Synthesis and Characterization of Sequence-Defined Stiff Oligomers Using the Sonogashira Reaction

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Meinen Eltern und Nico

"To achieve great things, two things are needed:
a plan, and not quite enough time."

after Leonard Bernstein

Die vorliegende Arbeit wurde von Januar 2015 bis Juli 2018 unter Anleitung von Prof. Dr. Michael A. R. Meier am Institut für Organische Chemie (IOC) des Karlsruher Instituts für Technologie (KIT) durchgeführt.

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Karlsruhe, 19.07.2018

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Abstract

Conjugated rod-like oligomers are interesting compounds for electronic applications. Several iterative procedures for the synthesis of monodisperse oligo(phenylene ethynylene)s (OPEs) were described, but only one example to sequence-defined OPEs is known to date. Sequence-defined conjugated oligomers offer the unique opportunity to investigate quantitative structure-property relationships.

In this work, a solution-based, linear procedure to sequence-defined OPEs is introduced. Therefore, several aromatic building blocks exhibiting a halogen and a protected triple bonds were synthesized. Different dialkoxy side chains served as solubilizing groups, displaying electron donating features. Furthermore, building blocks with electron accepting properties were prepared.

The rod-like oligomers were established by Sonogashira cross-coupling and subsequent deprotection of the triple bond enabling a further Sonogashira reactions in this iterative sequence. Initially, phenylacetylene as starting unit was converted with a building block yielding a monomer. With the formerly mentioned procedure, a monodisperse as well as a sequence-defined rod-like pentamer was synthesized over ten steps. The overall yield of the monodisperse pentamer amounted to 18% and a scale of 116 milligrams; the sequence-defined pentamer exhibited an overall yield of 3.2% and a scale of 73.6 milligrams. The final products and their respective intermediates were fully characterized by ^{1}H and ^{13}C NMR, mass and IR spectroscopy. Additionally, SEC and DSC were performed and the photophysical properties were investigated by UV/Vis spectroscopy.

A direct oligomerization approach with a chain stopper to monodisperse rod-like oligomers resulted in a broad oligomer mixture and clearly justifies the iterative reaction procedure.

In a second part of this work, monodisperse rod-like oligomers were connected to dyes with thermally activated delayed fluorescence function by Sonogashira cross-coupling. The oligomer-dye conjugates were fully characterized and might be useful compounds to investigate optoelectronic processes in organic solar cells.

Kurzzusammenfassung

Konjugierte Stäbchenmoleküle sind interessante Verbindungen für elektronische Anwendungen. Mehrere iterative Syntheseverfahren zu monodispersen Phenylalkin-Oligomeren wurden publiziert, aber nur ein Beispiel zu derartigen sequenzdefinierten Oligomeren existiert. Dabei könnten sequenzdefinierte, konjugierte Oligomere einen wichtigen Beitrag zur Erforschung von Struktur-Eigenschafts-Beziehungen liefern.

In dieser Arbeit wird ein lineares Syntheseverfahren zu sequenzdefinierten Phenylalkin-Oligomeren in Lösung vorgestellt. Dafür wurden verschiedene Bausteinmoleküle mit einem Halogen und einer geschützten Dreifachbindung synthetisiert. Verschiedene Dialkyloxysubstituenten zur besseren Löslichkeit weisen zusätzlich elektronenschiebende Eigenschaften auf. Des Weiteren wurden Elektronenakzeptor-Bausteine hergestellt.

Die Stäbchenmoleküle wurden über Zyklen von Sonogashira Kreuzkupplung und anschließender Entschützung der Dreifachbindung realisiert. Zunächst wurde Phenylacetylen als Starteinheit mit einem Bausteinmolekül umgesetzt und das entsprechende Monomer erhalten. Mit dem vorgestellten Syntheseverfahren konnten ein monodisperses und ein sequenzdefiniertes Pentamer in jeweils zehn Reaktionsschritten erhalten werden. Die Ausbeute für das monodisperse Pentamer belief sich dabei auf 18% und 116 Milligramm. Für das sequenzdefinierte Pentamer wurde eine Ausbeute von 3.2% und 73.6 Milligramm erhalten. Die finalen Produkte sowie die entsprechenden Intermediate wurden vollständig mit ^{1}H und ^{13}C-NMR, IR-Spektroskopie und Massenspektrometrie charakterisiert. Zusätzlich wurde SEC und DSC durchgeführt und die photophysikalischen Eigenschaften mit UV/Vis-Spektroskopie untersucht.

