. Jasper Michels

Zweitgutachter: Prof. Dr. Rudolf Zentel

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1. Introduction

The electrical conductivity of polyacetylene was discovered by HEEGER, MACDIARMID and SHIRAKAWA in 1970 and rewarded with the Nobel prize in 2000.[1–3] This discovery of conducting polymers put oligomer and polymer organic semiconductors in the focus of research. The next "big" discovery was made from TANG and VANSLYKE, the first thin layer organic light emitting diode (OLED) based on tris(8-hydroxychinolin)-aluminium(III) (Alq_3) (**1**) was assembled.[4]

In year 1989 Friend *et al.* found electroluminescence in poly(*p*-phenylene vinylene) (PPV). To use this discovery, they synthesized first a solution-processable precursor polymer, which still had no conjugated backbone and showed therefore no electroluminescence. Subsequently, they deposited the precursor polymer in thin films on substrates via spin-coating. After thermal treatment, the conjugated polymer was obtained and with that the first polymer light emitting diode (PLED) was build. [5]

Another way how the conjugated polymer can be processed was found by HEEGER and BRAUN in 1991. They discovered 2-((2-ethylhexyl)oxy)-5-methoxy-PPV (MEH-PPV), a PPV with lateral side chains, which is soluble in the conjugated form. With that they simplified the fabrication by depositing the semiconducting polymer directly out of solution. Thereby, it is possible to apply the polymer to a large area.[6]

Since then, the PLEDs were tried to be improved in efficiency and lifetime of the used components. Especially, a great potential for flat-panel displays was seen, because PLEDs offer a low-cost approach with reduced complexity in the manufacturing process.[7]

Different products are already commercially available, which use OLEDs in their displays, for example flat screen televisions, cameras, smartphones or tablets. Furthermore, they can be used in (large-area) light sources[8], organic field effect transistors (OFETs)[9], organic photovoltaic devices (OPVs)[10] or in biosensors.[11,12]

2. Theory

2.1. Organic semiconductors

Organic semiconductors can be subdivided into two general groups, small molecules (SM) and polymers, both consist of organic solids. Usually, small molecules are deposited by vacuum sublimation[4], whereas polymers are processed out of solution[6], using methods like spin-coating, dip-coating or printing. Using this, large areas can be coated with high quality films and less costs than by vacuum deposition.[13] By sublimation the small molecule based materials can be purified easily, which is one requirement for efficient and long living OLEDs.[13]

Both groups, SMs and polymers, possess a conjugated π electrons system, on which the ability to transport charges is based. With an increasing conjugated system the number of π and π* orbitals is increasing. This leads to an increased energy level of the highest occupied molecular orbital (HOMO) and a decreased energy level of the lowest unoccupied molecular orbital (LUMO), therefore the gap becomes smaller. The band gap determines the wavelength and therefore the colour of the emitted light (see Figure 1).[13]

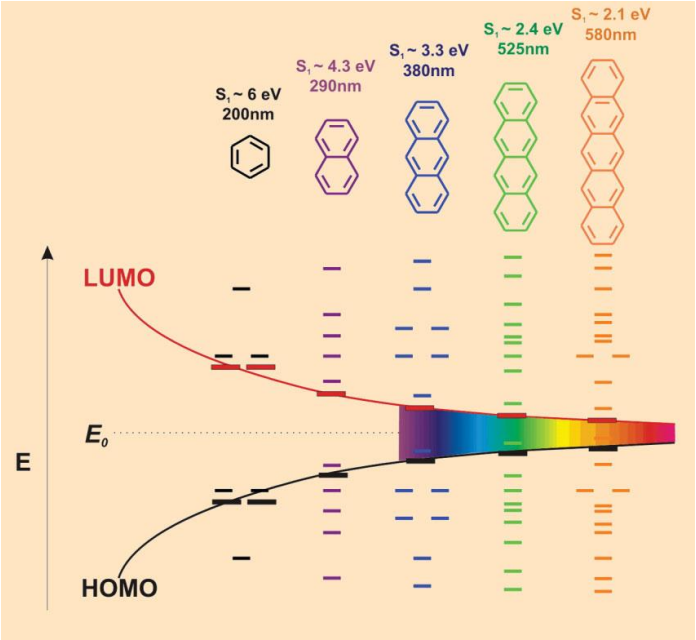


Figure 1: The gap between HOMO and LUMO becomes smaller with an increasing conjugated system. The length of the conjugated π-system and therefore the band gap determines the wavelength of the emitted light (taken from [13]).

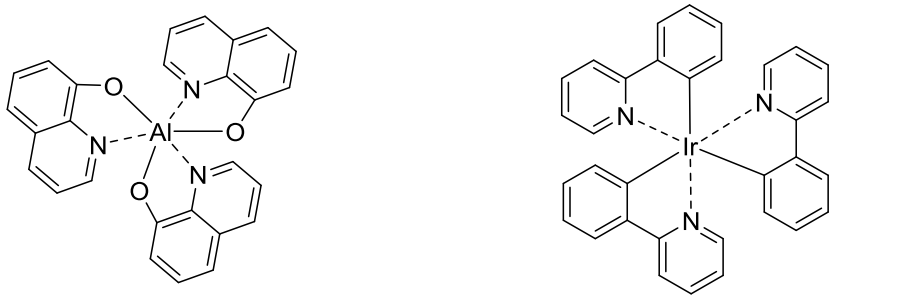
In a solid an infinite number of π and π* orbitals interact, the intermolecular interactions can be described by the band theory, with the valence and conduction band.[14] The size of the band gap is usually between 2,5—4 eV for organic semiconductors, is it bigger the organic molecule behaves like an isolator.[15]

Electron withdrawing or electron donating groups in organic molecules have an influence on the conjugated π-system and the energy levels and therefore on the size of the band gap.[15]

2.1.1. Small molecules

Most of the small molecules that are used in OLEDs are organic or metal containing materials.

The first technically installed emitter was tris(8-hydoxychinolin)-aluminium(III) (Alq_3) (**1**) (Figure 2). Another well-known emitter is tris[2-phenylpyridinato-C^2,*N*]iridium(III) ($Ir(ppy)_3$) (**2**)[16,17]. The emission of light takes place on the ligands.[16]



1

Tris(8-hydroxychinolin)-aluminium(III) (Alq_3)

2

Tris[2-phenylpyridinato-C^2,*N*]iridium(III) ($Ir(ppy)_3$)

Figure 2: Tris(8-hydroxychinolin)-aluminium(III) (Alq_3) (**1**) and tris[2-phenylpyidinato-C^2,*N*]iridium(III) ($Ir(ppy)_3$) **2** are the first examples of used small molecules in OLEDs.[16,17]

One advantages of small molecules is that they can be purified easily. On one hand, the evaporation deposition methods allow complicated device architectures with good performance.[18–20] Because of this benefits SM based devices are already used in commercial products like OPVs, or displays.[21]

On the other hand, caused by vapor deposition and purification by sublimation only a small amount (≈ 20 %) of the organic material is utilized.[22]

2.1.2. Polymers

Polymers that are used for organic devices have a reduced complexity in the manufacturing process with a higher utilization of the organic material, because they can be easily processed out of solution.[5,7]

There are many different ways to process the polymer out of solution, for example spin-coating[5], where the polymer solution is applied, while the substrate is rotating, dip-coating[23], the substrate is just dipped in the polymer solution and inkjet printing[24], here the polymer is printed via droplets on a surface.

As mentioned before, the conjugated π-system determines the wavelength and therefore the colour of emitted light by the polymer. By modifying the conjugated π-system with introduced sidechains, the colour of the emitted light can be varied (Figure 3).[6] PLEDs based on non-substituted poly(*p*-phenylene vinylene) (PPV) emit yellow-green light, whereas MEH-PPV emits orange-red light.

Furthermore, the solubility is improved, because unsubstituted PPV is an insoluble solid.[14,25]

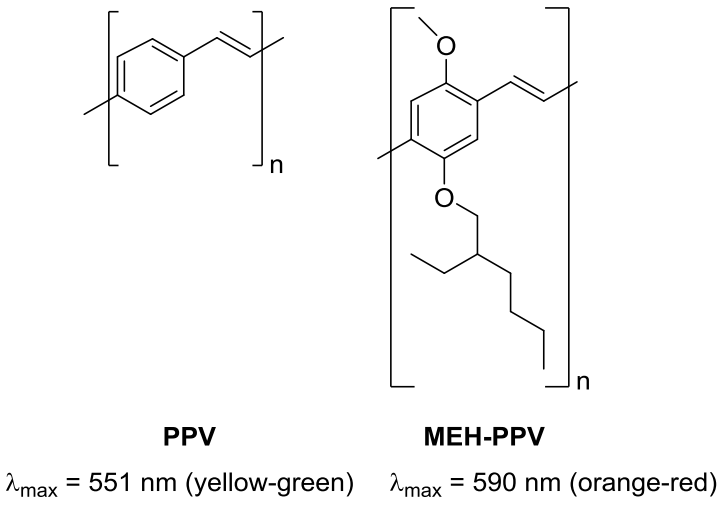
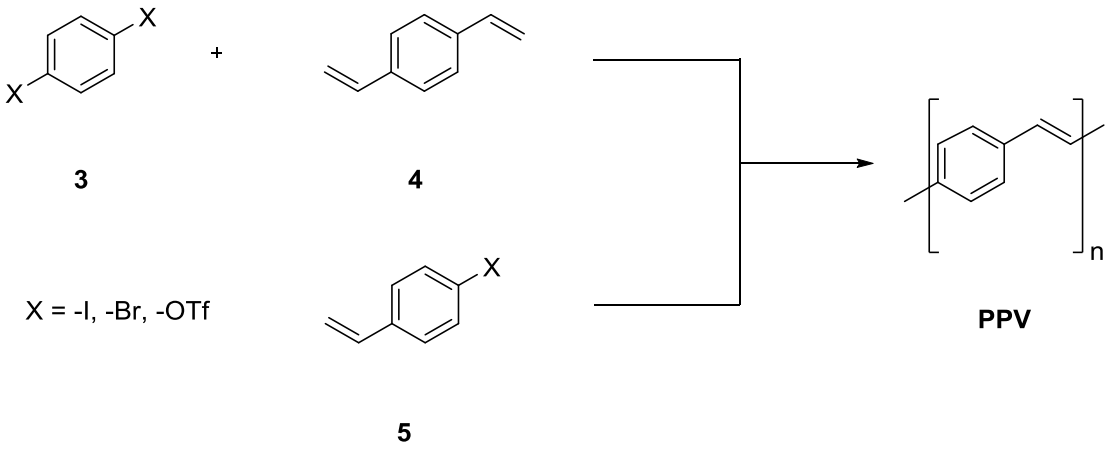


Figure 3: Depending on the sidechains attached to PPVs the emitted colour of the light in devices can be changed.

2.2. PPVs

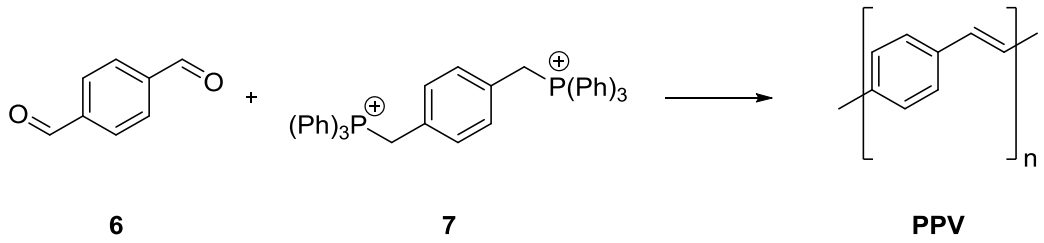
PPVs can be synthesized via different routes. One possible synthetic way are step-growth reactions, for example transition metal catalyzed polycondensations, like the HECK or SUZUKI reaction. One drawback of the reaction is that the catalyst has to be removed after the reaction, otherwise short circuits can occur, when voltage is applied to the device.[26] Furthermore, at lower conversion only di-, tri- and oligomers are formed. Only at high conversion high molecular weights are obtained.[27]

As an example the HECK reaction can either be performed with *p*-divinylbenzene (**3**) and *p*-di-halidebenzene (**4**), according to an AA-BB–polycondensation, or with the *p*-halidestyrene (**5**), according to an AB-polycondensation (Scheme 1).



Scheme 1: The HECK reaction to obtain PPV from different monomers. The top line shows the AA-BB-polycondensation and in the bottom route the AB-polycondensation.

Additional, an approach via WITTIG[28] or WITTIG-HORNER[29] reaction would be possible, where no catalyst is needed. Nevertheless, the problem with the low degree of polymerization is here still present. In the WITTIG reaction PPV is formed out of terephthalaldehyde (**6**) with triphenylphosphin oxide **7** (Scheme 2).[28] This reaction is *Z* selective for the formed double bond. This can be avoided by using WITTIG-HORNER, which gives the *E* product.

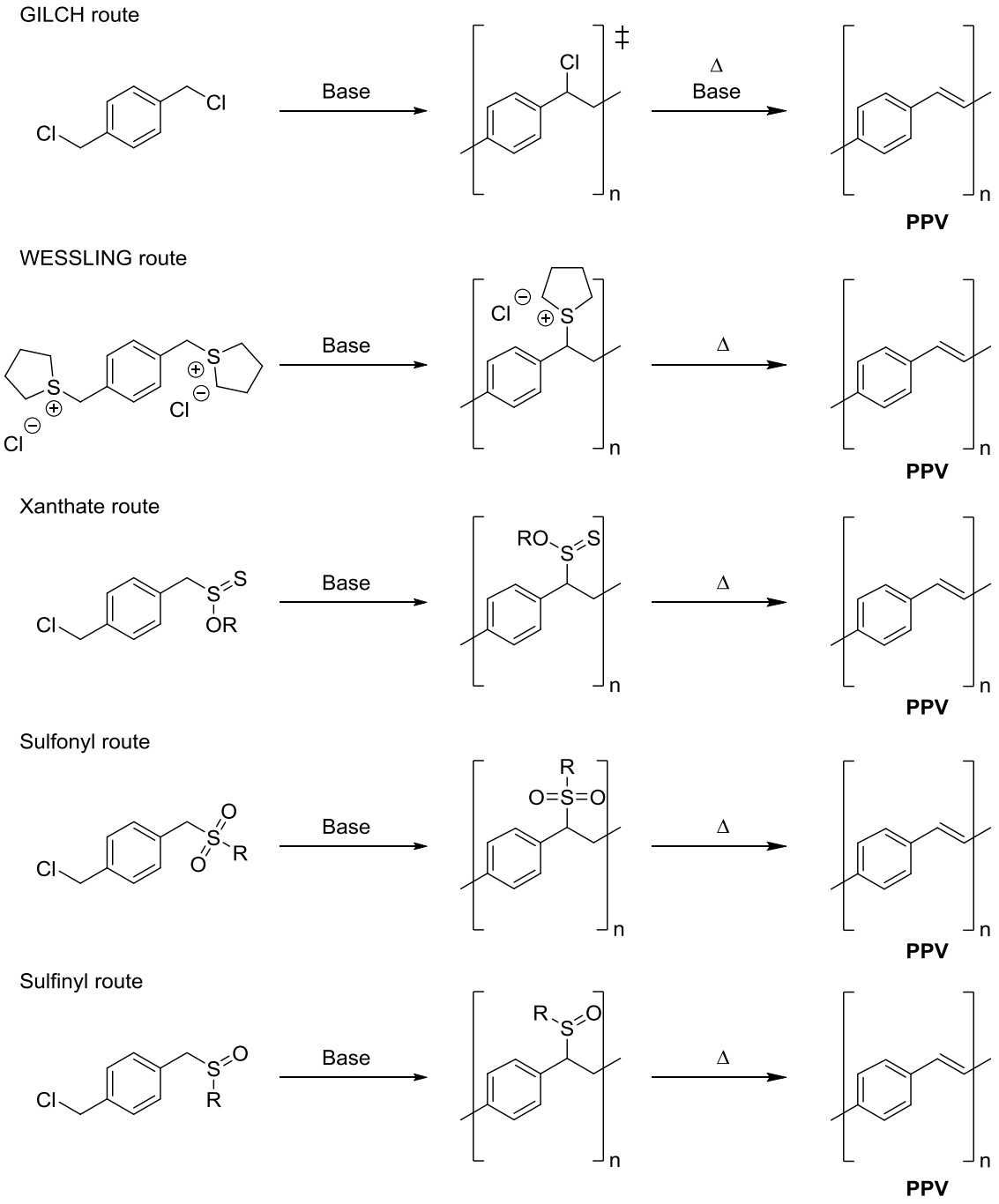


Scheme 2: The WITTIG-HORNER reaction of terephthalaldehyde **6** with triphenylphosphine **7** to PPV is shown.

Chain-growth reactions are also a possibility to obtain PPVs, following different precursor routes. FRIEND *et al.* used PPV as organic material for the first fabricated PLED. They synthesized a solution processable precursor polymer and deposited it via spin-coating as thin films on substrates. Afterwards, thermal treatment gave the conjugated polymer.[5]

This became the general synthetic approach in precursor routes, treating the monomers with base first, the leaving group is split off, giving the polymer that can be isolated and purified, since they are still soluble in common solvents, and therefore processable.[30] In the second step the polarizer groups are eliminated with base and/or thermal treatment, giving the conjugated PPVs. Examples for these precursor routes are the GILCH[25], WESSLING[31], xanthate[32], sulfonyl[33] or the sulfinyl route[30] (Scheme 3).

In general these routes differ in the polarizer, which remains in the polymer until it is eliminated in the second reaction step.



Scheme 3: Different precursor routes to obtain PPV via chain-growth reactions. In the first step the soluble polymer is formed, then the polarizer is eliminated in a second step, giving the conjugated polymer.

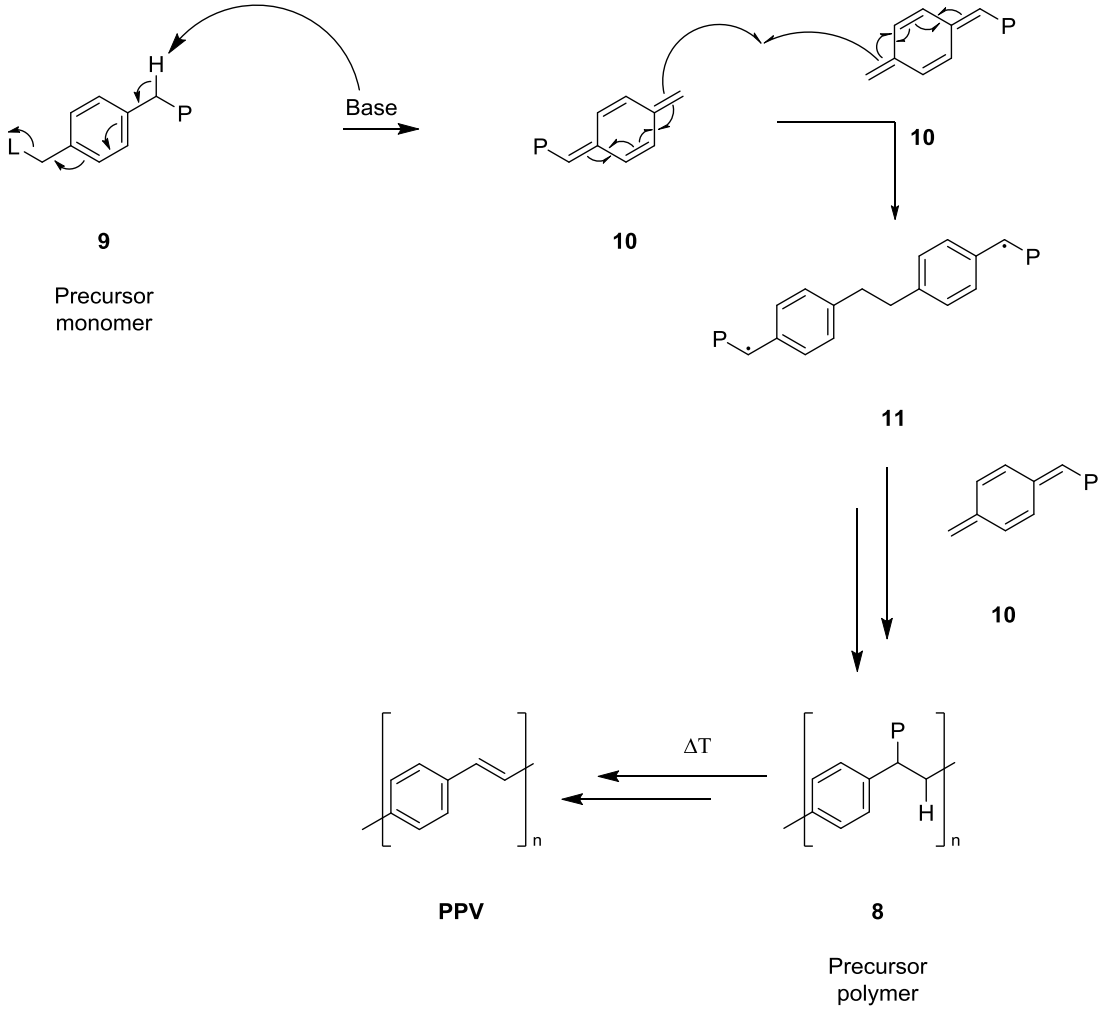
With each of these reactions it is possible to achieve a high molecular weight of the polymer.[27] In the GILCH route as well as in the WESSLING route symmetrical monomers are used, referring to the leaving group and the polarizer, in the other reactions they are different.

The GILCH route can be carried out in a one-pot reaction, because chloride is a good leaving group, leading to a fast reaction. Due to this, the precursor polymer is not accessible. With this precursor route gelation of the reaction mixture takes place very often. This leads to a non processable polymer.[34]

The other precursor routes make it possible to isolate the precursor polymer, but as the polarizer groups are relatively stable, they can remain in the polymer after the elimination step, giving a partially non-conjugated polymer.[34]

The polarizer has to be designed in a special way. On the one hand the bond has to be strong enough, that the precursor polymer can be isolated, on the other hand weak enough that it can be split off by thermal treatment.[35]

The general reaction mechanism is shown in Scheme 4, where P is the polarizer, L the leaving group, first the precursor polymer **8** and then PPV is formed.



Scheme 4: The radical polymerization of a precursor monomer **9** towards PPV, P is the polarizer and L the leaving group.

First a deprotonation in benzylic position of the monomer **9** takes place, inducing a 1,6-elimination and forming the *p*-quinodimethane **10**, which is the actual reactive monomer. Following, a free radical polymerization takes place, where the diradical **11** can react on both sides with an additional *p*-quinodimethane **10**, giving the precursor polymer **8**. [30,35,36]

A benefit is that after each propagation step a diradical is present again, leading to a polymer with a high molecular weight. Therefore a classic termination of the chain is not possible, rather a still unknown termination takes place.