Ein direkter Oligomerisierungsversuch zu monodispersen Stäbchenmolekülen mit einem Kettenstopper führte zu einem Gemisch aus vielen Oligomeren und rechtfertigt die iterative Reaktionsführung.

In dieser Arbeit wurden außerdem Stäbchenmoleküle mit Farbstoffen, die eine thermisch aktivierte verzögerte Fluoreszenz aufweisen, mittels Sonogashira Reaktion verknüpft und vollständig charakterisiert. Mit diesen Verbindungen könnten optoelektronische Vorgänge in organischen Solarzellen untersucht werden.

Contents

1. Nature versus Synthetic Chemistry – an Introduction

According to the international union of pure and applied chemistry (IUPAC), a polymer is “a substance composed of macromolecules” revealing that it usually consists of molecules with varying molecular weight.[1] The synthesis of a monodisperse macromolecule *i.e.* a high molecular weight compound with distinct molecular weight, is still a challenge for polymer chemists. In nature, however, a few macromolecules such as peptides, proteins or deoxy- and ribonucleic acid (DNA/RNA) exhibit not only a defined molecular weight but rather a definite arrangement of monomer units (*i.e.* sequence). These macromolecules are therefore termed “sequence-defined”.[2] Sometimes, the expression “sequence” is exclusively used for the previously mentioned compounds of biological origin.[3] Nowadays, it is also utilized for synthetic representatives – either oligomers or polymers – with a definite order of monomer units.[4] Whilst synthetic chemists can theoretically apply an unlimited quantity of building blocks, sequence-defined macromolecules in nature are restricted to the natural amino acids in peptides or proteins and the purine and pyrimidine bases in RNA or DNA. The building set for peptides and proteins totals to more than 20 amino acids, *i.e.* 20 canonic and at least two further proteinogenic ones.[5] This differentiation is based on the biosynthesis of amino acids, the so called gene expression. Interestingly, DNA – and more specifically a triplet of nucleobases – serves as code for amino acids and through transcription to messenger RNA (mRNA) and translation, peptides are formed.[6] The schematic overview of the gene expression is depicted in Figure 1: DNA is a polynucleotide, which appears as a double helix.[7] A nucleotide consists of a phosphate, a pentose (*i.e.* deoxyribose for DNA, ribose for RNA) and a purine or pyrimidine base. DNA is composed of the purine bases adenine and guanine and the pyrimidine bases cytosine and thymine (compare Figure 1 on the right). The bases are complementary, forming two hydrogen bonds between adenine and thymine and three hydrogen bonds between guanine and cytosine.[7] These Watson-Crick base pairs enable, *inter alia*, the double helix structure. The nucleotides are connected by phosphodiester bonds, which are formed by the enzyme DNA polymerase in biological systems.[8] Through transcription, the information of the DNA is transferred to mRNA.[9] RNA

differs from DNA not only in the sugar component but also in the nucleobases and occurs usually as a single strand.[10] The complementary base of adenine is uracil instead of thymine (depicted in orange in Figure 1). Although RNA appears as a single-stranded polynucleotide, it can exhibit a secondary structure, *e.g.* by pairing complementary bases (Watson-Crick) within the same single-strand. The mRNA is a special form of RNA, which is translated within the ribosome complex to the respective peptide or protein.[11] Interestingly, the ribosome itself consists to a significant part of ribosomal RNA (rRNA) and is therefore a rRNA/protein complex. Translation requires a further RNA species: the transfer RNA (tRNA), which carries the respective amino acids.[12] Furthermore, the tRNA exhibits a specific tertiary structure with an anticodon loop for the complementary mRNA. As mentioned earlier, three nucleobases code one amino acid: $4^3 = 64$ combinations are therefore theoretically possible, but only 20 canonic amino acids exist.[13] DNA serves therefore as data storage, which inspired chemists to reproduce this ability in synthetic molecules.[14]