If the mechanism follows a radical polymerization, as it is shown in Scheme 4, or an anionic mechanism, depends on the used solvent.[30]

3. Task

PPVs can be used in organic light emitting diodes or photovoltaic devices. For this application the polymer has to fulfill certain requirements, such as processability from solution to produce homogenous films, which is highly dependent on the molecular weight and the solubility. Especially the so-called GILCH route often leads to non-processable polymers due to geled particles in the solution formed during the reaction.[37]

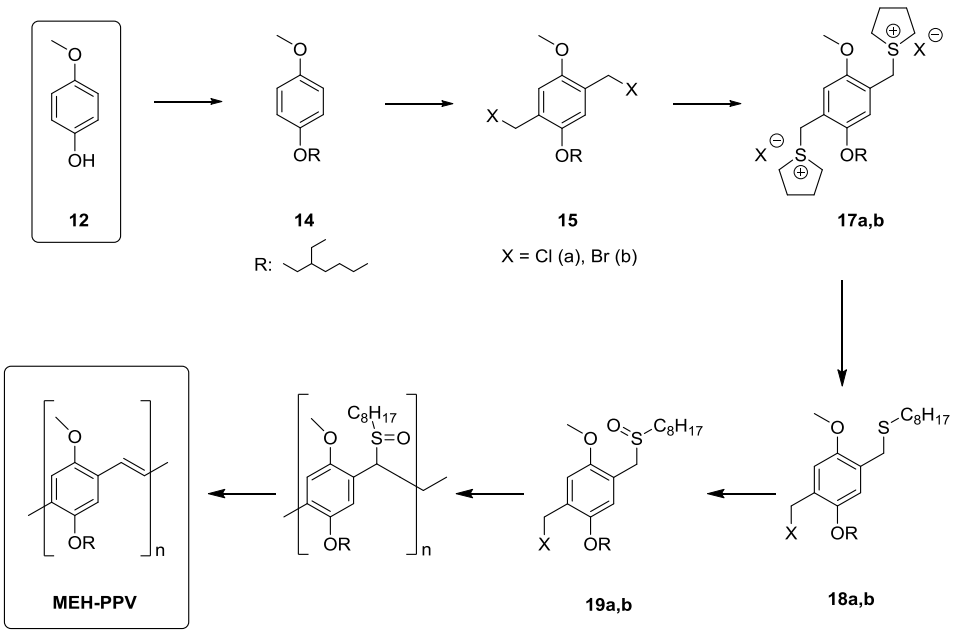
This problem does not occur when other precursor routes like the sulfinyl are followed, most likely because prepolymer formation and elimination are separated.

As the synthesis of MEH-PPV, a widely used and a well-known polymer, lacks reproducibility, the scope of this thesis is to transfer the synthetic procedure developed by LUTSEN *et al.*[38] for 2-methoxy-5-(3′,7′-dimethyloctyloxy)-PPV (MDMO-PPV) via the sulfinyl route to MEH-PPV. Furthermore, the influence of different halides (chloride and bromide) as leaving groups on the yield, purity and reproducibility of the obtained polymers are investigated. Eventually a conclusion whether the sulfinyl route is a useful way to obtain MEH-PPV is made.

4. Results and discussion

4.1. Synthesis plan

Scheme 5 shows the planned synthetic steps towards PPV via the sulfinyl route starting from 4-methoxyphenol (**12**).



Scheme 5: The planned route to synthesise MEH-PPV starting from 4-methoxyphenol (**12**). After five reaction steps the precursor monomer **19** is formed, which will then be polymerized and eliminated.

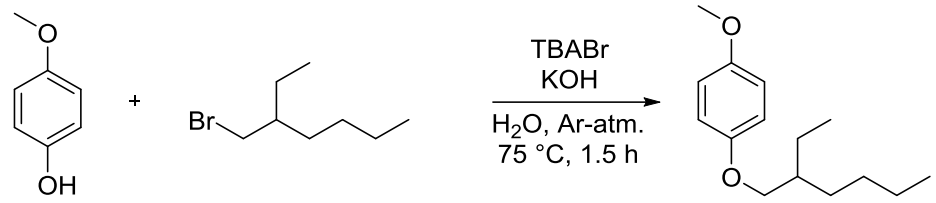
In the first step of the reaction pathway the second side chain should be introduced giving the ether **14**, followed by a halidemethylation leading to **15**. The halides are then exchanged against tetrahydrothiophene (**16**) giving the salts **17a** and **17b**, in order to facilitate the next reaction step. The following reaction should lead to the sulfanes **18a** and **18b**, by exchanging one tetrahydrothiophene group in **17a** and **b** is against a sulfane group and the other tetrahydrothiophene group by the halide. It is expected that two configurational isomers form, in the interest of clarity only one is shown here. The last step in the reaction cascade is the oxidation of the sulfur atom, resulting in the precursor monomers **19a** and **b**, which will then be polymerized, elimination of the polarizer gives the desired MEH-PPV.

In the following section the results of the precursor monomers **19a** and **b** syntheses are shown and discussed, starting with the influence of chloride and bromide as leaving group. Afterwards, the polymer synthesised via the GILCH route will be discussed. All shown reactions, if not stated differently, were carried out based on a procedure for MDMO-PPV, that is already known in literature.[38] Moreover, MEH-PPV should be synthesized via the GILCH route, to compare the resulting polymers.

4.2. Chloride as substituent during the precursor monomer synthesis

4.2.1. Synthesis of 1-((2-ethylhexyl)oxy)-4-methoxybenzene (14).

In reaction step of 1-((2-ethylhexyl)oxy)-4-methoxybenzene (**14**) (MEH-ether) is synthesized, starting from 4-methoxyphenol (**12**). With 3-(bromomethyl)heptane (**13**) and KOH the second aliphatic side chain is introduced, tetra-*n*-butylammonium bromide (TBABr) is used as phase transfer catalyst (Scheme 6).



12 **13** **14**

Scheme 6: Synthesis of 1-((2-ethylhexyl)oxy)-4-methoxybenzene (**14**) with 4-methoxyphenol (**12)**, 3-(bromomethyl)-heptane (**13**), KOH as base and tetra-*n*-butylammonium bromide (TBABr) as phase transfer catalyst.

According to a literature procedure from NEEF and FERRARIS[39] this synthesis was performed, however some synthetic conditions were changed. In the literature all components were mixed from the start and heated to 100 °C for 3 days. In this work 4-methoxyphenol (**12**) was first heated with base to ensure full deprotonation. Then 3-(bromomethyl)heptane (**13**) was added. Furthermore, **12** was used in an excess, instead of **13**, because 4-methoxyphenol (**12**) can be removed easily via aqueous (aq.) work-up. 3-(bromomethyl)heptane (**13**) as excess compound would require high-vacuum distillation after the work up to remove remaining **13**.

After extraction of the aqueous phase and removal of the solvent the pure product was obtained in 87.1 % yield (lit.[39]: 83 %).

In the ^{1}H-NMR spectrum in Figure 4 no characteristic signals of 3-(bromomethyl)heptane (**13**) (3.4 ppm (dd, Br-CH_2)) can be found.

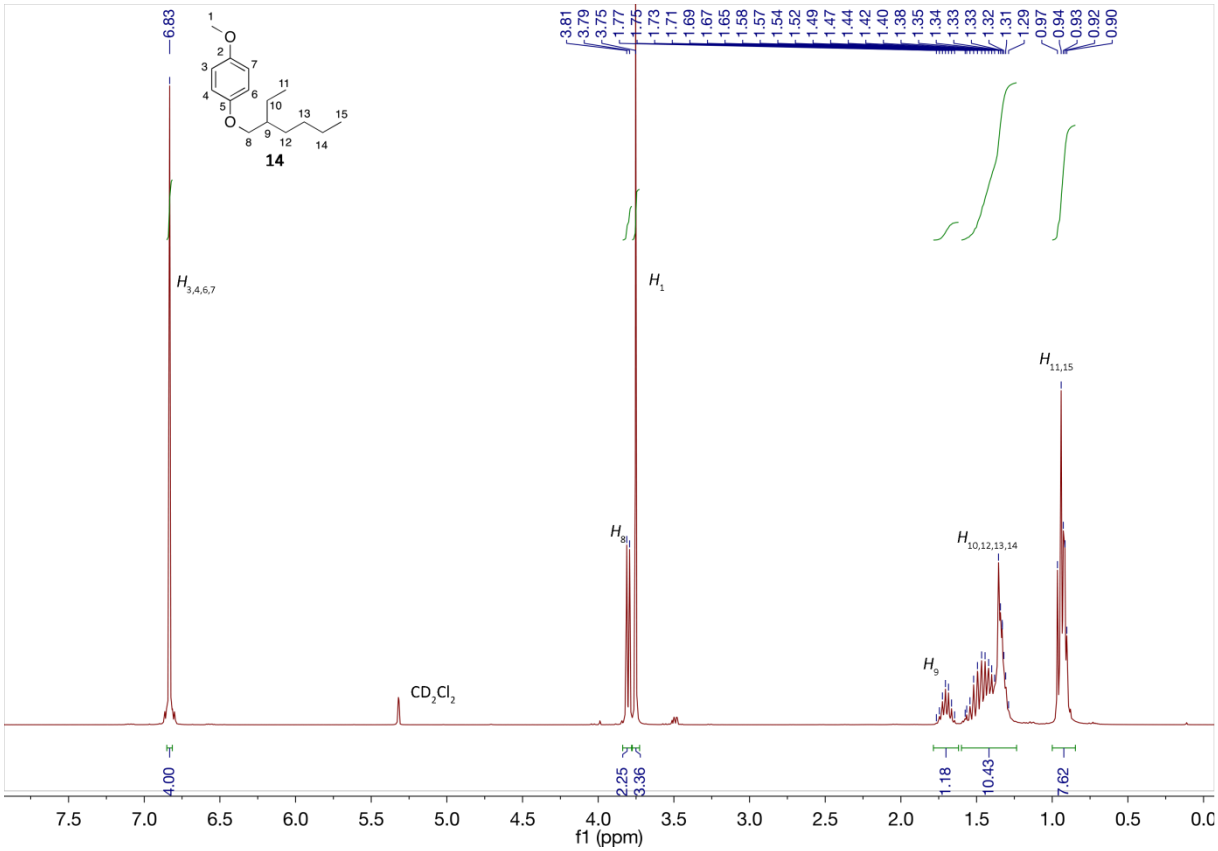


Figure 4: ^{1}H-NMR spectrum of the obtained pure MEH-ether **14** in CD_2Cl_2.

The signals are assigned to the structure with the subscript numbers, a detailed assignment is performed in the experimental part.

Furthermore, the successful linkage of alkyl to oxygen has been proved with 2D-NMR methods. Hetero nuclear multiple-bond correlations (HMBC) spectra are able to show long range correlation between ^{1}H- and ^{13}C-atoms. In this case a correlation between H_8 and C_5 can be seen, which confirms the success of the reaction (highlighted in Figure 5). For representation only these signals are assigned, while a detailed assignment of the signals is performed in the experimental part.

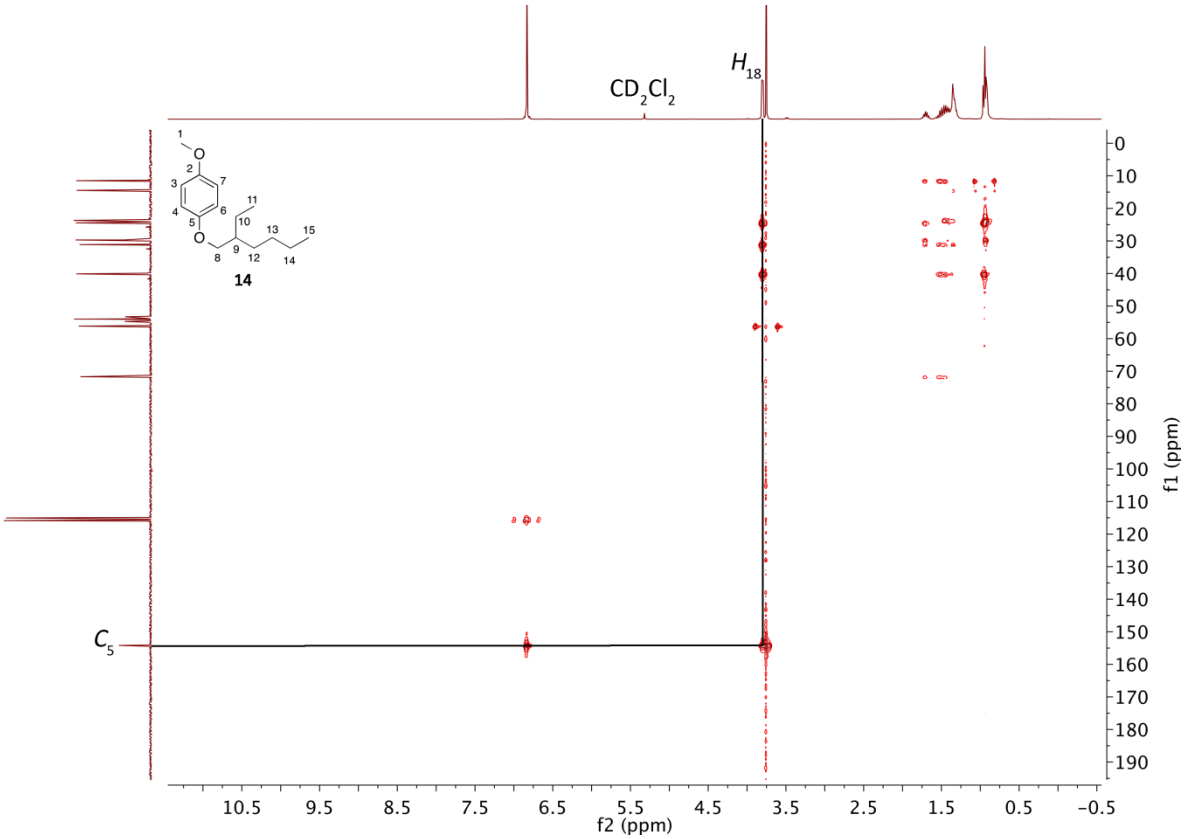
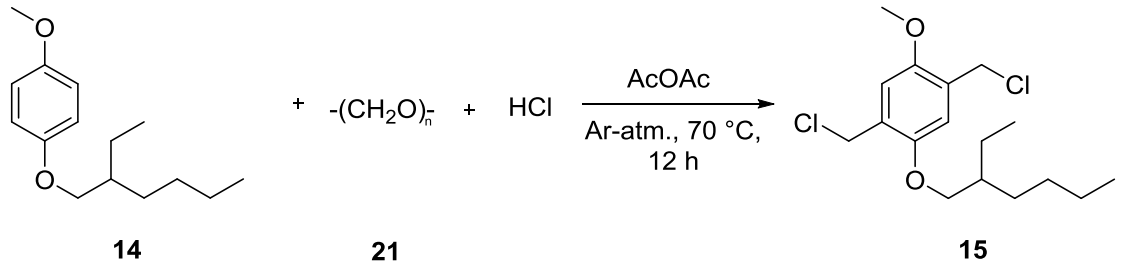


Figure 5: The HMBC-NMR correlation spectrum of MEH-ether **14** is displayed, the correlation between H_8 and C_5 is highlighted.

4.2.2. Synthesis of 1,4-bis(chloromethyl)-2-((2-ethylhexyl)oxy)-5-methoxybenzene (15).

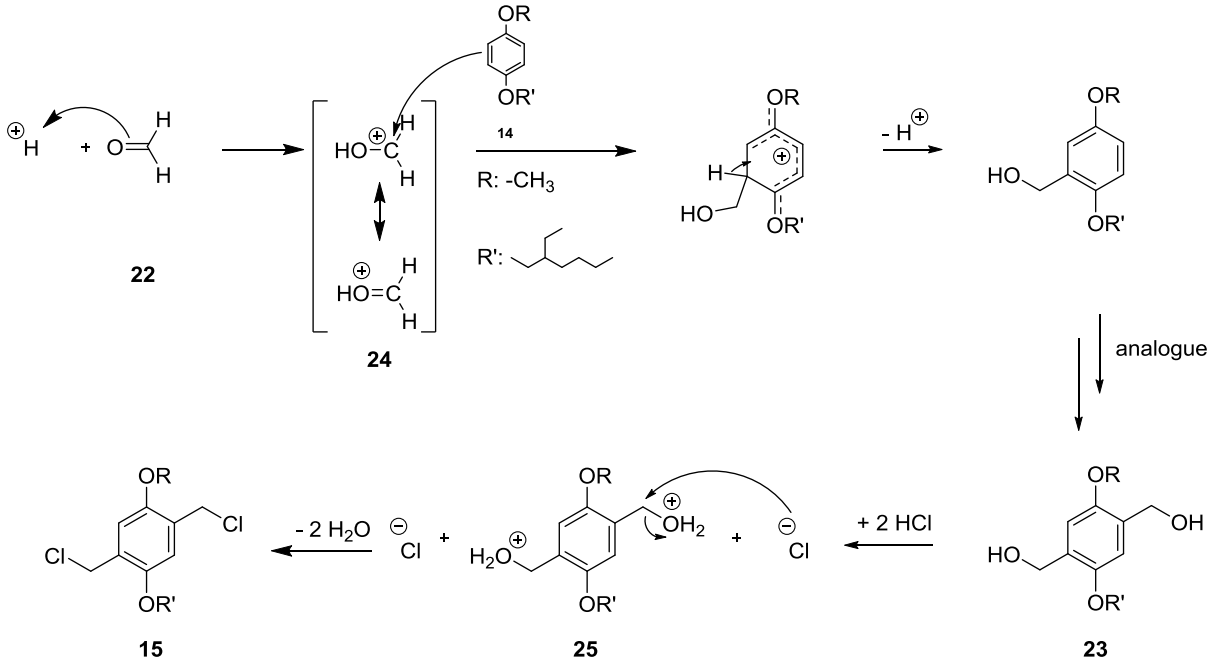
In the following reaction a chloromethylation with the obtained MEH-ether **14** is perfomed. Thereby, the ether **14** reacts with paraformaldehyde (**21**) and aqueous hydrochloric acid in acetic anhydride to 1,4-bis(chloromethyl)-2-((2-ethylhexyl)oxy)-5-methoxybenzene (**15**) (Scheme 7).



Scheme 7: The chloromethylation of 1-((2-ethylhexyl)oxy)-4-methoxybenzene (**14**) with paraformaldehyde (**21**) and aqueous hydrochloric acid in acetic anhydride giving 1,4-bis(chloromethyl)-2-((2-ethylhexyl)oxy)-5-methoxybenzene (**15**).

This synthesis was executed following a literature procedure from NEEF and FERRARIS[39], whereby hydrochloric acid instead of hydrobromic acid in glacial acetic acid was used. Acetic anhydride was used in an excess to remove H_2O from the aqueous hydrochloric acid solution and to ensure a high H^+ concentration.

Paraformaldehyde (**21**) belongs to the substance class of polyacetales, which are known to degrade in acids. By mixing **21** with hydrochloric acid formaldehyde (**22**) is formed. In the acidic medium **22** reacts with 1-((2-ethylhexyl)oxy)-4-methoxybenzene (**14**) in an electrophilic aromatic substitution (Scheme 8).



Scheme 8: The mechanism of the electrophilic aromatic substitution of **14** with paraformaldehyde (**22**) and acid catalysis. In a second step the benzylic hydroxyl groups in **23** undergo nucleophilic substitution with hydrogen chloride giving a chloromethyl group.

Hydrogen chloride protonates formaldehyde (**22**), which leads to a resonance structure including the carbenium ion **24**. This allows an attack of the aromatic electrons at the positively charged carbon atom. The positive charge is delocalized over the whole benzene ring. By splitting of a proton the aromaticity is re-established.

In the next step the benzylic carbons undergo a nucleophilic substitution, whereby the hydroxyl groups are exchanged through chloride groups. This reaction is catalysed by the acidic medium. The oxygen atom in the benzylic position in **23** is protonated, which increases the leaving potential of the nucleofuge H_2O and forming a partial positive charge at the benzylic carbon atom, allowing an easier nucleophilic attack of the chloride ion in **25**.

In the nucleophilic substitution of the hydroxyl group by the chloride H_2O is released, which reacts with acetic anhydride to acetic acid. This ensures a high H^+-concentration in the reaction mixture.

An aqueous work-up was performed to wash out the acid and a crystalline raw product was obtained. Recrystallization from 2-propanol instead of *n*-hexane gave the pure crystalline product with 79.3 % yield (lit.[39]: 65.02 %).

The ^{1}H-NMR spectrum of the pure product is shown in Figure 6, the protons of the benzylic carbon atoms are assigned with $H_{16,17}$.

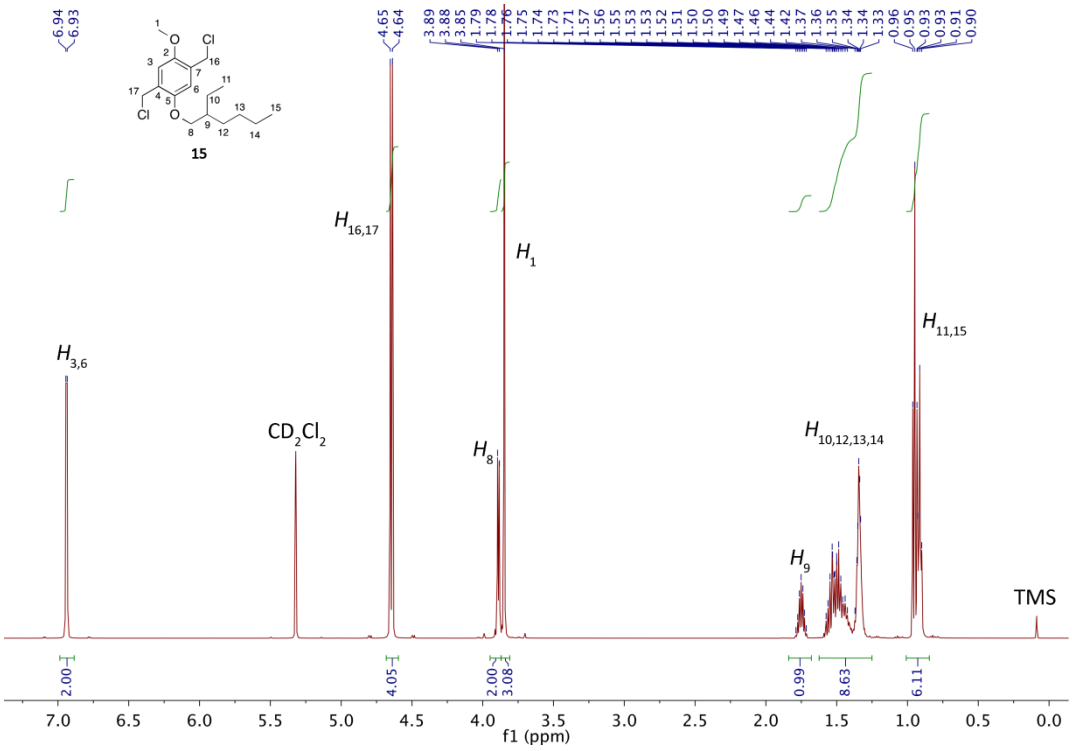


Figure 6: The ^{1}H-NMR spectrum of 1,4-bis(chloromethyl)-2-((2-ethylhexyl)oxy)-5-methoxybenzene (**15**) in CD_2Cl_2.

The success of the chloromethylation can be seen by correlation between $H_{16,17}$ and $C_{3,6}$ in the HMBC-correlation spectrum (highlighted in Figure 7).

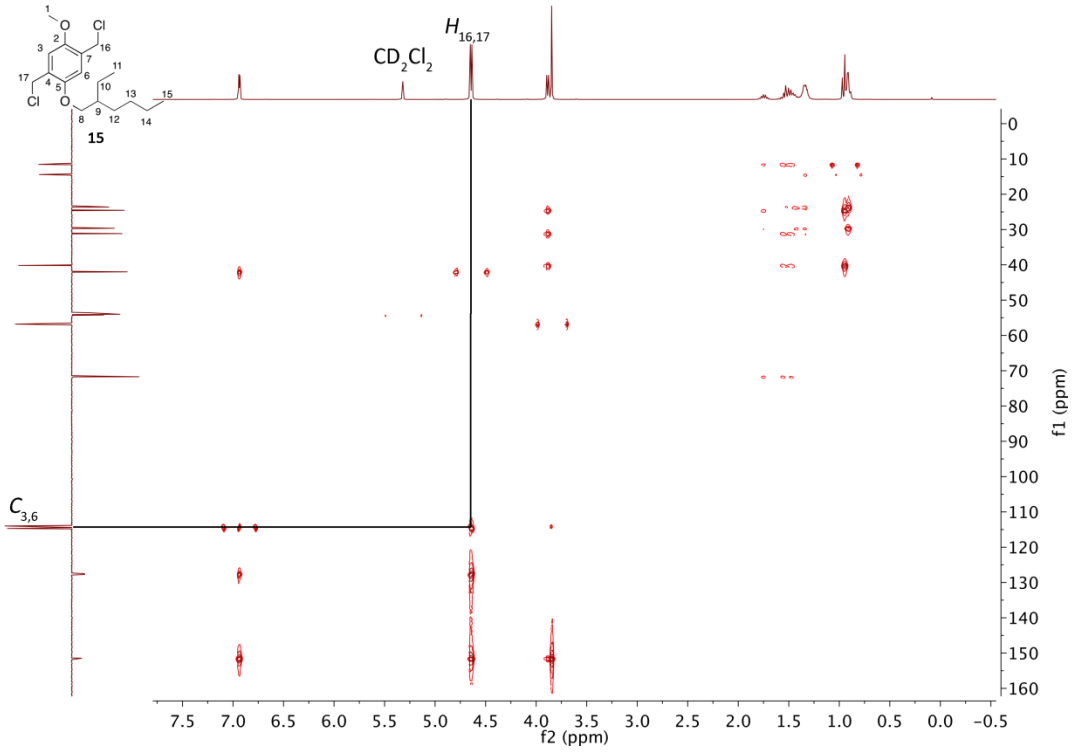
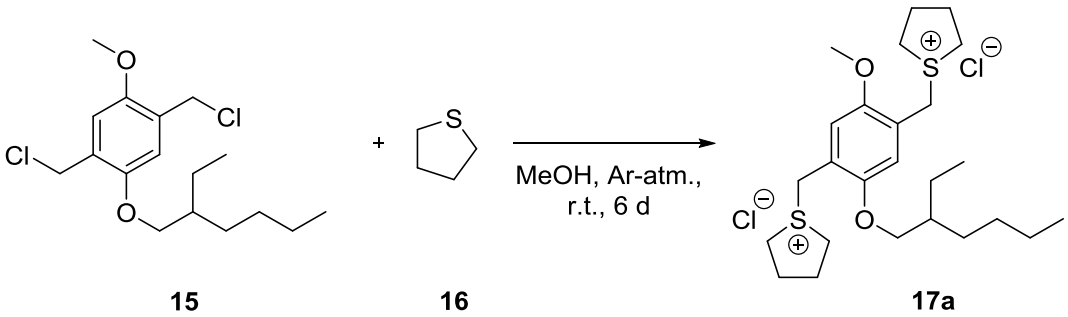


Figure 7: HMBC-spectrum of 1,4-bis(chloromethyl)-2-((2-ethylhexyl)oxy)-5-methoxybenzene (**15**) in CD_2Cl_2. The important correlation between $H_{16,17}$ and $C_{3,6}$ is highlighted.

4.2.3. Synthesis of 1,1'-((2-((2-ethylhexyl)oxy)-5-methoxy-1,4-phenylene)bis(methylene))bis-(tetrahydro-1*H*-thiophen-1-ium)chloride (17a).

In the third reaction step the chlorides are exchanged by tetrahydrothiophene (**16**) forming the salt **17a** (Scheme 9).

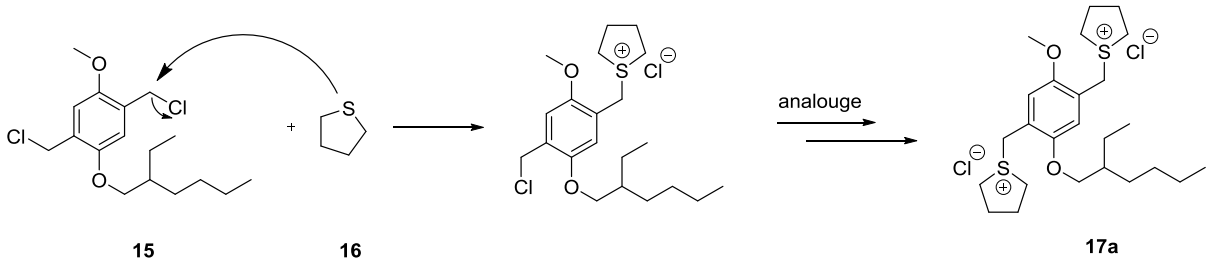


Scheme 9: On 1,4-bis(chloromethyl)-2-((2-ethylhexyl)oxy)-5-methoxybenzene (**15**) chlorides are exchanged by tetrahydrothiophene (**16**) in methanol, forming 1,1'-((2-((2-ethylhexyl)oxy)-5-methoxy-1,4-phenylene)bis(methylene))bis-(tetrahydro-1*H*-thiophen-1-ium)chloride (**17a**).

The exchange with tetrahydrothiophene (**16**) was done on the basis of the work of ZAQUEN *et al.*[40], although in literature the reaction was performed with 2-methoxy-5-(3′,7′-dimethyloctyl-oxy)- instead of 1-((2-ethylhexyl)oxy)-4-methoxy-side chains, giving the MDMO sulfinyl monomer.

The reaction was quenched after 6 days, by adding cold acetone (– 20 °C) to the mixture. It was observed, that the solubility of the salt **17a** in acetone is extensively increasing with the (solvent) temperature. This leads to the problem of decreasing yield when the equipment is warming up to fast while filtering off the precipitate. This could be an explanation for 23.3 % yield (lit.[40]: 60.04 %).

The mechanism of the reaction is not known in literature up to now. In the Scheme 10 a possible reaction mechanism is shown.



Scheme 10: Proposed mechanism for the exchange of both chlorides against tetrahydrothiophene (**16**), forming the salt **17a**.

Due to the higher electronegativity of the chloride the carbon atom is partially positively charged, allowing the free electron pair of the sulfur in **16** to nucleophilically attack the benzylic carbon atom in **15**. Chloride is released and the salt **17a** is formed with chloride as counter ion. This corresponds to the mechanism of a nucleophilic substitution.

The ^{1}H-NMR spectrum of the product **17a** is shown in Figure 8.

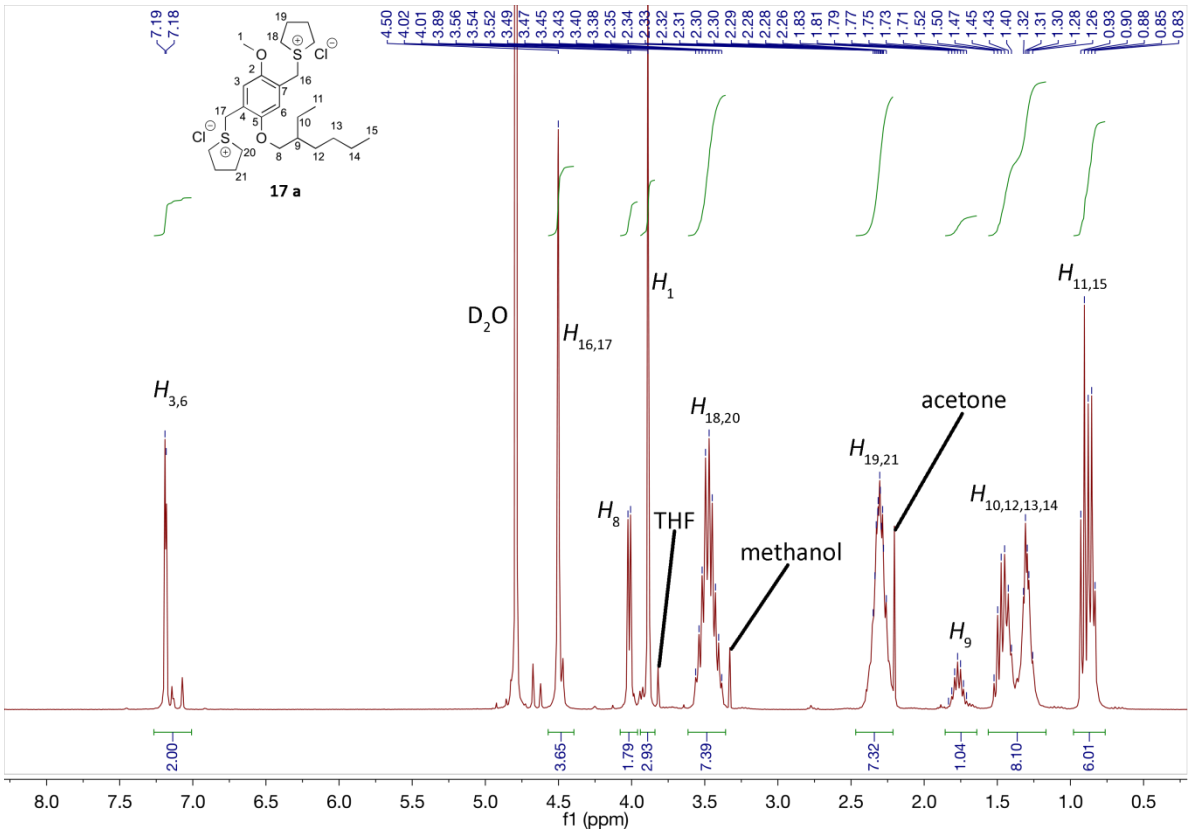


Figure 8: Pictured is the ^{1}H-NMR of 1,1'-((2-((2-ethylhexyl)oxy)-5-methoxy-1,4-phenylene)bis(methylene))bis(tetrahydro-1*H*-thiophen-1-ium)chloride (**17a**) in D_2O with assigned protons and traces of solvents.

Since the **17a** is a salt, D_2O was used as deuterated solvent so it is not possible to compare the ^{1}H-NMR spectrum of **17a** with the spectra of the previous products. The protons are assigned in Figure 8 with the subscript numbers, traces of remaining solvent were assigned separately. The signals at 3.5 ppm and 2.3 ppm can be assigned to a tetrahydrothiophene group, indicating a successful reaction.

The linkage of the tetrahydrothiophene group to the benzylic carbon atoms, has been proved via HMBC-NMR spectroscopy (see Figure 9) by a correlation of $H_{16,17}$ and $C_{18,20}$, which is highlighted.

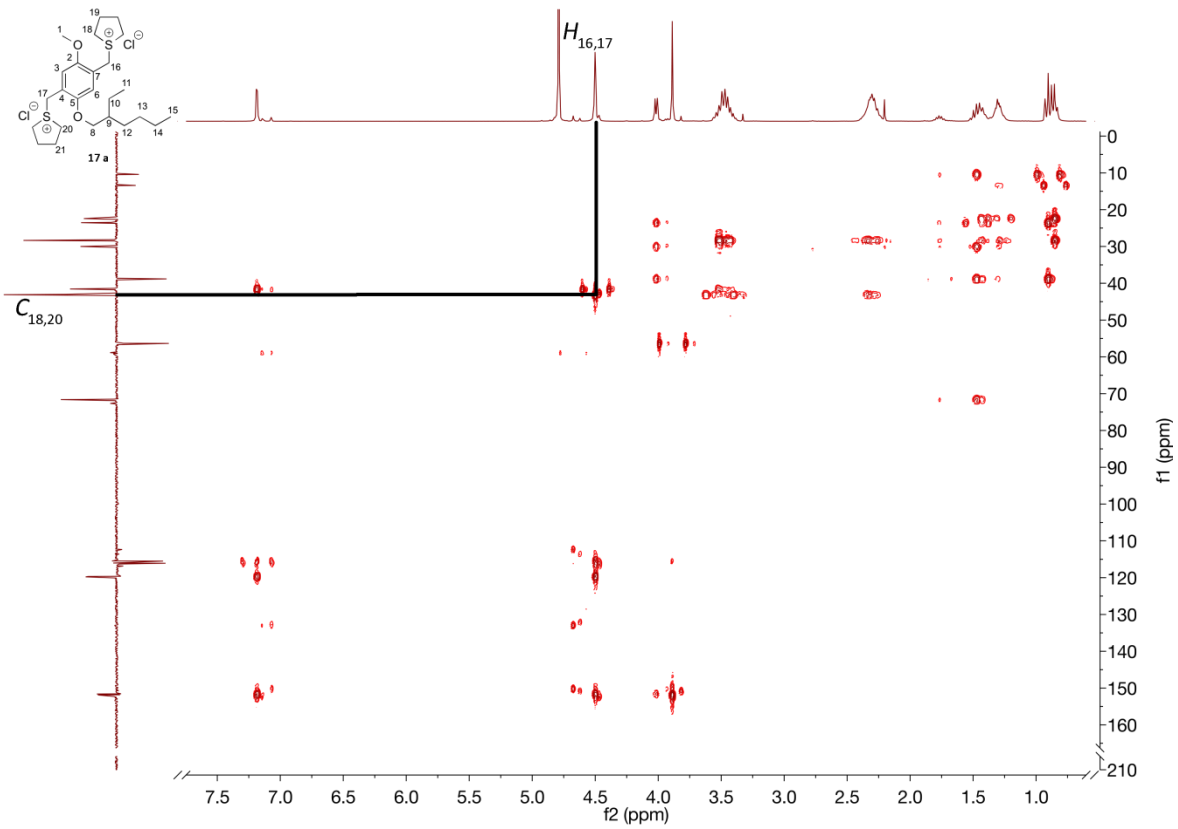
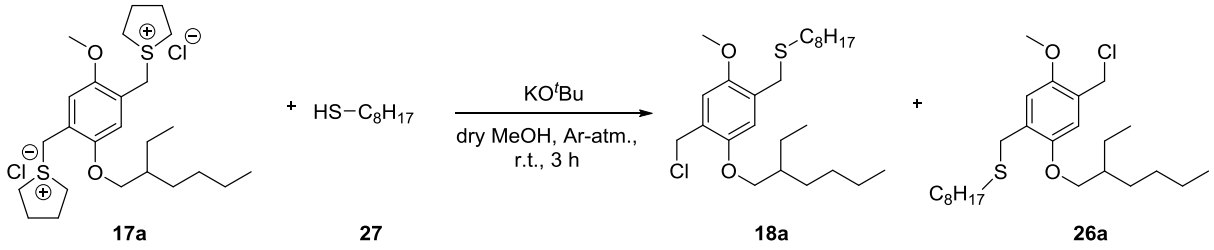


Figure 9: HMBC-NMR spectrum of **17a** in D_2O, the correlation between $H_{16,17}$ and $C_{18,20}$ and the carbons $C_{18,20}$ of the tetrahydrothiophene group is highlighted.

4.2.4. Synthesis of the configurational isomeric sulfanes 18a and 26a.

The obtained chloride-salt **17a** is mono substituted in the following reaction by *n*-octanethiol (**27**) in presence of potassium *tert*-butoxide as base in dry methanol. The other tetrahydrothiophene group is resubstituted by chloride, as it is shown in Scheme 11.

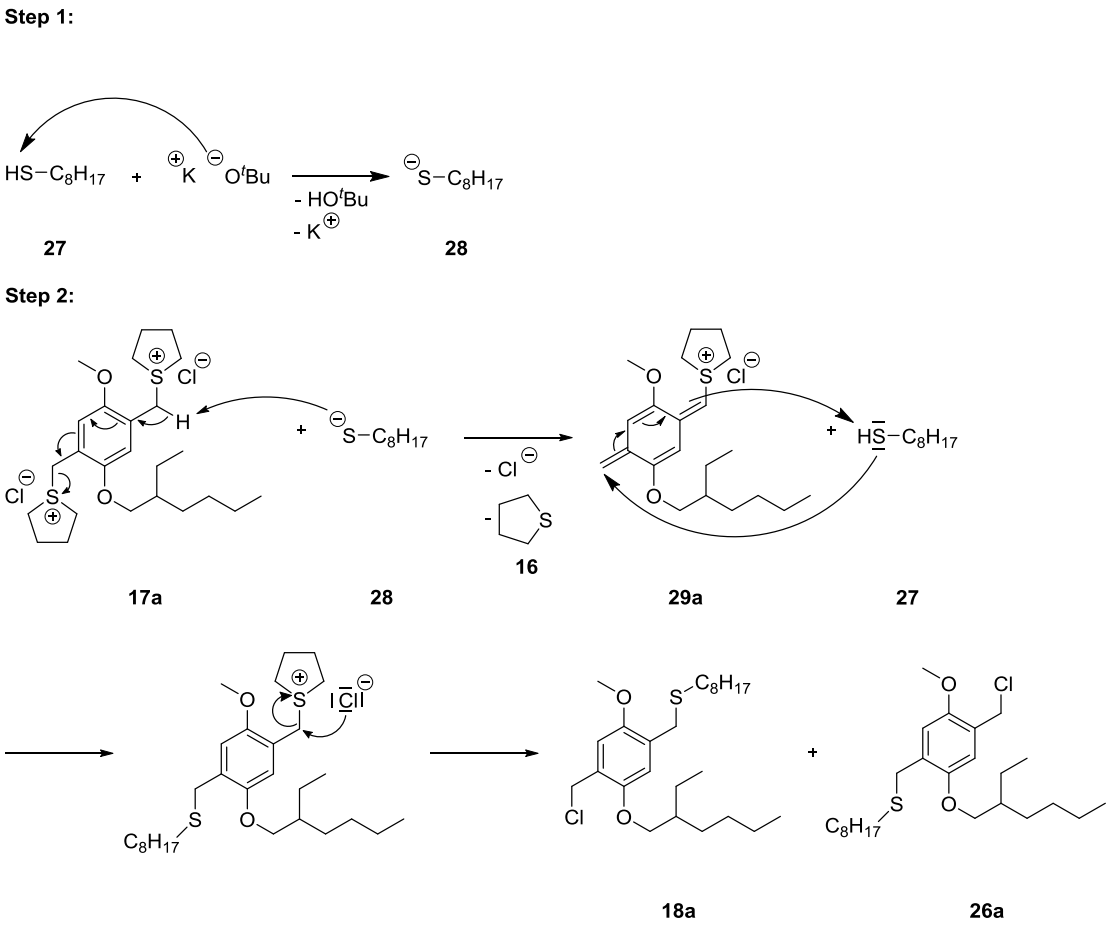


Scheme 11: The exchange of one tetrahydrothiophene group against *n*-octanethiol (**27**) forming the sulfanes **18a** and **26a**, while the other tetrahydrothiophene group is resubstituted by chloride.

The reaction was performed based on a literature procedure of ZAQUEN *et al.*[40] and JUNKERS *et al.*[41].

The stoichiometry of the used reactants is an important factor in this reaction, in order to substitute one tetrahydrothiophene group against chloride and the other one against a sulfane group. Nevertheless, it is possible that the bis-chloride or the bis-sulfane are formed as side products.

In the first step of the reaction, *n*-octanethiol (**27**) was stirred with the base, to achieve full deprotonation of the thiol. Afterwards, this solution was added to the salt **17a** to perform the exchange of the tetrahydrothiophene groups. VAN BREEMEN *et al.* proposed the following mechanism for this reaction (Scheme 12).[42]



Scheme 12: The mechanism for the exchange of tetrahydrothiophene groups, giving the configurational isomeric sulfanes **18a** and **26**. The mechanism is shown for one isomer.

In the first step the thiol **27** is deprotonatd by the base. The thiolate **28** deprotonates the salt **17a** in benzylic position forming the *p*-quinodimethane **29** and the thiol **27**. Tetrahydrothiophene **16** and one chloride are split off. A free electron pair of thiol **27** attacks the *p*-quinodimethane **29a** in benzylic position, where no tetrahydrothiophene group is connected. Afterwards, chloride performs a nucleophilic substitution on the other benzylic carbon atom and the tetrahydrothiophene group is split off just as well, giving sulfanes **18a** and **26a**.

The work-up procedure was changed compared to literature.[40] The washing step of the organic layer was done first in order to remove potassium chloride and *tert*-butanol formed during the reaction. After this step the solvent used for extraction was removed and *n*-octane was added for azeotropic distillation to remove the tetrahydrothiophene (**16**). The azeotropic distillation is more difficult when the formed salt is still in the crude product mixture. Based on these performed deviations the pure product was obtained with 59.0 % yield (lit.[40]: 96.9 %).

The ^{1}H-NMR spectrum of the product mixture is shown in Figure 10, the signals are assigned with the subscript numbers to the structure, traces of remaining solvent were assigned separately. The observed multiplicity of the signals differs from the expectations. Slightly differences in chemical shift, resulting from the isomers can lead to overlapping signals which then appear as multiplets.

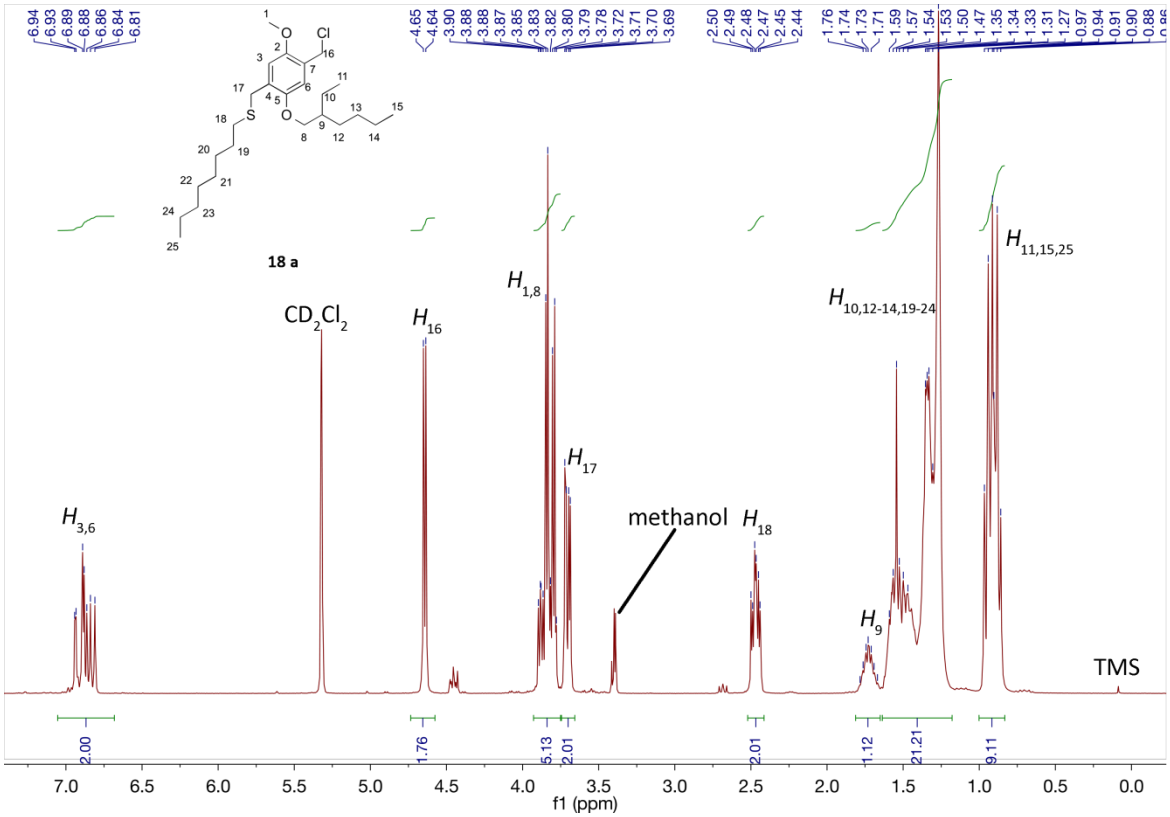


Figure 10: The ^{1}H-NMR spectrum of the formed sulfanes (**18a**) and (**26a**) in CD_2Cl_2, for representation only the chemical structure of one isomer is shown.

Due to the different electronegativity of chlorine and sulfur, the benzylic protons are in different chemical environments. The signals at 4.6 ppm and 3.7 ppm can be assigned to these benzylic protons, indicating the success of the reaction.

In the HMBC-NMR spectrum (Figure 11) a correlation signal of H_{17} and C_{18} can be seen, which proves a successful linkage of thiol **27** to the benzylic carbon.

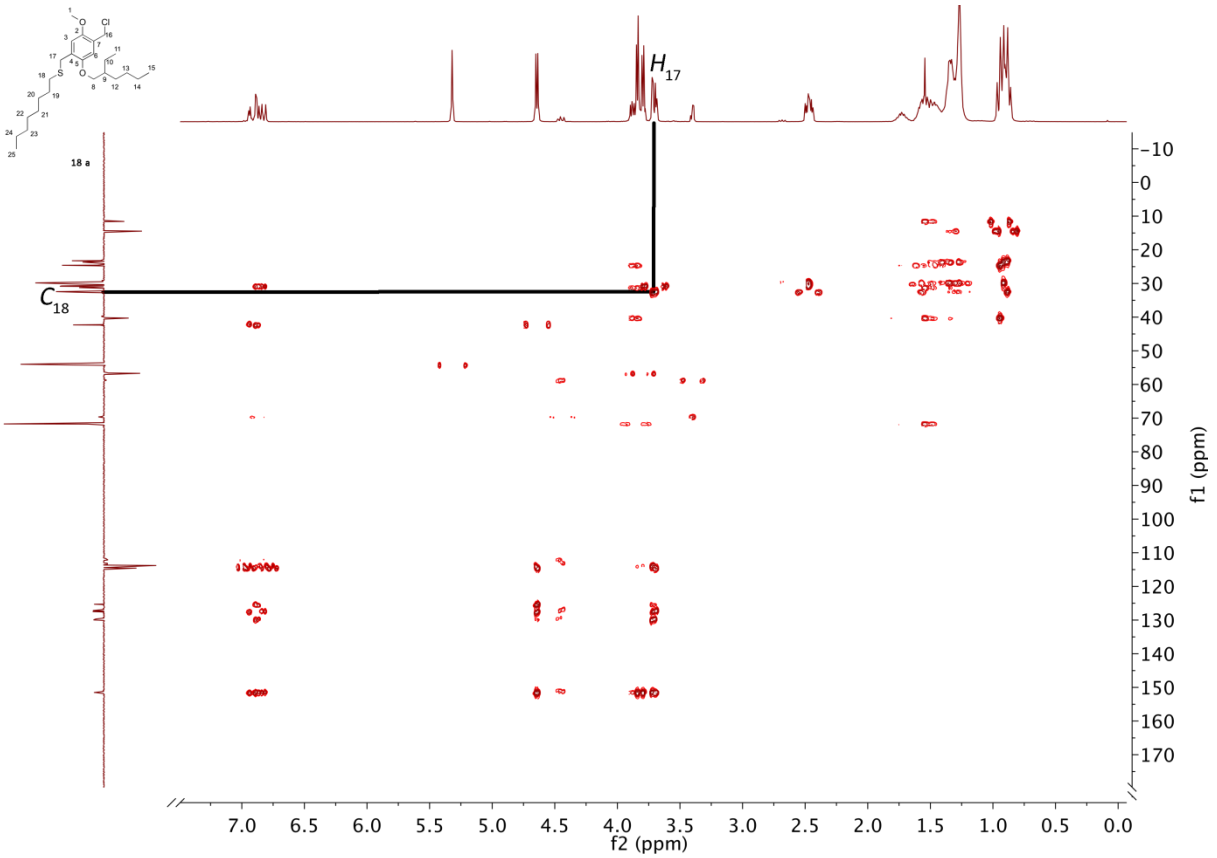


Figure 11: The HMBC-NMR correlation spectrum of sulfane **18a** and **26a** is shown, the correlation between H_{17} and C_{18} is highlighted.

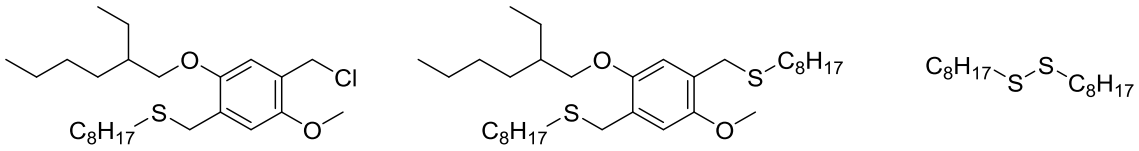
A detailed assignment of the chemical shifts was performed in the experimental section.

Because the mono- and bis-substituted products differ not much in their chemical shift in the ^{1}H-NMR-spectrum mass spectrometry was performed to prove the mono-substituted product was obtained from the reaction. A field desorption (FD) spectrum was recorded having the advantage that no molecule fragmentation takes place, rather cluster are formed. Based on this the following possible side products of the reaction were assumed (Figure 12).

The spectrum is pictured in Figure 13. The molecular weight of sulfanes **18a** and **26a** is 443.13 g·mol^{-1}, peaks with 442.3 m/z, 884.6 m/z and 1329.7 m/z can be assigned to the desired products.

If thiol **27** binds to both benzylic positions bis-sulfane **30** is obtained with a molecular weight of 552.96 g·mol^{-1}. The peak with 552.7 m/z as well as with 1104.8 m/z can be assigned to this side product.

Another possibility is a redox reaction of the thiol **27** giving the disulfide **31** with a molecular weigth of 290.57 g·mol^{-1}. The peak with 290.4 m/z can be assigned to this disulfide **31**.



18a | **30** | **31**

443.13 g/mol | 552.96 g/mol | 290.57 g/mol

Figure 12: Based on the mass spectrum these side products, which can be formed during the reaction, were assumed.

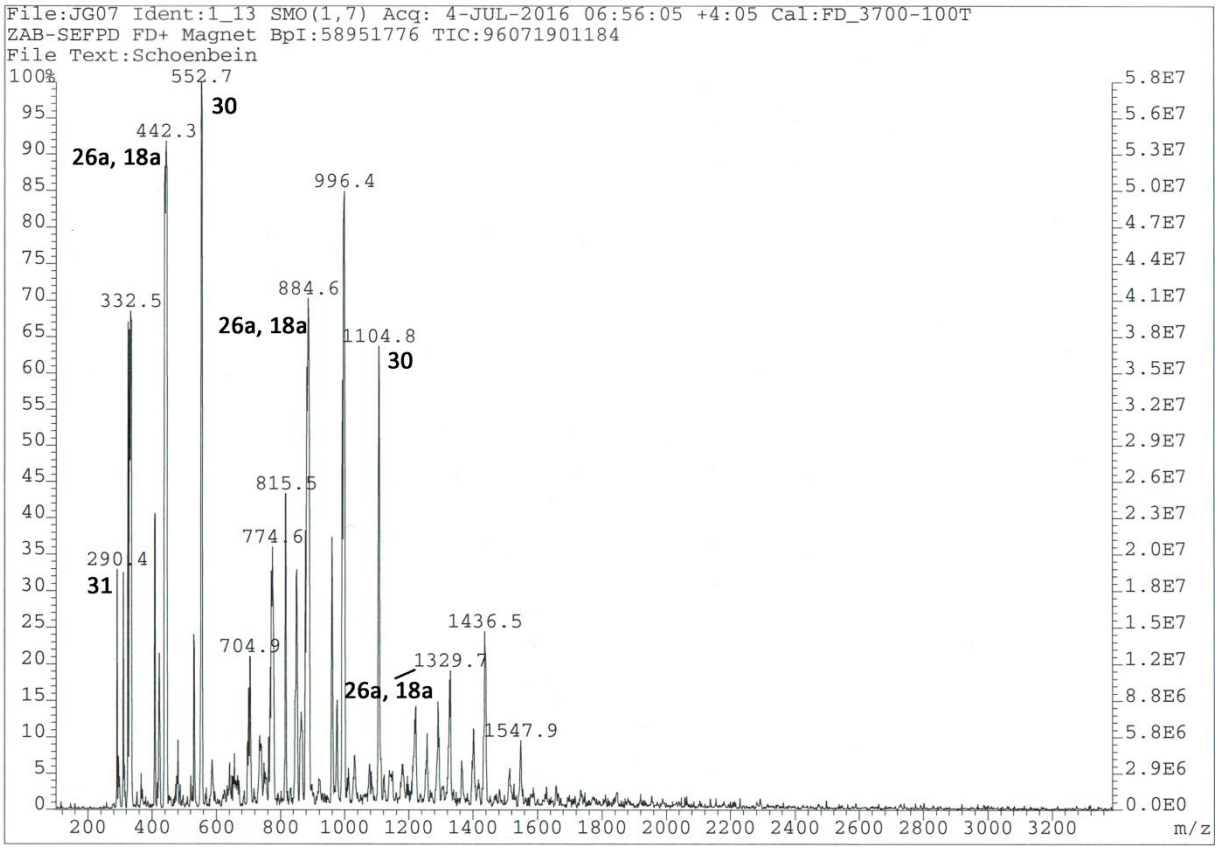
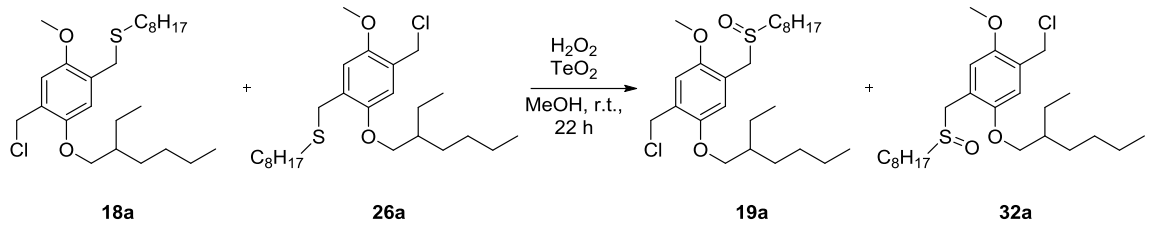


Figure 13: The field desorption spectrum of sulfane **18a** and **26a** with assigned peaks.

4.2.5. Synthesis of the precursor monomer 19a and 32a by oxidation of the sulfanes 18a and 26a.

In last reaction step towards the precursor monomer the sulfur atom in sulfane **18a** and in its configurational isomer **26a** are oxidized with aqueous hydrogen peroxide solution and tellurium dioxide as catalyst in methanol (Scheme 13).



Scheme 13: Sulfanes **18a** and **26a** react with aqueous hydrogen peroxide solution in methanol, catalyzed by tellurium dioxide, giving the precursor monomers **19a** and **32a**.

The synthesis was performed based on a literature procedure published by ANDERSON *et al.*[37]. The progress of the reaction was monitored via TLC (*n*-hexane : EtOAc, 6 : 4). Tellurium dioxide was added as catalyst to facilitate the oxidation of the sulfur atom. The reaction was quenched by adding saturated NaCl solution, as described in literature.

After work-up a yellow oil was obtained and ^{1}H-NMR spectrum showed it was a mixture of different compounds (Figure 14).

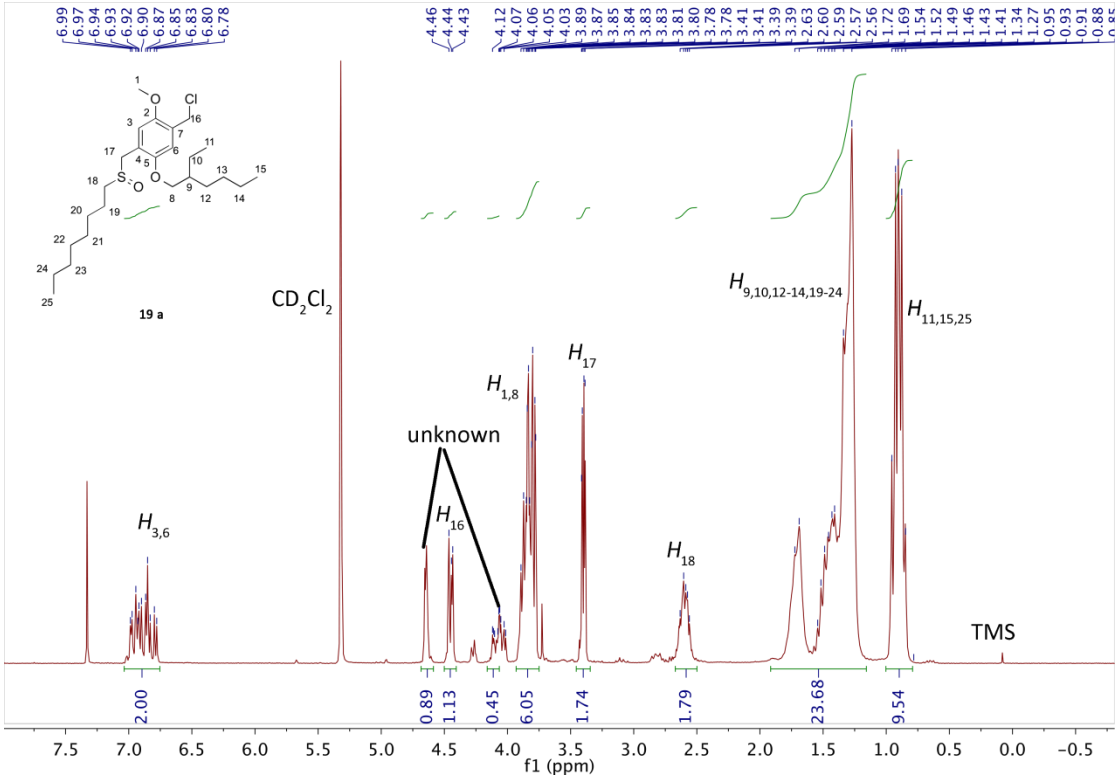


Figure 14: The ^{1}H-NMR spectrum of the raw products of **19a** and **32a** in CD_2Cl_2 is shown. For a better clarity only the chemical structure of one isomer is shown, as it is not expected to see big differences in chemical shift for both isomers.

As a mixture of products was obtained, column chromatography (SiO_2 0.040 – 0.063 mm, *n*-hexane : EtOAc, 6 : 4) was performed. The products **19a** and **32a** could not be isolated. TLCs (*n*-hexane : EtOAc, 6 : 4) of the different fractions showed many spots, which indicates product degradation on the column.

Because the pure monomer could not be isolated, no sulfinyl polymerization towards MEH-PPV-precursor polymer was performed, neither the elimination to fully eliminated MEH-PPV.

4.3. Bromide as substituent during the precursor monomer synthesis

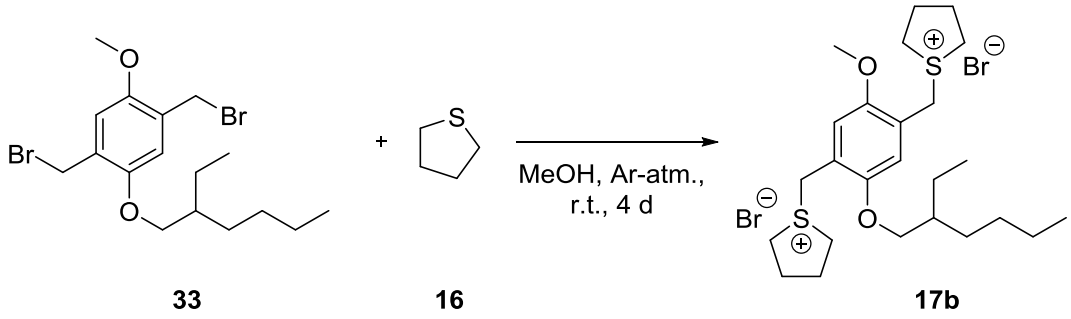
In the following section bromide as leaving group in the monomer synthesis will be discussed in detail. These reactions are not known to literature yet, the performance was based on literature for the synthesis of MDMO-PPV[40] with chloride as leaving group. If not stated otherwise the yields are also compared to these literature procedures. With the following reactions it should be investigated, whether the yield of the subsequent polymerization can be improved (lit.: 72 %[40]) using bromide as substituent instead of chloride.

It is expected that the precursor sulfinyl monomer with bromide as leaving group polymerizes faster, because it is more reactive due to the higher leaving potential of bromide.

The bis-bromide **33** is equal to 1,4-bis(chloromethyl)-2-((2-ethylhexyl)oxy)-5-methoxy-benzene (**15**) in the reaction mechanism of its synthesis. The chemical was already in stock and therefor used for the following reactions.

4.3.1. Synthesis of 1,1'-((2-((2-ethylhexyl)oxy)-5-methoxy-1,4-phenylene)bis(methylene))bis-(tetrahydro-1*H*-thiophen-1-ium)bromide (17b).

Both bromides of **33** were exchanged by tetrahydrothiophene (**16**) in methanol giving the salt **17b** (Scheme 14).



33 **16** **17b**

Scheme 14: The substitution of bromides by tetrahydrothiophene (**16**) in methanol, giving the salt **17b**.

In deviation to the literature of ZAQUEN *et al.*[40] the reaction was performed with 1-((2-ethyl-hexyl)oxy)-4-methoxy-side chains.

The reaction was quenched after 4 days, by adding cold acetone (– 20 °C) to the mixture. The solubility of the formed salt **17b** in acetone is extensively increasing with the (solvent) temperature. This leads to the problem of decreasing yield when the equipment is warming up too fast while filtering off the precipitate. 52.8 % yield (lit.[40]: 60.04 %) were achieved.

The synthesis of the chloride salt **17a** gave 23.3 % yield. A reason for the higher yield while using bromide as leaving group could be the higher leaving potential of bromide compared to

chloride. Furthermore, bromide and the thioether **16** are classified as soft, regarding the hard and soft acids and bases (HSAB) concept, so the reaction is preferred compared to the same reaction with chloride, which is not as soft as bromide.

It can be assumed that the mechanism for this reaction, which is not known in literature up to now, is equivalent to the mechanism (Scheme 10) of the chloride salt **17a**.

The ^{1}H-NMR spectrum of the formed salt **17b** is shown in Figure 15, the protons are assigned with subscript numbers, traces of solvent are also shown. The signals at 3.5 ppm and 2.3 ppm can be assigned to the tetrahydrothiophene group. This indicates a successful reaction.

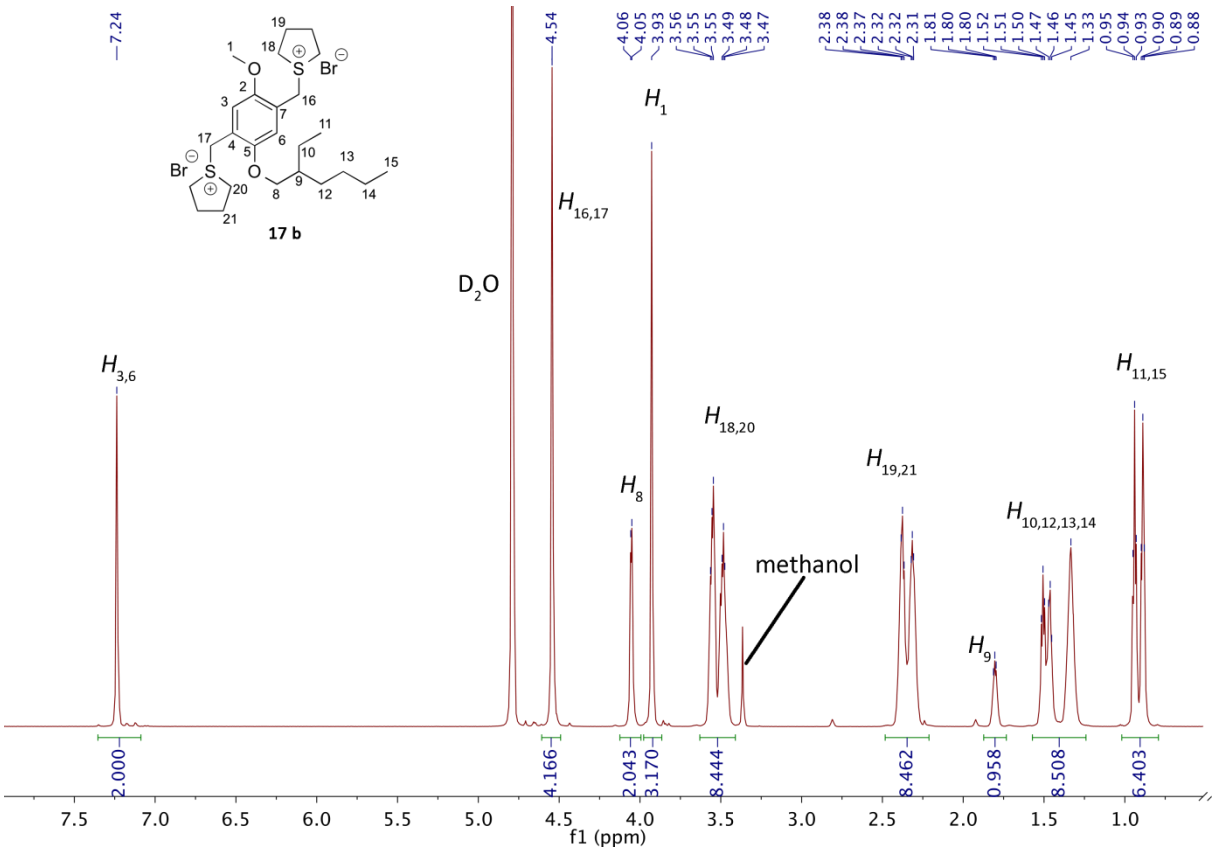


Figure 15: ^{1}H-NMR of bromide salt **17b** in D_2O, with assigned protons and traces of solvent.

By correlation of $H_{16,17}$ and $C_{18,20}$ in HMBC-NMR spectrum (Figure 16) the linkage of the tetrahydrothiophene groups to the benzylic carbon atoms can be proved.

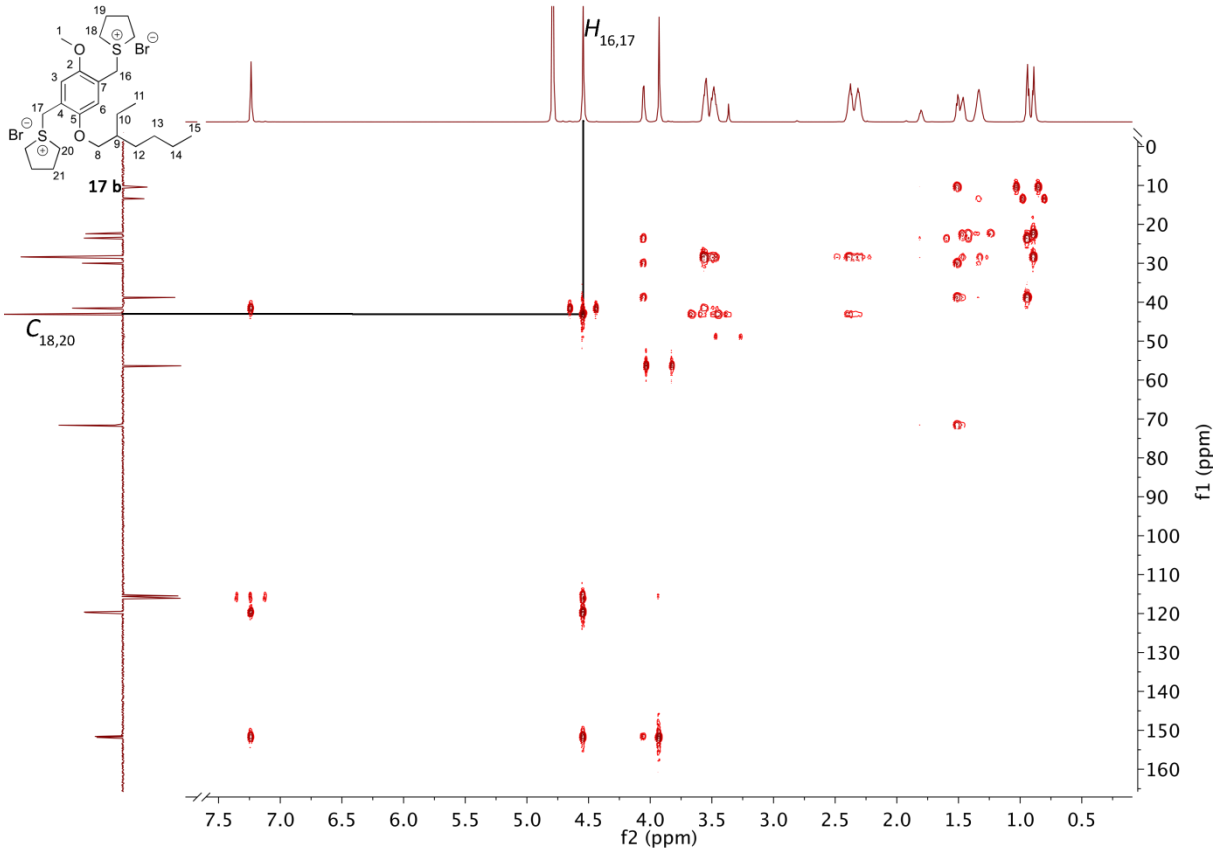
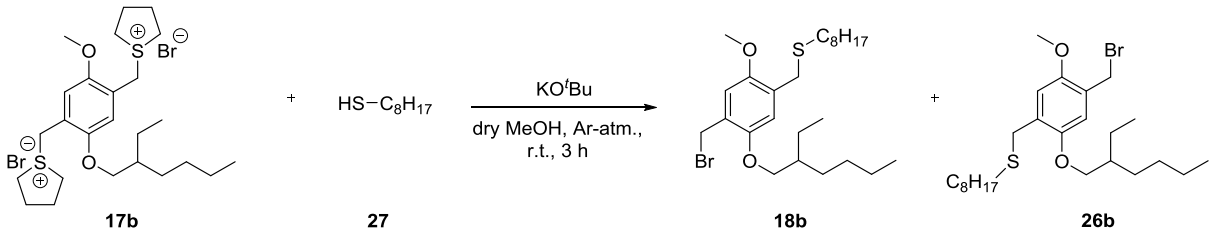


Figure 16: The correlation of $H_{16,17}$ and $C_{18,20}$ is highlighted in the HMBC-NMR spectrum of salt **17b** in D_2O.

4.3.2. Synthesis of the bromo-sulfanes 18b and 26b.

In the following reaction an exchange of the tetrahydrothiophene groups is performed in salt **17b**, using *n*-octanethiol (**27**) and potassium *tert*-butoxide in methanol forming the bromo-sulfanes **18b** and **26b** (Scheme 15). Thereby one tetrahydrothiophene group is exchanged by *n*-octanethiol (**27**) and the other group resubstituted by bromide.



Scheme 15: The bromide salt **17b** reacts with *n*-octanethiol (**27**) and base in methanol, giving the sulfanes **18b** and **26b**. One tetrahydrothiophene group is resubstituted by bromide, while the other one is exchanged by *n*-octanethiol (**27**).

Based on a literature procedure of ZAQUEN *et al.*[40] and JUNKERS *et al.*[41] the reaction was performed. Besides the desired main product it is also possible, that the bis-bromide or the bis-sulfane is formed during the reaction.

It can be assumed that the mechanism for this reaction is equivalent to the one for the chloride equivalents **17a** and **26a** (Scheme 12).

The work-up of the reaction was performed in deviation to literature[40]. After evaporating the solvent the organic layer was washed first, in order to remove potassium bromide and *tert*-butanol, which were formed during the reaction. The solvent for extraction was evaporated and an azeotropic distillation with *n*-octane was performed to remove tetrahydrothiophene (**16**) from the products **18b** and **26b**. The product was obtained with a yield of 78.2 % (lit.[40]: 96.9 %).

Using the bromide salt **17b** the yield could be improved compared to the chloride salt **17a** as reactant (59.0 %). This may be due to the higher leaving potential of bromide, compared to chloride.

In ^{1}H-NMR spectrum of the product mixture of **18b** and **26b** the signals are assigned to the structure with subscript numbers, traces of solvent were also assigned (Figure 17). Differences in chemical shift, resulting from the formed isomers, can lead to overlapping signals which then appear as multiplets.

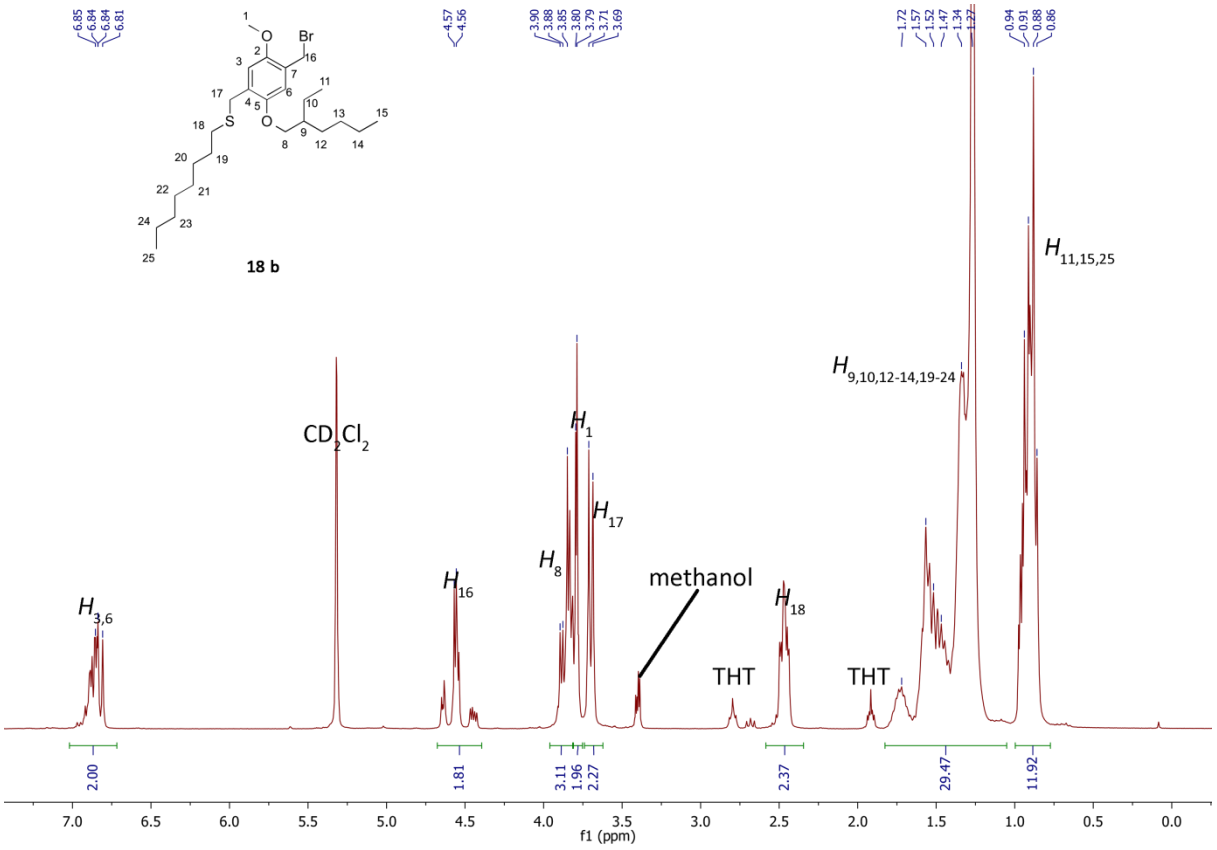


Figure 17: ^{1}H-NMR spectrum of sulfanes **18b** and **26b** in CD_2Cl_2, for representation only the chemical structure of one isomer is shown.

The signals at 4.6 ppm and 3.7 ppm can be assigned to the benzylic protons which are in different chemical environments. Due to the difference in electronegativity between sulfur and bromine different substituents on the benzylic carbon atoms can be assumed, indicating the success of the reaction.

The signals at 2.8 ppm and 1.9 ppm can be assigned to remaining tetrahydrothiophene (**16**) in the product. High vacuum distillation and repeated azeotropic distillation did not remove the traces.

The success of the reaction can be proven by 2D-NMR spectroscopy. By a correlation between H_{17} and C_{18} in the HMBC-NMR spectrum the linkage between thiol **27** and the benzylic carbon can be verified.

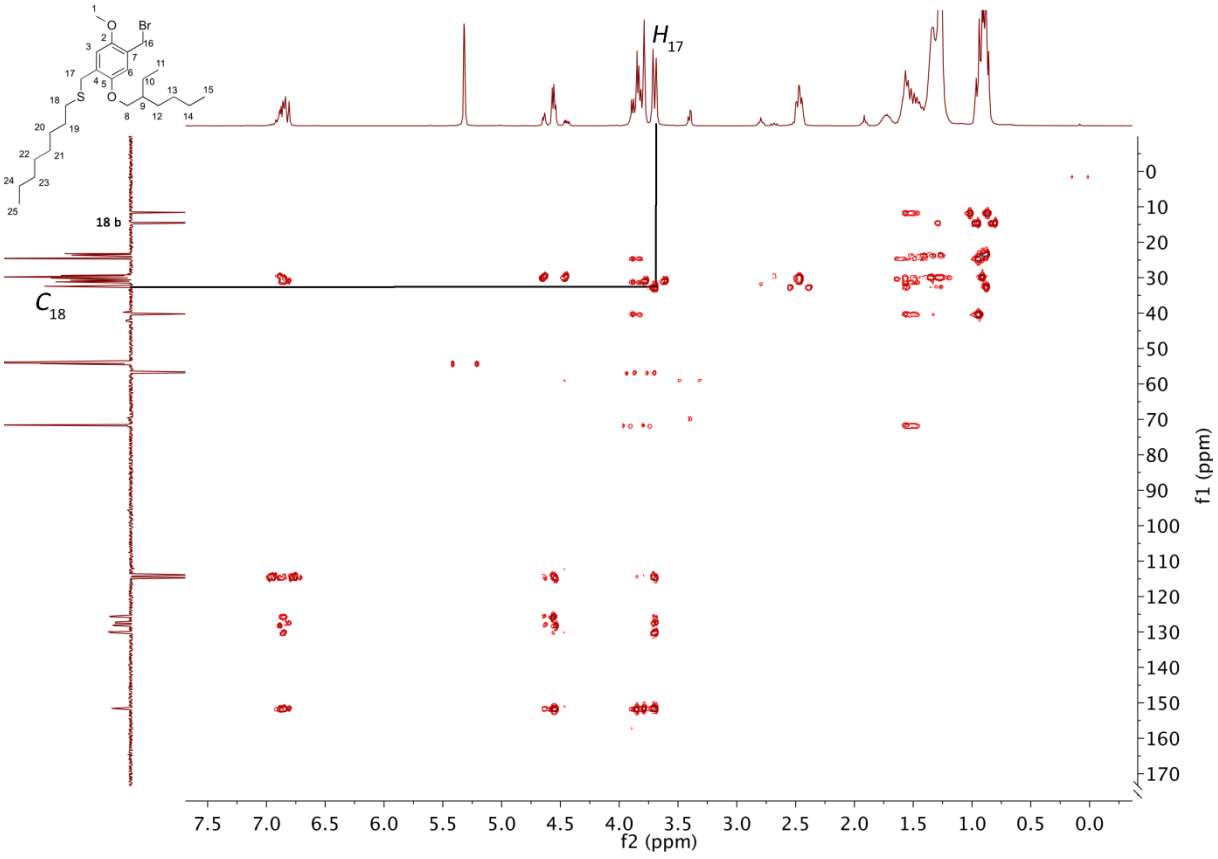


Figure 18: HMBC-NMR correlation spectrum of sulfanes **18b** and **26b** in CD_2Cl_2, the correlation between H_{17} and C_{18} is highlighted, only one isomer is displayed.

To prove the existence of the mono-substituted products **18b** and **26b** mass spectrometry was performed, where the products can be assigned to the molecule and molecule cluster peaks. The molecular weight of sulfanes **18b** and **26b** is 487.58 g·mol^{-1}, peaks with 488.6 m/z, 975.2 m/z and 1445.7 m/z can be assigned to them (Figure 20).

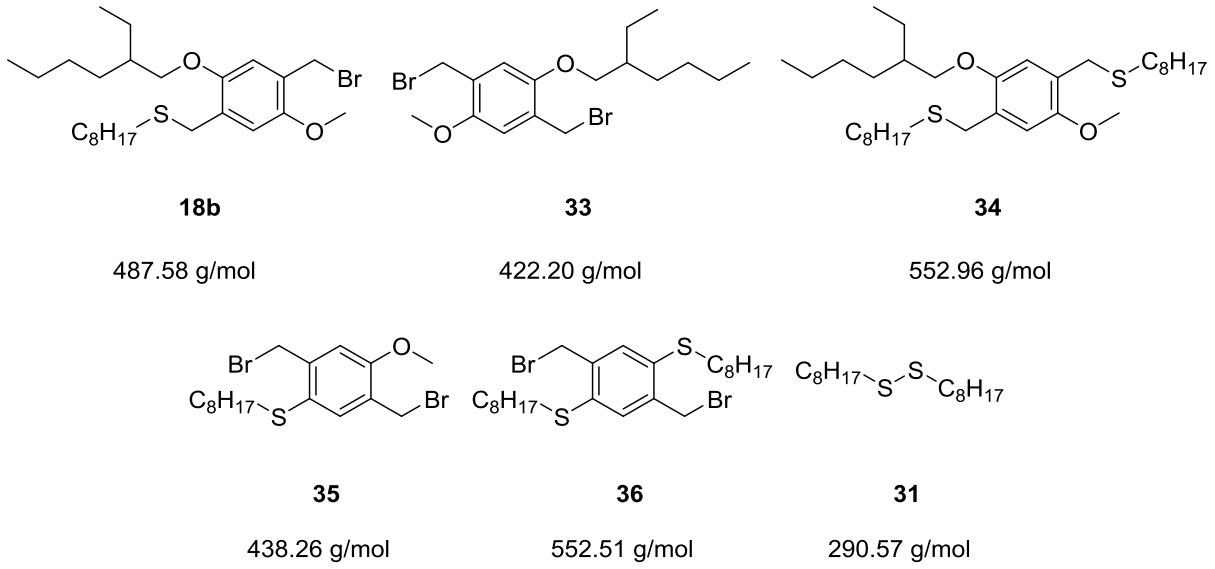


Figure 19: The structures and molecular weights of possible side products formed during the reaction are shown.

The molecular weight and structure of possible side products of the reaction are shown in Figure 19, other peaks can be assigned to them. For representation only one isomer of each chemical structure is shown.

The bis-bromide **33** is formed through the resubstitution of both tetrahydrothiophene groups by bromide, giving back the starting reactant **33** with a molecular weight of 422.20 g·mol^{-1}, peaks with 424.6 m/z, 847.7 m/z can be assigned to it.

When both tetrahydrothiophene groups are exchanged by *n*-octanethiol (**27**) the bis-sulfane **34** is formed, with a molecular weight of 552.96 g·mol^{-1}, peaks with 552.8 m/z and 1105.4 m/z can be assigned to it.

If thiol **27** substitutes one sidechain via an *ipso*-substitution the side products **35** can be obtained with a molecular weight of 438.26 g·mol^{-1} the peaks with 438.8 m/z as well as the peak with 1318.4 m/z can be assigned to it.

If thiol **27** substitutes both sidechains via an *ipso*-substitution the product **36** with a molecular weight of 552.51 g·mol^{-1} is formed. To this product, peaks with 552.8 m/z and 1105.4 m/z can be assigned.

The disulfide **31** can be formed by a redox reaction from thiol **27**. The molecular weight of disulfide **31** is 290.57 g·mol$^{-1,}$ the peak with 290.7 m/z can be assigned to it.

The mass spectrum shows, that even when the reaction is performed with optimal stoichiometry, the bis-substituted products **33** and **34** cannot be prevented and many various side products can be formed.

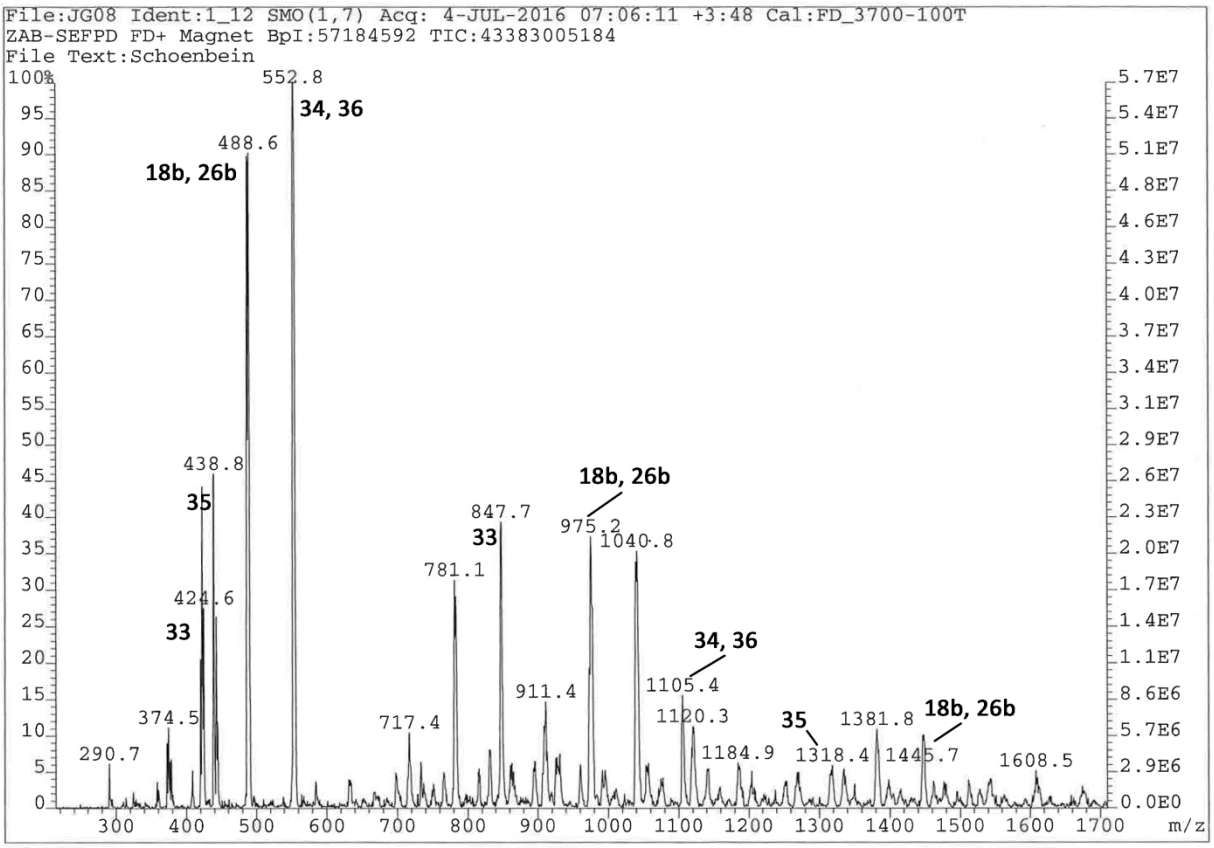
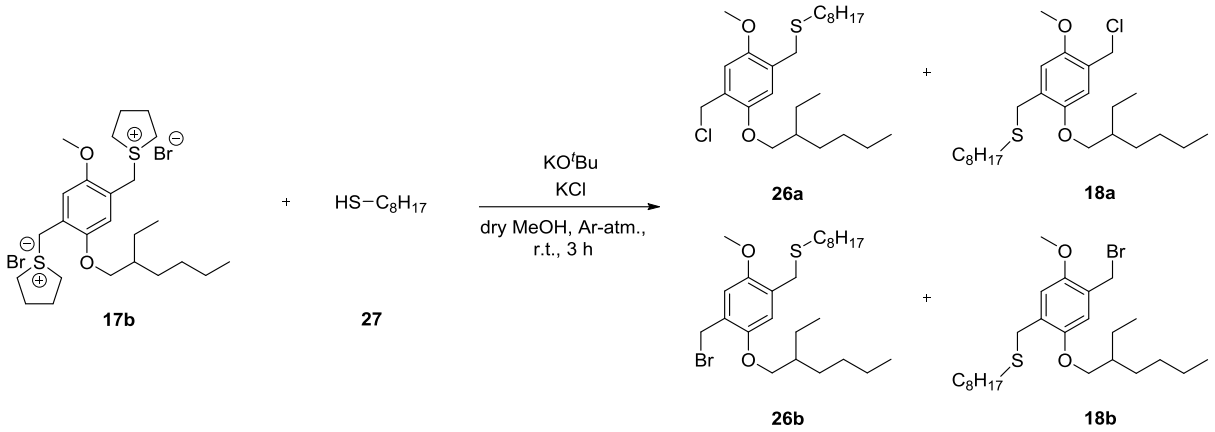


Figure 20: The mass spectrum of sulfanes **18b** and **26b** with assigned peaks.

4.3.3. Synthesis of different sulfanes 18a, 18b, 26a and 26b by adding potassium chloride.

In order to exchange one tetrahydrothiophene group by thiol **27** and the other group by chloride, the previous reaction was performed again with potassium chloride in an excess (Scheme 16). Since bromide has the higher leaving potential than chloride, this reaction was perfomed to investigate, whether bromide is able to substitute the tetrahydrothiophene group in presence of chloride.



Scheme 16: In salt **17b** one tetrahydrothiophene group is exchanged by octanethiol (**27**), the other one is exchanged by a chloride or bromide, forming the sulfanes **18a**, **18b**, **26a** and **26b**.

The performance of the reaction was based on literature of ZAQUEN *et al.*[40] and JUNKERS *et al.*[41]. Potassium chloride was added in excess to the reaction mixture. This attempt to change the halides was performed, due to the fact that chloride has a lower leaving potential and therefore sulfane **18a** and **26a** are more stable. Additionally it was not clear, why the yield in the exchange reaction (see chapter 4.3.2) was lower, than the one in literature. One reason could be, that bromide is a too good leaving group and would therefore not bind again to the benzylic carbon. Potassium chloride was then added to offer a second, worse leaving group, which should bind to the benzylic carbon more easily.

The mechanism is equivalent to the shown mechanism in Scheme 12. Chloride as well as bromide are able to substitute the second tetrahydrothiophene group, despite the fact that chloride is the better nucleophile.

Compared to literature[40] the work-up was changed. After evaporation of the solvent the organic layer was washed first to remove potassium bromide and potassium chloride. After the solvent for extraction was evaporated, *n*-octane was added to remove tetrahydrothiophene (**16**) via azeotropic distillation.

In Figure 21 the ^{1}H-NMR spectrum of the obtained sulfanes **18a**, **18b**, **26a** and **26b** is shown. The signals are assigned to the structure with subscript numbers, traces of solvent were also assigned. Two products with an isomer each and different bis-substituted side products with chloride and bromide can be formed during the reaction. This leads to different chemical shifts, which can lead to overlapping signals that can appear as multiplets.

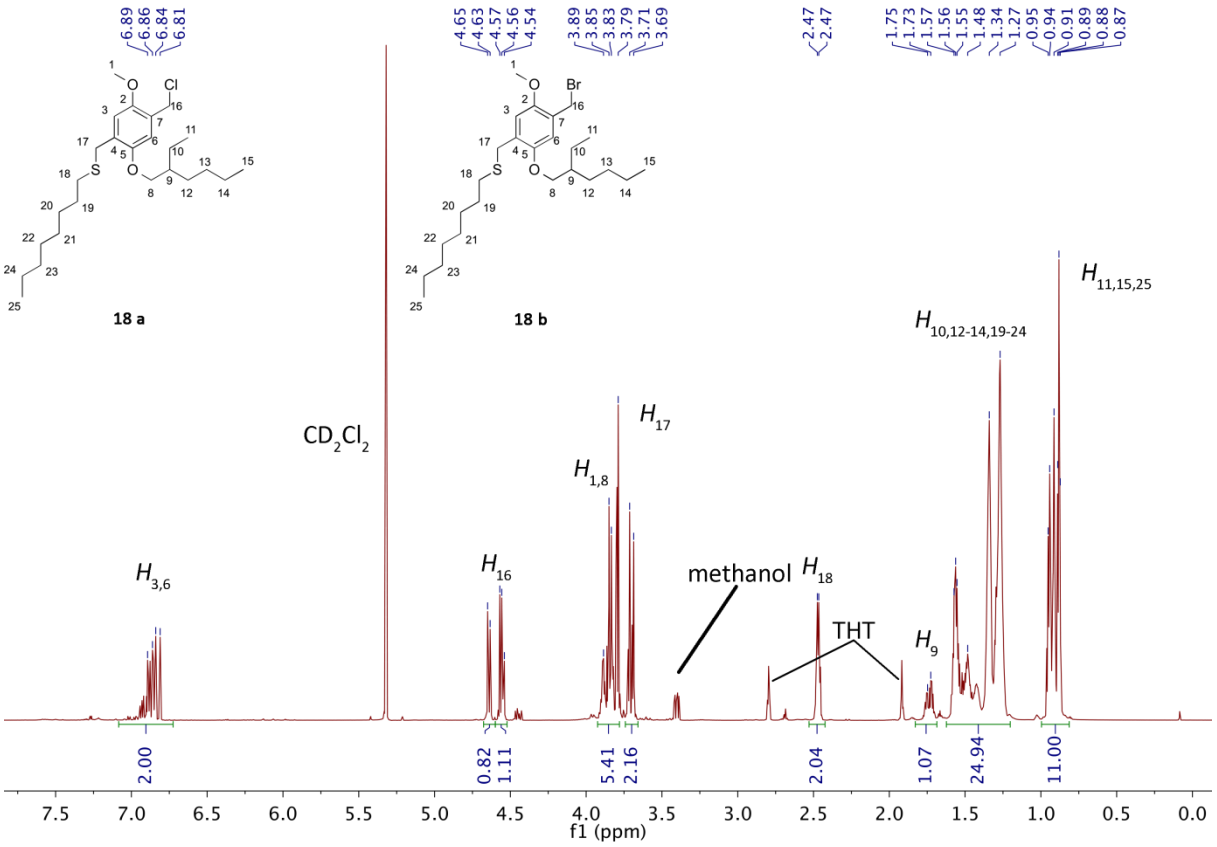


Figure 21: ^{1}H-NMR spectrum of sulfanes **18a**, **18b**, **26a** and **26b** in CD_2Cl_2, for representation only the chemical structure of one isomer is shown. The peaks are assigned to the structure with subscript numbers, traces of solvent are also shown.

The signals at 4.6 ppm and 3.7 ppm can be assigned to the benzylic protons of sulfanes **18a**, **18b**, **26a** and **26b** . This indicates an exchange of both tetrahydrothiophene groups against a halide and thiol **27**.

With the chemical shifts of the benzylic protons it cannot be stated whether chloride or bromide did the exchange of one tetrahydrothiophene group. This is visualized by superimposition of the ^{1}H-NMR spectra of theproduct mixture and both bis-halides **15** and **33**, all measured in CD_2Cl_2 (Figure 22). For a better representation the area between 4.9 ppm and 6.4 ppm was cut out.

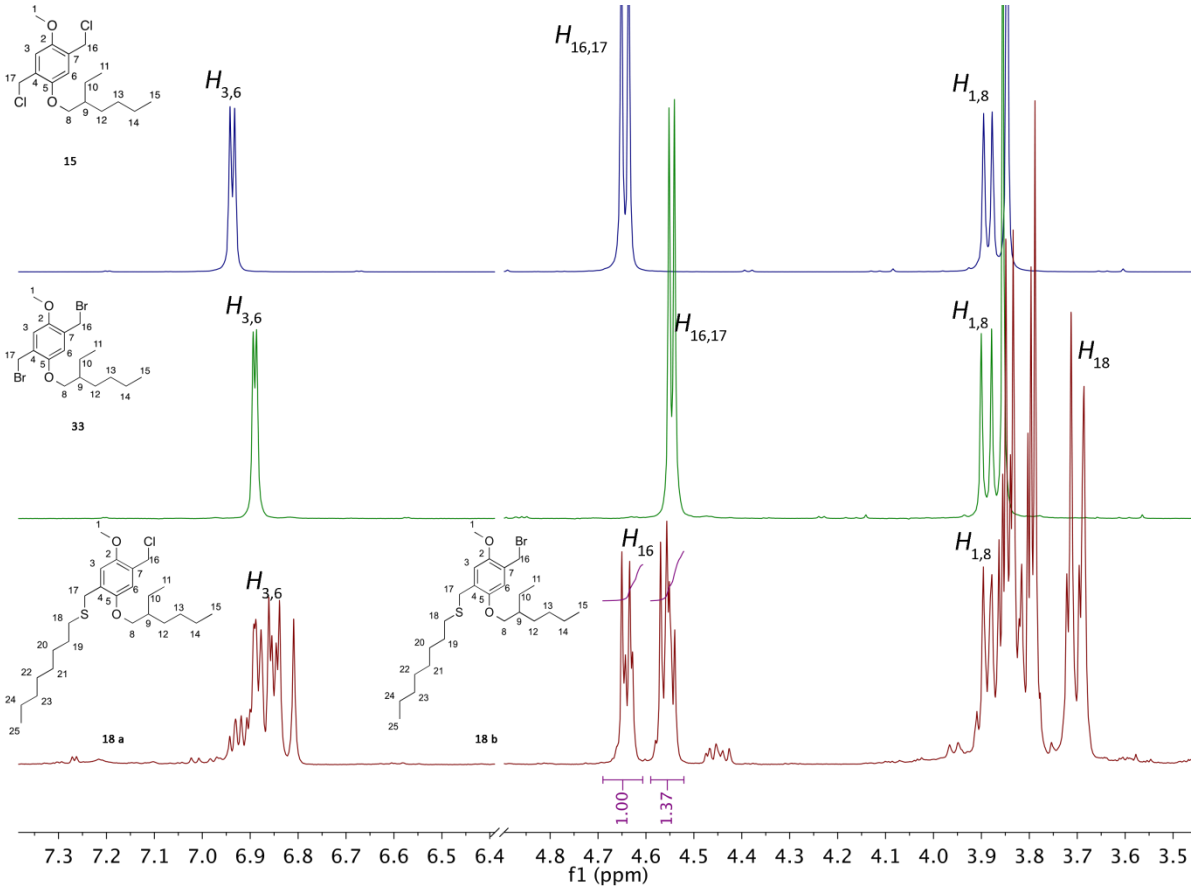


Figure 22: Superimposition of the spectra of the product mixture, bis-chloride **15** and bis-bromide **33** in CD_2Cl_2. The area between 4.9 ppm and 6.4 ppm was cut out, for better representation.

This comparison indicates that the chloro-sulfanes **17a** and **26a** as well as the bromo-sulfanes **17b** and **26b** are formed during the reaction. Using the integrals for the benzylic protons (Figure 22) the ratio of the different halides in the mixture can be determined to 1.00 : 1.37. The reaction gave 42.2 % of chloro-sulfanes **17a** and **26a** and 57.8 % bromo-sulfanes **17b** and **26b** leading to an average molecular mass of 469.58 g·mol^{-1} and average 85.8 % yield (lit.[40]: 96.9 %). As more bromides **17b** and **26b** were formed, the assumption, that chloride binds easier is not supported. It could not be clarified why more of **17b** and **26b** formed.

The successful linkage of thiol **27** to the benzylic carbons has been proven by HMBC-NMR via the correlation of H_{17} and C_{18} (Figure 23).

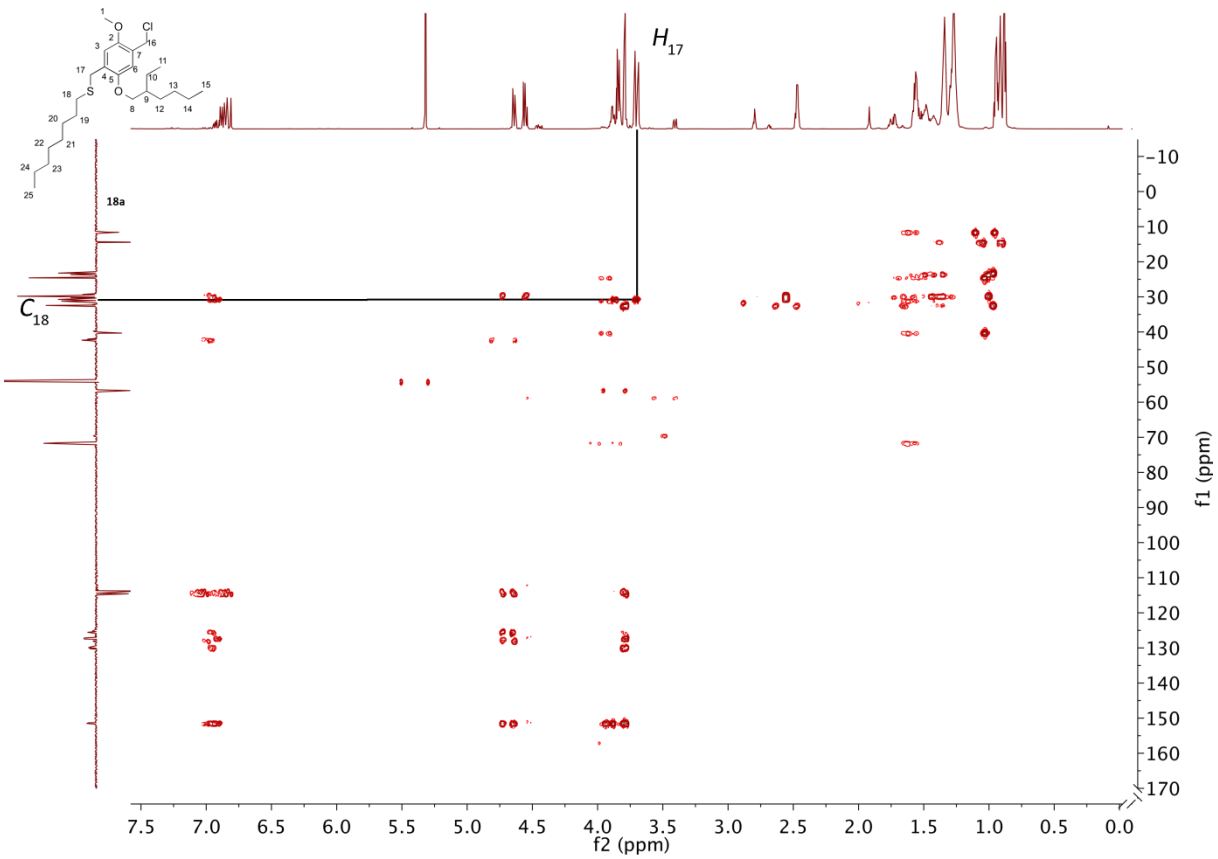
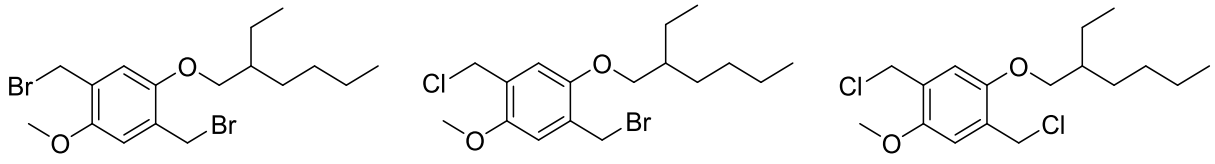


Figure 23: HMBC-NMR correlation spectrum of sulfanes **18a**, **18b**, **26a** and **26b** in CD_2Cl_2. The correlation between H_{17} and C_{18} is highlighted.

To prove the existence of the mono-substituted chloro-products **18a** and **26a** mass spectrometry was performed. The molecular weight of chloride-sulfanes **18a** and **26a** is 443.13 g·mol^{-1} therefore the peak with 442.6 m/z can be assigned to **18a** and **26a** (Figure 25).

The molecular weight of the bromo-sulfanes **18b** and **26b** is 487.58 g·mol^{-1}, the peaks with 486.6 m/z and 975.2 m/z can be assigned to them.

The molecular weights and structures of possible side products that can be formed during the reaction are shown below (Figure 24), other peaks can be assigned to them. Only one isomer of each chemical structure is pictured.



33 422.20 g/mol

37 377.75 g/mol

15 333.29 g/mol

Figure 24: The structures and molecular weights of side products, which can be formed during the reaction are shown.

The bis-bromide **33** is formed through the resubstitution of both tetrahydrothiophene groups by bromide, giving back the starting reactant **33** with a molecular weight of 422.20 g·mol^{-1}, peaks with 422.4 m/z, 847.4 m/z can be assigned to it. The bis-chloride **15** is formed equivalently, giving **15** with a molecular weight of 333.29 g·mol^{-1}, the peak with 995.4 m/z can be assigned to it. The molecular weight of **37**, with both chloride and bromide as substituents is 377.78 g·mol^{-1} the peak with 376.3 m/z can be assigned to it.

The other possible side products were already discussed in chapters 4.2.4 and 4.3.2.

The mass spectrometry shows, that various side products can be formed during the reaction.

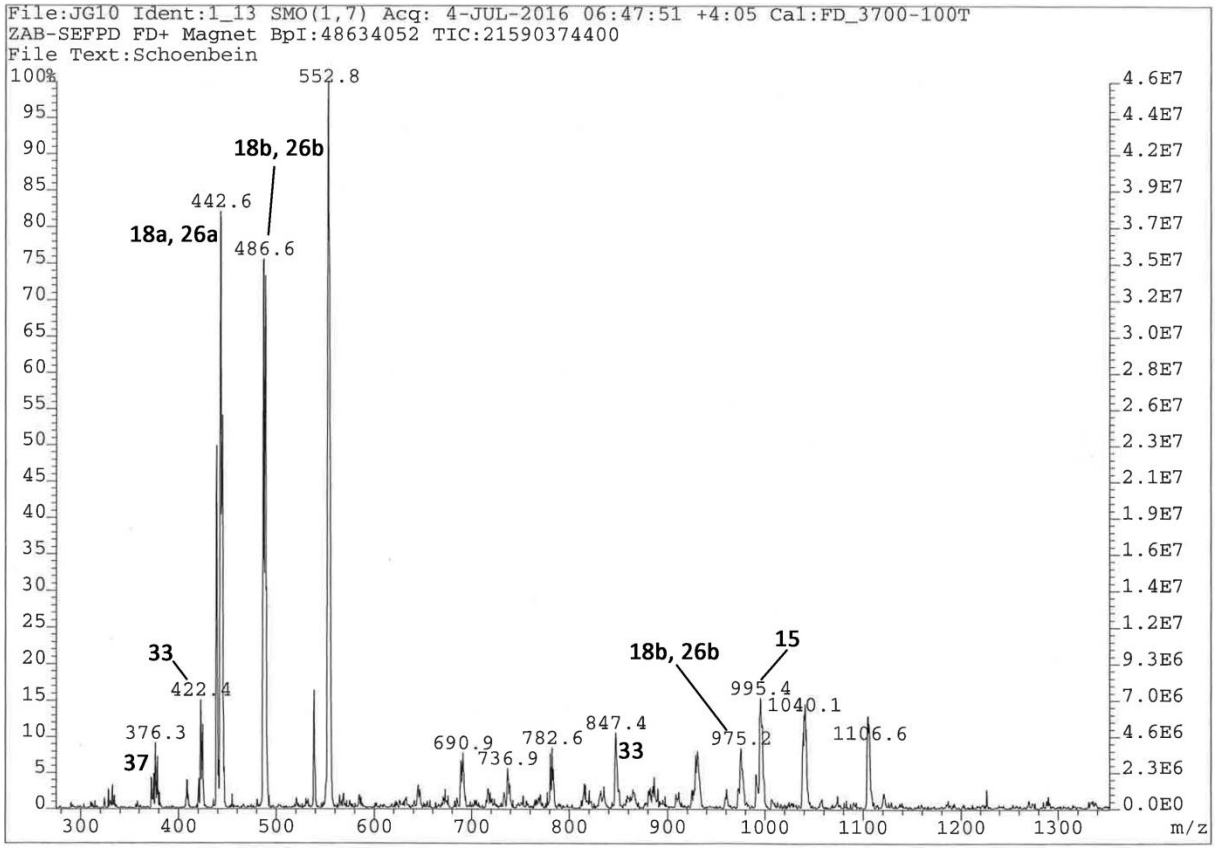
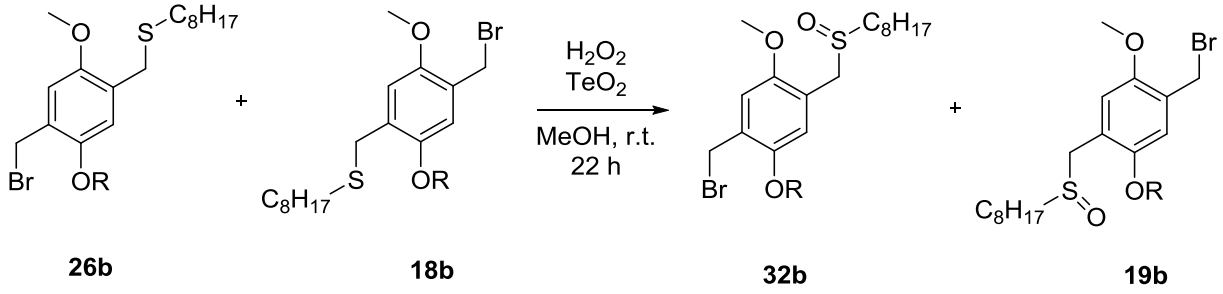


Figure 25: The mass spectrum of the sulfanes **18a**, **18b**, **26a** and **26b** is displayed. A lot of side products were formed in the reaction.

Since a mixture of different substances was obtained in this reaction, the oxidation was only performed with the pure bromo-sulfanes **18b** and **26b**.

4.3.4. Synthesis of the precursor monomers 19b and 32b.

In the following reaction the obtained sulfanes **18b** and **26b** are oxidized with aqueous hydrogen peroxide solution and tellurium dioxide as catalyst in methanol, giving the sulfinyl monomers **19b** and **32b** (Scheme 17).



Scheme 17: Oxidation of sulfanes **18b** and **26b** with aqueous hydrogen peroxide solution and tellurium dioxid in methanol, sulfinyl monomers **19b** and **32b**.

The reaction was executed based on the literature procedure of ANDERSON *et al.*[37]. Tellurium dioxide was added with the intent to facilitate the oxidation of the sulfur atom. The progress of the reaction was monitored via TLC (*n*-hexane : EtOAc, 6 : 4).

The reaction was quenched by adding saturated NaCl solution, as described in literature.[37]

After work-up the ^{1}H-NMR spectrum of the crude product showed that it was a mixture of different compounds (Figure 26). The signals are assigned to the structure with subscript numbers, traces of solvent and unknown peaks were also assigned.

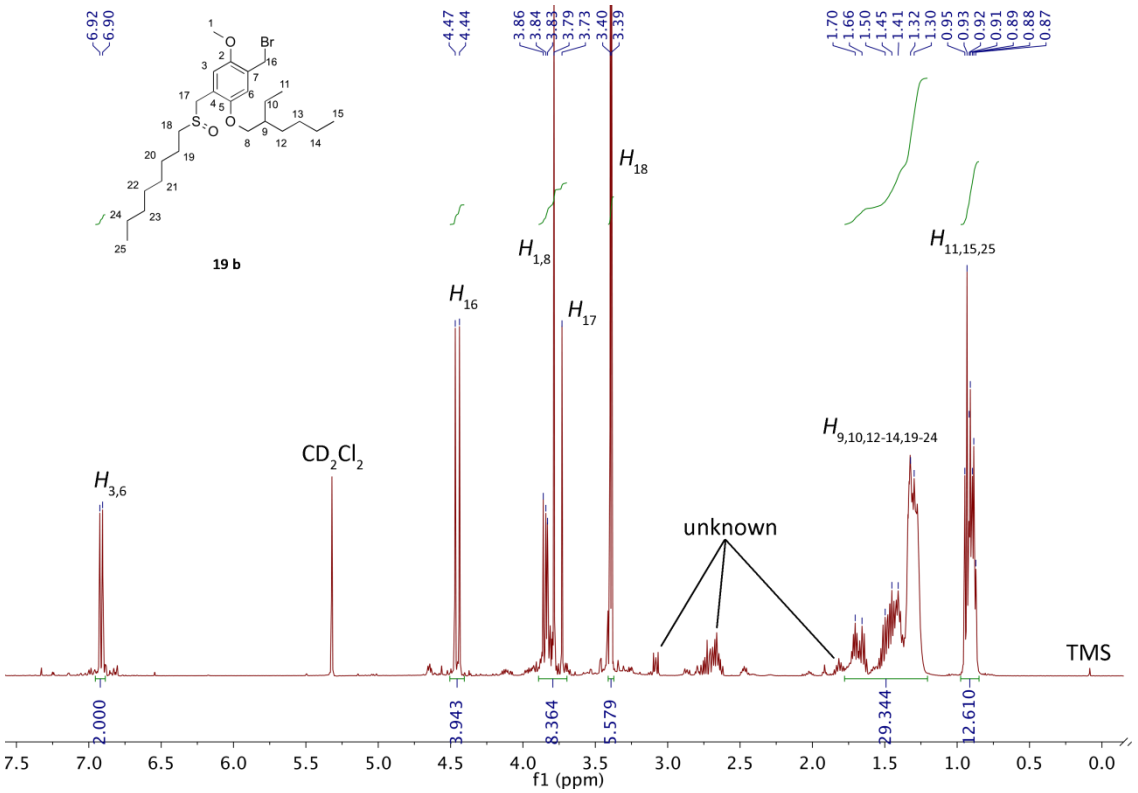


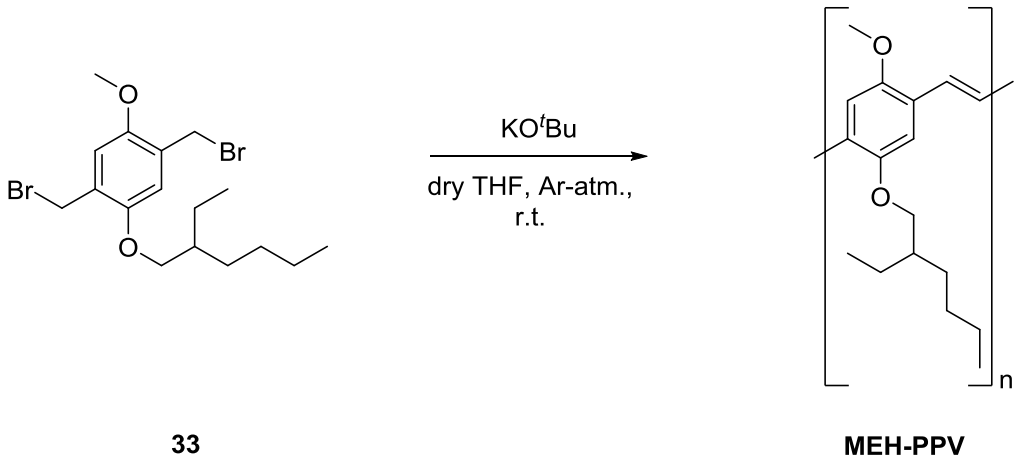
Figure 26: The ^{1}H-NMR spectrum of the obtained crude sulfinyls **19b** and **32b** in CD_2Cl_2, only the chemical structure of one isomer is shown.

A mixture of different compounds is seen in the ^{1}H-NMR spectrum, therefore column chromatography (SiO_2 0.040–0.063 mm, *n*-hexane : EtOAc, 6 : 4) was performed. It was not possible to isolate the product. Degradation of the product is presumed, because TLCs (*n*-hexane : EtOAc, 6 : 4) of the different fractions showed many spots.

Because the pure monomer could not be obtained, neither sulfinyl polymerization towards MEH-PPV-precursor polymer, nor the elimination to fully conjugated MEH-PPV was performed.

4.4. GILCH polymerization

MEH-PPV was synthesized via the GILCH route. The monomer 1,4-bis(bromomethyl)-2-((2-ethylhexyl)oxy)-5-methoxybenzene (**33**) was polymerized in dry tetrahydrofuran (THF) with KO^{t}Bu as base, as it is shown in the Scheme 18.



33 **MEH-PPV**

Scheme 18: Achieving MEH-PPV through the polymerization of bis-bromide **33** in dry THF with base via the GILCH route.

The polymerization was performed with a monomer concentration of 15 mmol·L^{-1} based on the work of SCHWALM.[34] Gelation of the reaction mixture took place immediately after adding the monomer. Precipitation of the geled polymer would have lead to a non-processable polymer, so stirring was continued for another day because this gelation is known to occur due to a very strong entanglement of the polymer chains.[43] As the very high viscosity did not decrease after one day, solvent was added to reduce the concentration. Additional stirring lead to a viscous solution without gel particles. The polymer was precipitated in methanol, filtered off, dried and dissolved in $CHCl_3$ (7 mg·mL^{-1}) in order to precipitate it again. Thereby small oligomers and salt, which might have been trapped during the first precipitation, were washed out, giving 86.7 % yield (lit.[34]: 80–90 %). With PS as standard and THF as eluent gel permeation chromatography (GPC) gave $\bar{M}_n$ = 55 388.30 g·mol^{-1} and $\bar{M}_w$ = 1 086 110.00 g·mol^{-1}.

In Figure 27 the ^{1}H-NMR of the obtained MEH-PPV is shown.

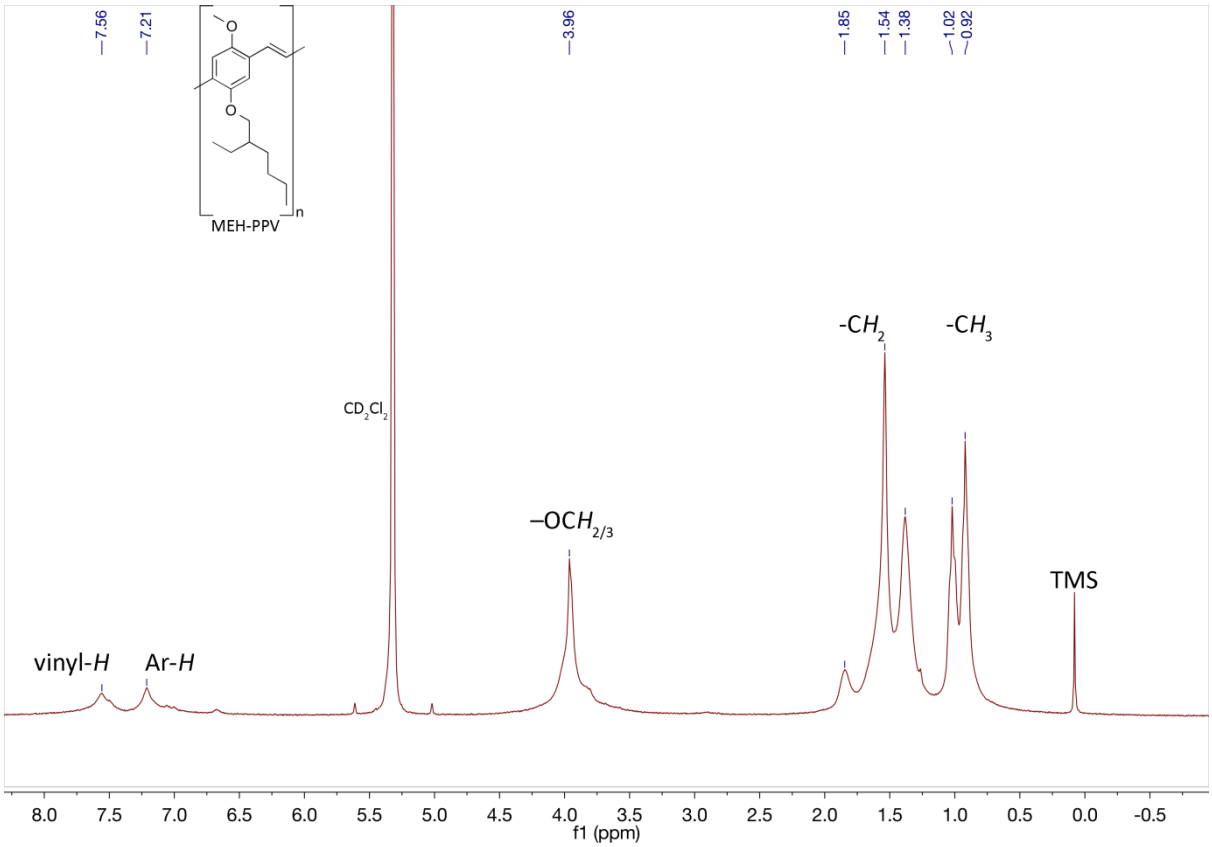


Figure 27: ^{1}H-NMR of the obtained MEH-PPV via the GILCH route in CD_2Cl_2.

5. Conclusion and outlook

The scope of this work was to transfer the synthetic procedure for MDMO-PPV via the sulfinyl route to MEH-PPV. Starting from 4-methoxyphenol (**12**) it was possible to introduce the second lateral sidechain and after a chloromethylation the GILCH monomer **15** was obtained. In the following reactions the GILCH monomers **15** and **33** were used with chloride(**15**) as well as bromide (**33**) as leaving group. The aim was to investigate whether bromide is giving higher yields in the polymerization step than chloride, as it is known from the GILCH route.[34]

The halides were successfully substituted by tetrahydrothiophene, giving the salts **17a** and **17b**. Based on its higher leaving potential, the bromide salt **17b** was formed faster and with higher yield. Afterwards, the configurational isomeric sulfanes **18a**, **18b**, **26a** and **26b** were achieved, by substituting one tetrahydrothiophene group against thiol **27** and the other one by the counter ion chloride or bromide respectively. The bromide sulfanes **18b** and **26b** gave a higher yield than the chloride sulfanes **18a** and **26a**. Additionally, by adding an excess of potassium chloride to this reaction mixture it was investigated, if a quantitative exchange of the halide can enforced. Finally, the sulfinyl monomer was obtained by oxidizing the sulfanes **18a**, **18b**, **26a** and **26b** with hydrogen peroxide in presence of a catalyst. This gave several side products, which could not be isolated and identified, but based on mass spectrometry some possible side products were assumed. To purify the products column chromatography was performed, but neither the products were obtained, nor could the crude products be recovered.Since sulfinyl monomers **19a**, **19b**, **32a** and **32b** were not obtained pure, neither the polymerization, nor the elimination to MEH-PPV were performed.

The scope of further investigations should be to modify the reaction conditions towards higher selectivity, so less side products are formed. The catalyst in the oxidation step of sulfanes **18a**, **18b**, **26a** and **26b** could be changed, for example to triflic anhydride, which shows selectivities bigger than 90 %.[44]

Once the pure sulfinyl monomer is obtained the polymerization can be carried out. Then the non-conjugated polymer and the elimination step can be investigated separately, probably leading to non-geled and thereby better processable polymers. Moreover, it can be investigated if the halides that are used as leaving group are having an effect on the polymerization. As molecular weight is an important factor for smooth films the molecular weights of sulfinyl and GILCH MEH-PPVs should be compared. Finally, it has to be discussed, whether the quality of the obtained MEH-PPV in terms of molecular weight, solubility, degree of elimination/conjugation justifies the additional executed reactions, compared to the GILCH route.

6. Experimental

6.1. Materials and Instrumentation

All chemicals and solvents were purchased from Fischer Scientific or Sigma Aldrich and were used as obtained, if not stated differently. Deuterated solvents were purchased from Deutero GmbH.

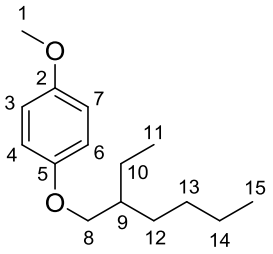
FD mass spectra were recorded with a ZAB2-SE-fpd (VG Instruments) with associated software OPUS B3.7/1X.

SEC measurements were performed in THF with a PSS SecCurity system (Agilent Technologies 1260 Infinity). SDV columns (PSS) with dimensions of 300 × 80 mm, 10 µm particle size, and pore sizes of 106, 104, and 500 Å were employed. The DRI Shodex RI-101 detector (ERC) and UV−vis 1260-VWD detector (Agilent) were used for detection. Calibration was achieved using poly(styrene) standards provided by Polymer Standards Service.

For nuclear magnetic resonance analysis ^{1}H and ^{13}C NMR spectra recorded on a Bruker AVANCE III 300, 500, 700 or 850 MHz spectrometer. All spectra were measured at 298 K. The spectra were calibrated against the solvent signal and analyzed using MestReNova 8 from Mestrelab Research S.L..

6.2. Monomer syntheses

6.2.1. Synthesis of 1-((2-ethylhexyl)oxy)-4-methoxybenzene (14)



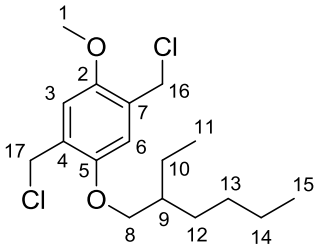
14

4-methoxyphenol (3.75 g, 30.21 mmol, 1.14 eq), KOH (5.20 g, 92.68 mmol, 3.50 eq), tetrabutyl-ammonium bromide (0.37 g, 0.001 mol) and water (30.0 mL) were mixed in a two-necked round-bottom-flask, an Ar-atmosphere was established and the reaction mixture was heated for 1.5 h to 75 °C. To this solution 3-(bromomethyl)heptane (5.11 g, 26.46 mmol, 1.00 eq) was added dropwise. The reaction was heated to reflux for 19 h. After allowing the reaction to cool to ambient temperature, the layers were separated followed by one time extraction of the aqueous phase with hexane (75.0 mL). The organic layer was washed three times with de-ionized (dI) water (300.0 mL), pre-dried with sat. NaCl solution (75.0 mL) and dried over $MgSO_4$. Evaporation of the solvent gave 4.51 g (19.08 mmol, 72.1 %) of an orange oil.

^{1}H-NMR (300 MHz, CD_2Cl_2): δ = 6.83 (m, 4H, $H_{3,4,6,7}$), 3.81 (s, 1H, H_8), 3.79 (s, 1H, H_8), 3.75 (s, 3H, H_1), 1.71 (hept, 1H, H_9), 1.62—1.21 (m, 8H, $H_{10,12,13,14}$), 1.03—0.81 (m, 6H, $H_{11,15}$) ppm.

^{13}C-NMR (75 MHz, CD_2Cl_2): δ = 154.24 (C_2), 154.20 (C_5), 115.87(C_6), 115.05(C_3), 71.69 (C_8), 56.15 (C_1), 40.11 (C_9), 31.12, 29.70, 24.45, 23.69, 14.48 (C_{15}), 11.49 (C_{11}) ppm.

6.2.2. Synthesis of 1,4-bis(chloromethyl)-2-((2-ethylhexyl)oxy)-5-methoxybenzene (15)



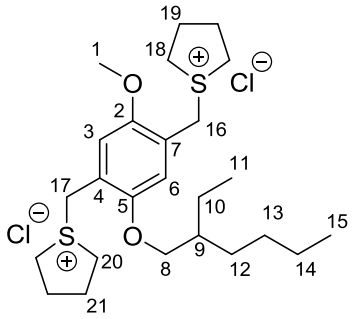
15

1-((2-ethylhexyl)oxy)-4-methoxybenzene (19.48 g, 82.41 mmol, 1.00 eq), paraformaldehyde (6.71 g, 223.44 mol, 2.71 eq) and aq. hydrogen chloride solution (15.91 mL, 637.10 mmol, 7.73 eq) were added to a three-necked round-bottom flask. After an Ar-atmosphere was established, acetic anhydride (82.2 mL, 869.23 mmol, 10.55 eq) was added to this solution and the mixture was heated to 70 °C for 12 h. After cooling to ambient temperature, ice water (500.0 mL) was added and the mixture was extracted two times with $CHCl_3$ (300.0 mL, 50.0 mL). The combined organic layers were combined, washed three times with dI water (600.0 mL), neutralised with sat. $NaHCO_3$ solution (200.0 mL), washed with dI water (100.0 mL) again and pre-dried with sat. NaCl solution (400.0 mL). After drying over $MgSO_4$ the solvent was evaporated giving a yellow solid. After recrystallization from *i*-propanol 20.91 g (64.68 mmol, 78.5 %) of colorless crystals were obtained.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ = 6.94 (s, 1H, H_6), 6.93 (s, 1H, H_3), 4.64 (d, 4H, $H_{16,17}$), 3.89 (s, 1H, H_8), 3.88 (s, 1H, H_8), 3.85 (s, 3H, H_1), 1.75 (hept, 1H, H_9), 1.65—1.20 (m, 8H, $H_{10,12,13,14}$), 0.96 (t, 3H, H_{15}), 0.91 (t, 3H, H_{11}) ppm.

^{13}C-NMR (75 MHz, CD_2Cl_2): δ = 151.52 (C_2), 151.44 (C_5), 127.71, 127.47, 114.67 (C_6), 113.96 (C_3), 71.68 (C_8), 56.78 (C_1), 42.03 ($C_{16,17}$), 41.99 ($C_{16,17}$), 40.16 (C_9), 31.13, 29.64, 24.54, 23.62, 14.42 (C_{15}), 11.54 (C_{11}) ppm.

6.2.3. Synthesis of 1,1'-((2-((2-ethylhexyl)oxy)-5-methoxy-1,4-phenylene)bis(methylene))bis-(tetrahydro-1*H*-thiophen-1-ium)chloride (17a)



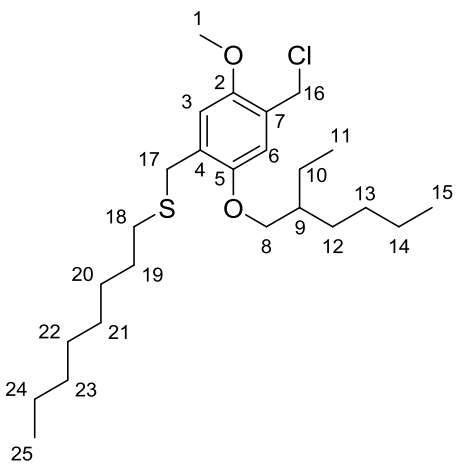
17a

A solution of 1,4-bis(chloromethyl)-2-((2-ethylhexyl)oxy)-5-methoxybenzene (9.95 g, 29.85 mmol, 1.00 eq) in methanol (100.0 mL) was prepared under an Ar-atmosphere and tetrahydrothiophene (13.2 mL, 149.71 mmol, 5.02 eq) was added. The mixture was stirred at room temperature for 6 days, then cooled down with an ice/NaCl bath and acetone (330.0 mL, −20 °C) was added. A colorless solid precipitated, which was filtered off. The solid was dissolved in methanol (30.0 mL) and precipitated in acetone (150.0 mL, −20 °C) again, giving 3.76 g (7.38 mol, 23.3 %) of a colorless solid.

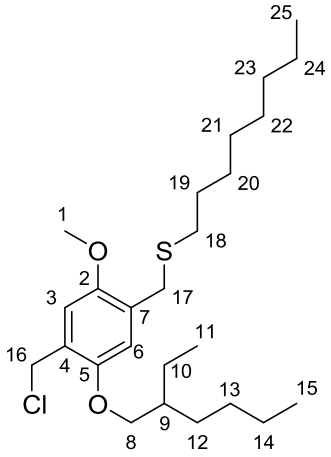
^{1}H-NMR (300 MHz, D_2O): δ = 7.19 (s, 1H, H_6), 7.18 (s, 1H, H_3), 4.50 (s, 4H, $H_{16,17}$), 4.02 (s, 1H, H_8), 4.01 (s, 1H, H_8), 3.89 (s, 3H, H_1), 3.56-3.38 (m, 8H, $H_{18,20}$), 2.38-2.24 (m, 8H, $H_{19,21}$), 1.77 (hept, 1H, H_9), 1.52—1.28 (m, 8H, $H_{10,12,13,14}$), 0.90 (t, 3H, H_{15}), 0.85 (t, 3H, H_{11}) ppm.

^{13}C-NMR (176 MHz, D_2O): δ = 151.87 (C_2), 151.60 (C_5), 119.79 , 119.67, 116.07 (C_6), 115.50 (C_3), 71.62 (C_8), 56.34 (C_1), 43.10 ($C_{18,20}$), 43.03 ($C_{18,20}$), 41.68 ($C_{16,17}$), 41.55 ($C_{16,17}$), 38.81 (C_9), 30.00, 28.43 ($C_{19,21}$), 28.35 ($C_{19,21}$), 23.55, 22.42, 13.41 (C_{15}), 10.43 (C_{11}) ppm.

6.2.4. Synthesis of (4-(chloromethyl)-5-((2-ethylhexyl)oxy)-2-methoxybenzyl)(octyl)-sulfane (26a) and (4-(chloromethyl)-2-((2-ethylhexyl)oxy)-5-methoxybenzyl)(octyl)-sulfane (18a).



18a



26a

A solution of 1,1'-((2-((2-ethylhexyl)oxy)-5-methoxy-1,4-phenylene)bis(methylene))bis(tetrahydro-1*H*-thiophen-1-ium)chloride (2.99 g, 6.03 mmol, 1.00 eq) in dry methanol (18.0 mL) and a solution of *n*-octanethiol (1.05 mL, 6.03 mmol, 1.00 eq) with KO^{t}Bu (699.76 mg, 6.24 mmol, 1.00 eq) in dry methanol (12.0 mL) were prepared under Ar-atmosphere in two flasks. The base solution was stirred at room temperature for 30 minutes added dropwise to the solution of x. The reaction was allowed to stir for three hours at room temperature. The solvent was evaporated, octane (5 x 15.0 mL) was added to remove tetrahydrothiophene via azeotropic distillation. The crude product was dissolved in CH_2Cl_2 (12.0 mL), washed three times with diluted NaCl solution (sat. NaCl solution : H_2O, 1 : 10; 12 mL), dried over $MgSO_4$ and the solvent was evaporated. Octane (2 x 15.0 mL) was added to remove traces of tetrahydrothiophene via azeotropic distillation, giving 1.58 g (3.56 mmol, 59.0 %) of a yellow oil.

^{1}H-NMR (300 MHz, CD_2Cl_2): δ = 6.93 (s, 1H, H_6), 6.89 (s, 1H, H_3), 4.65 (s, 2H, H_{16}), 3.88 (s, 1H, H_8), 3.88 (s, 1H, H_8), 3.83 (s, 3H, H_1), 3.71 (s, 2H, H_{17}), 2.48 (t, 2H, H_{18}), 1.72 (hept, 1H, H_9), 1.59—1.27 (m, 20H, $H_{10,12\text{-}14,19\text{-}24}$), 0.97-0.86 (m, 9H, $H_{11,15,25}$) ppm.

^{13}C-NMR (214 MHz, CD_2Cl_2): δ = 151.52 (C_2), 151.46 (C_5), 127.48, 127.17, 114.65 (C_6), 113.85 (C_3), 71.73 (C_8), 56.75 (C_1), 42.15 (C_{16}), 40.25 (C_9), 32.61(C_{18}), 30.15 (C_{17}), 29.82, 24.58, 23.67, 23.24, 14.44 (C_{15}), 11.57 (C_{11}) ppm.

6.2.5. Synthesis 1-(chloromethyl)-5-((2-ethylhexyl)oxy)-2-methoxy-4-((octylsulfinyl)methyl)-benzene (32a) and 1-(chloromethyl)-2-((2-ethylhexyl)oxy)-5-methoxy-4-((octylsulfinyl)-methyl)benzene (19a).

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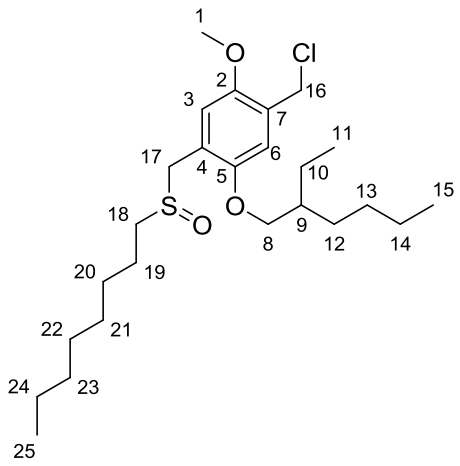
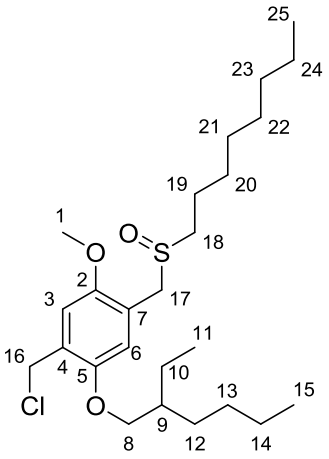


19a

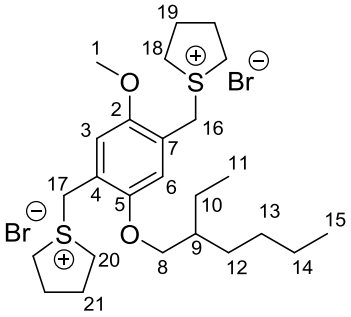


32a

(4-(chloromethyl)-5-((2-ethylhexyl)oxy)-2-methoxybenzyl)(octyl)sulfane (1.58 g, 3.56 mmol, 1.00 eq) was mixed with tellurium dioxide (94.52 mg, 0.21 mmol, 0.06 eq) in methanol (24.5 mL) and aq. H_2O_2 solution (35 %, 1.7 mL, 55.56 mmol, 15.61 eq) was added. The mixture was stirred at room temperature for 22 hours, then sat. NaCl solution (13.0 mL) was added. The reaction mixture was extracted three times with $CHCl_3$ (15.0 mL) and dried over $MgSO_4$. Evaporation of the solvent gave 1.40 g (3.05 mmol, 85.7 %) of the raw product. It was tried to isolate the pure product via column chromatography (SiO_2; *n*-hexane : EtOAc, 6 : 4), but this did not work and the crude product could not be recovered.

^{1}H-NMR (300 MHz, CD_2Cl_2): δ = 6.94 (s, 1H, H_6), 6.90 (s, 1H, H_3), 4.46 (s, 2H, H_{16}), 3.84 (s, 1H, H_8), 3.83 (s, 1H, H_8), 3.80 (s, 3H, H_1), 3.39 (s, 2H, H_{17}), 2.60 (t, 2H, H_{18}), 1.69 (hept, 1H, H_9), 1.55—1.27 (m, 20H, $H_{10,12\text{-}14,19\text{-}24}$), 0.95-0.85 (m, 9H, $H_{11,15,25}$) ppm.

6.2.6. Synthesis of 1,1'-((2-((2-ethylhexyl)oxy)-5-methoxy-1,4-phenylene)bis(methylene))bis-(tetrahydro-1*H*-thiophen-1-ium)bromide (17b).



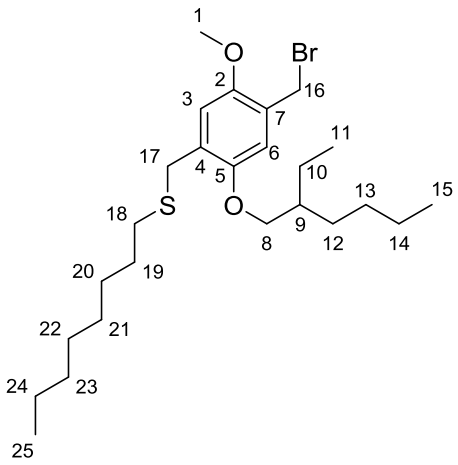
17b

Under Ar-atmosphere a solution of 1,4-bis(bromomethyl)-2-((2-ethylhexyl)oxy)-5-methoxy-benzene (15.04 g, 35.62 mmol, 1.00 eq) in methanol (120.0 mL) was prepared. To this solution tetrahydrothiophene (16.1 mL, 182.60 mmol, 5.12 eq) was added dropwise, the mixture was stirred at room temperature for 4 days and afterwards cooled down with an ice/NaCl bath. Acetone (400.0 mL, −20 °C) was added and a colorless solid precipitated, which was filtered off, giving 11.09 g (18.53 mmol, 52.1 %) of colorless crystals.

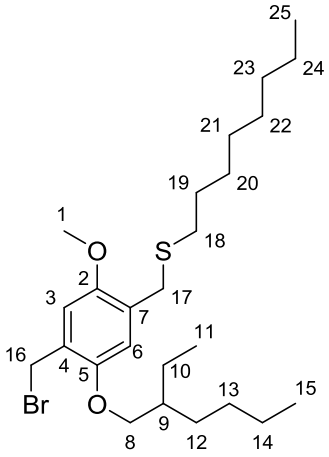
^{1}H-NMR (300 MHz, D_2O): δ = 7.21 (s, 2H, $H_{3,6}$), 4.51 (s, 4H, $H_{16,17}$), 4.03 (s, 1H, H_8), 4.01 (s, 1H, H_8), 3.90 (s, 3H, H_1), 3.57-3.40 (m, 8H, $H_{18,20}$), 2.36-2.25 (m, 8H, $H_{19,21}$), 1.78 (hept, 1H, H_9), 1.52—1.29 (m, 8H, $H_{10,12,13,14}$), 0.91 (t, 3H, H_{15}), 0.86 (t, 3H, H_{11}) ppm.

^{13}C-NMR (176 MHz, D_2O): δ = 151.83 (C_2), 151.56 (C_5), 119.74 , 119.61, 116.07 (C_6), 115.47 (C_3), 71.61 (C_8), 56.34(C_1), 43.11 ($C_{18,20}$), 43.03 ($C_{18,20}$), 41.67, 41.54, 38.78(C_9), 29.98, 28.44 ($C_{19,21}$), 28.36 ($C_{19,21}$), 23.53, 22.42, 13.42 (C_{15}), 10.43 (C_{11}) ppm.

6.2.7. Synthesis of (4-(bromomethyl)-5-((2-ethylhexyl)oxy)-2-methoxybenzyl)(octyl)-sulfane (26b) and (4-(bromomethyl)-2-((2-ethylhexyl)oxy)-5-methoxybenzyl)(octyl)-sulfane (18b).



18b



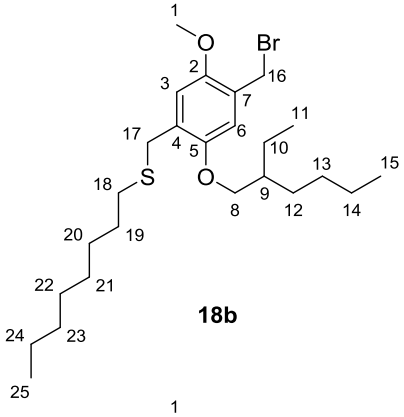
26b

In two flasks a solution of 1,1'-((2-((2-ethylhexyl)oxy)-5-methoxy-1,4-phenylene)bis-(methylene))bis(tetrahydro-1*H*-thiophen-1-ium)bromide (1.00 g, 1.67 mmol, 1.00 eq) in dry MeOH (6.0 mL) and a solution of *n*-octanethiol (0.29 mL, 1.67 mmol, 1.00 eq) with KO^{t}Bu (210.27 g, 1.87 mmol, 1.12 eq) in dry methanol (4.7 mL) were prepared under an Ar-atmosphere. The base solution was stirred at room temperature for 24 minutes and added dropwise to the solution of x. The mixture was stirred for three hours at room temperature, then the solvent was evaporated, octane (5 x 25.0 mL) was added to remove tetrahydrothiophene via azeotropic distillation. This gave colorless and yellow solids, which were dissolved in CH_2Cl_2 (6.0 mL), washed three times with diluted NaCl solution (sat. NaCl solution : H_2O, 1 : 10; 12.0 mL), dried over $MgSO_4$. Evaporation of the solvent gave 640.84 mg (1.31 mmol, 78.4 %) of a viscous yellow oil, which crystallized after 24 hours.

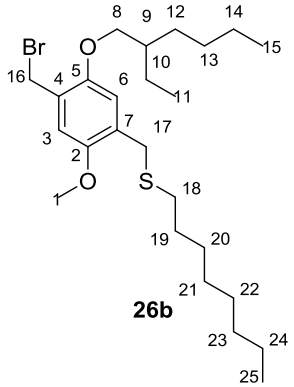
^{1}H-NMR (300 MHz, CD_2Cl_2): δ = 6.85 (s, 1H, H_6), 6.84 (s, 1H, H_3), 4.57 (s, 2H, H_{16}), 3.85 (s, 1H, H_8), 3.83 (s, 1H, H_8), 3.79 (s, 3H, H_1), 3.70 (s, 2H, H_{17}), 2.47 (t, 2H, H_{18}), 1.72 (hept, 1H, H_9), 1.57—1.27 (m, 20H, $H_{10,12\text{-}14,19\text{-}24}$), 0.94-0.86 (m, 9H, $H_{11,15,25}$) ppm.

^{13}C-NMR (214 MHz, CD_2Cl_2): δ = 151.60 (C_2), 151.44 (C_5), 128.10, 127.32, 114.68 (C_6), 113.98 (C_3), 71.55 (C_8), 56.76 (C_1), 40.24 (C_9), 32.42 (C_{18}), 30.76 (C_{17}), 29.81 (C_{16}), 24.58, 23.65, 23.23, 14.44 (C_{15}), 11.57 (C_{11}) ppm.

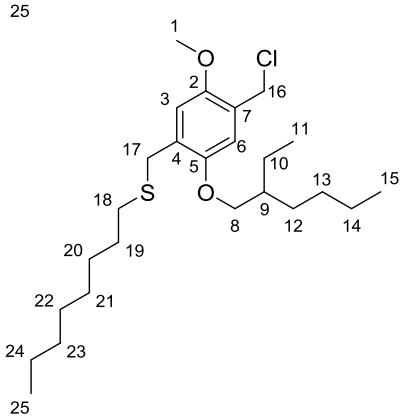
6.2.8. Synthesis of (4-(chloromethyl)-5-((2-ethylhexyl)oxy)-2-methoxybenzyl)(octyl)-sulfane (26a), (4-(chloromethyl)-2-((2-ethylhexyl)oxy)-5-methoxybenzyl)(octyl)-sulfane (18a), (4-(chloromethyl)-5-((2-ethylhexyl)oxy)-2-methoxybenzyl)(octyl)-sulfane (26b) and (4-(chloromethyl)-2-((2-ethylhexyl)oxy)-5-methoxybenzyl)(octyl)-sulfane (18b).



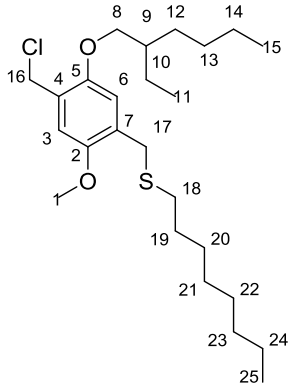
18b



26b



18a

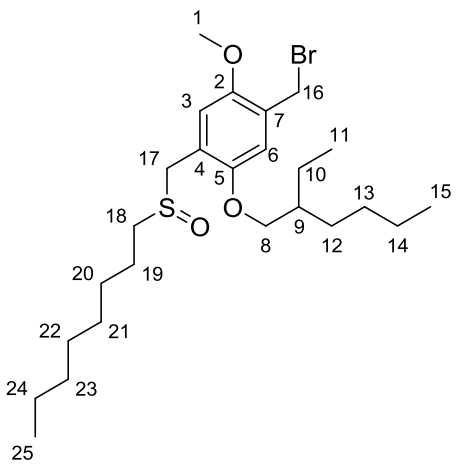


26a

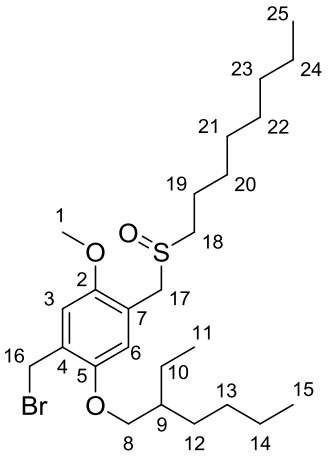
1,1'-((2-((2-ethylhexyl)oxy)-5-methoxy-1,4-phenylene)bis(methylene))bis(tetrahydro-1*H*-thiophen-1-ium)bromide (1.01 g, 1.69 mmol, 1.00 eq) was mixed with KCl (403.20 mg, 5.41 mmol, 3.20 eq) in dry methanol (6.0 mL). In a second flask *n*-octanethiol (0.29 mL, 1.67 mmol, 0.99 eq) was mixed with KO^{t}Bu (210.27 mg, 1.87 mmol, 1.12 eq) in dry MeOH (4.7 mL), both under an Ar-atmosphere. The base solution was stirred at room temperature for 24 minutes and added dropwise to the solution of x. The reaction was stirred at room temperature for three hours, then the solvent was evaporated and octane (5 x 5.0 mL) was added to remove tetrahydrothiophene via azeotropic distillation. The crude product was dissolved in CH_2Cl_2 (6.0 mL), diluted NaCl solution (sat. NaCl solution : H_2O, 1 : 10; 3.0 mL) was added, the solution turned orange overnight and showed fluorescence at 365 nm. The solution was washed three times with diluted NaCl solution (sat. NaCl solution : H_2O, 1 : 10; 4.0 mL), dried over $MgSO_4$ and the solvent was evaporated. Octane (10.0 mL) was added twice to this oil and distilled again. This gave 682.69 mg (1.54 mmol, 92.2 %) of an orange solid.

^{1}H-NMR (850 MHz, CD_2Cl_2): δ = 6.89 (s, 1H, H_6), 6.84 (s, 1H, H_3), 4.60 (s, 2H, H_{16}), 3.85 (s, 1H, H_8), 3.83 (s, 1H, H_8), 3.79 (s, 3H, H_1), 3.70 (s, 2H, H_{17}), 2.47 (t, 2H, H_{18}), 1.73 (hept, 1H, H_9), 1.57—1.27 (m, 20H, $H_{10,12\text{-}14,19\text{-}24}$), 0.94-0.87 (m, 9H, $H_{11,15,25}$) ppm.

6.2.9. Synthesis 1-(bromomethyl)-2-((2-ethylhexyl)oxy)-5-methoxy-4-((octylsulfinyl)methyl)-benzene (32b) and 1-(bromomethyl)-5-((2-ethylhexyl)oxy)-2-methoxy-4-((octylsulfinyl)-methyl)benzene (19b).



19b



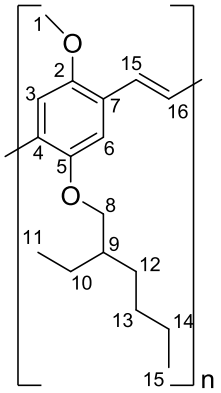
32b

A solution of (4-(bromomethyl)-5-((2-ethylhexyl)oxy)-2-methoxybenzyl)(octyl)sulfane (2.45 g, 5.03 mmol, 1.00 eq) and tellurium dioxide (108.55 mg, 0.68 mmol, 0.14 eq) in methanol (32.0 mL) were prepared. To this solution was added aq. H_2O_2 solution (35 %, 0.9 mL, 29.47 mmol, 5.64 eq), leading to a turbid reaction mixture. After three days, the solution became yellow and a solid precipitated. To the reaction mixture sat. NaCl solution (30.0 mL) was added and extracted three times with $CHCl_3$ (30.0 mL), then dried over $MgSO_4$. Evaporation of the solvent gave 2.31 g (4.59 mmol, 91.4 %) of the raw product. It was tried to isolate the pure product via column chromatography (SiO_2; *n*-hexane : EtOAc, 6 : 4), the product could not be isolated.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ = 6.92 (s, 1H, H_6), 6.90 (s, 1H, H_3), 4.46 (s, 2H, H_{16}), 3.84 (s, 1H, H_8), 3.83 (s, 1H, H_8), 3.79 (s, 3H, H_1), 3.73 (s, 2H, H_{17}), 3.39 (t, 2H, H_{18}), 1.70 (hept, 1H, H_9), 1.56—1.28 (m, 20H, $H_{10,12\text{-}14,19\text{-}24}$), 0.95-0.86 (m, 9H, $H_{11,15,25}$) ppm.

6.3. Polymer syntheses

6.3.1. Synthesis of Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]



MEH-PPV

A solution of 1,4-bis(bromomethyl)-2-((2-ethylhexyl)oxy)-5-methoxybenzene (0.63 g, 1.492 mol, 1.00 eq) in dry THF (80.0 mL) and a solution of KO^{t}Bu (0.84 g, 7.486 mol, 5.02 eq) in dry THF (20.0 mL) were prepared at room temperature under Ar-atmosphere and a gas exchange with Ar was performed for both solutions. The base solution was added over one minute to the stirred monomer solution. The mixture was allowed to stir at room temperature for one day. THF (40.0 mL) was added to the solution and stirred for an additional day. Afterwards, the mixture was heated to reflux for 2.5 hours. After stirring for additional three days at room temperature, the solution was poured in to methanol (300.0 mL) and the precipitated red polymer fibres were filtered off. The collected polymer was dried at 40 °C in vacuum, then dissolved in $CHCl_3$ (7 mg·mL^{-1}) under Ar-atmosphere and exclusion from light. The polymer was precipitated in methanol (120.0 mL), the red fibres were filtered off and dried at 40 °C in vacuum giving 310.05 mg (1.12 mmol, 79.9 % yield, based on the repeat unit).

^{1}H-NMR (300 MHz, CD_2Cl_2): δ = 7.56 (2H, $H_{15,16}$), 7.21 (1H, $H_{3,6}$), 3.96 (5H, $H_{1,8}$), 1.85 (1H, H_9), 1.54—1.27 (m, 8H, $H_{10,12\text{-}14}$), 1.02-0.92 (m, 6H, $H_{11,15}$) ppm.

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List of abbreviations

MEH	2-((2-ethyl¬hexyl)¬oxy)-5-methoxy-
MDMO	2-methoxy-5-(3',7'-di¬methyl¬octyl¬oxy)-
4-MP	4-methoxyphenol
aq.	Aqueous
atm.	Atmosphere
δ	chemical shift
conc.	Concentrated
dI	Deionized
eq	Equivalents
et al.	Lat.: *et alii* and others
FD	Field desorption
gpc	Gel permeation chromatography
HSAB	Hard and soft acids and bases
HMBC	Hetero nuclear multiple bond correlation
HOMO	Highest occupied molecular orbital
H_2O_2	Hydrogen peroxide
L	Leaving group
LUMO	lowest unoccupied molecular orbital
M_w	Mass average molar mass
MeOH	Methanol
S_N	Nucleophilic substitution
M_N	Number average molar mass
NMR	Nuclear magnetic resonance spectroscopy
OFET	Organic field effect transistor
OLED	Organic light emitting diode
OPV	Organic photovoltaic device
PPV	Poly(*p*-phenylene vinylene)
PPV	Poly-(p-phenylen-vinylen)e
PDI	Polydispersity index
KOH	Potassium hydroxide
KO^tBu	Potassium-*tert*-butoxide
sat.	Saturated
SM	Small molecule
NaCl	Sodium chloride
THF	Tertrahydrofuran
THT	Tetrahydrothiophene
TBABr	Tetra-n-butylammonium bromide
TLC	Thin layer chromatography
Alq3	Tris(8-hydoxychinolin)-aluminium(III)
Ir(ppy)3	Tris[2-phenylpyridinato-C^2,*N*]iridium(III)
2D NMR	Two-dimensional nuclear magnetic resonance spectroscopy

List of schemes

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