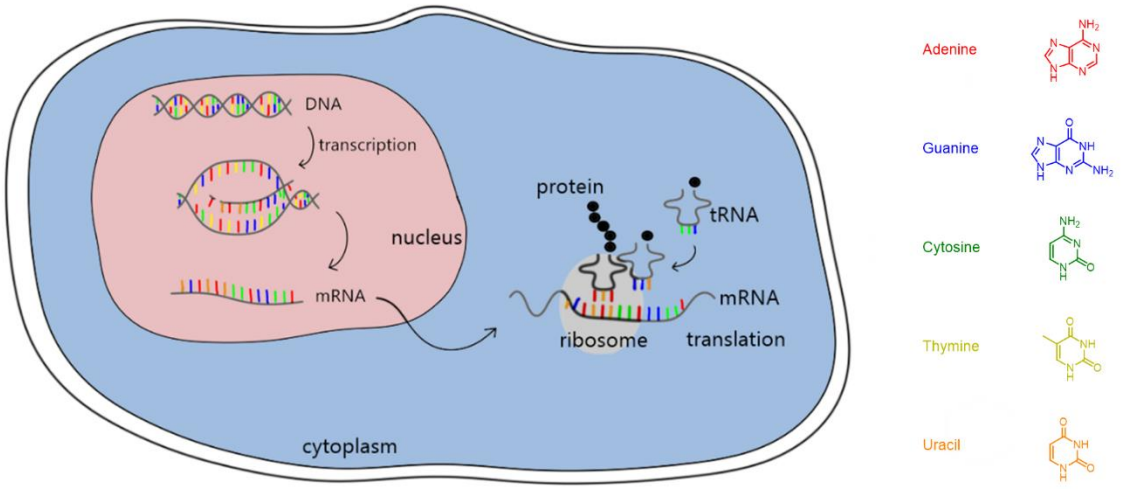


Figure 1: Schematic overview of the gene expression. The transcription from DNA to mRNA takes place in the nucleus. The mRNA is transferred to the cytoplasm, where translation to the protein occurs. The translation process proceeds in the ribosome, where the amino acid or the elongating peptide chain is bound to tRNA. The nucleobases are depicted on the right.

In nature, the error rate during gene expression is comparably low: it is composed of the error rate of transcription, which is around 10^{-5}, and translation, which is approximately 10^{-4}.[15] Consequently, transcription is a bit more precise and one mistake occurs every 100,000 incorporations of nucleotides. During translation,

one mistake occurs every 10,000 incorporations of amino acids. This high precision in biological systems is also desirable for synthetic chemists. While biologists can use the machinery of biology by reproducing DNA *via* polymerase chain reaction, chemists have developed solid phase syntheses.[16] Initially, an insoluble support was utilized by Merrifield for peptide synthesis, termed solid phase peptide synthesis (SPPS).[17] The insoluble polymer exhibits a linker unit, where a first amino acid can be attached. Through iterative coupling reactions and deprotection, a peptide can be formed. Monoprotected amino acids are utilized and inserted in excess to guarantee full conversion. In this way, purification is performed by simple washing. Subsequent deprotection enables a further coupling reaction with a second protected amino acid. When the desired sequence is obtained after several steps, the solid support can be cleaved. In comparison to nature, SPPS is limited: peptides with more than 30 to 50 amino acids are usually difficult to obtain *via* SPPS.[15] Furthermore, any conversion lower than 100% has a severe impact not only on the yield but also on the purity of the peptide, which is purified by high-performance liquid chromatography (HPLC) after cleavage. Still, for synthetic chemistry SPPS was a significant step towards sequence-defined oligomers and offered the possibility to automatize the syntheses. The same strategy was later also applied for oligonucleotide and oligosaccharide synthesis.[18] But not only biomacromolecules can be synthesized with the aid of a solid support. Nowadays, solid phase organic synthesis (SPOS) is a helpful tool when performing iterative synthesis procedures.[19] Therefore, SPOS is also used for the synthesis of sequence-defined oligomers in the field of polymer chemistry. Poly(phosphate)s based on phosphoramidite monomers were synthesized *via* a DNA synthesizer by Lutz *et al.* generating a macromolecule with a degree of polymerization (DP) of 104.[20] Du Prez *et al.* compared the synthesis of carbamate-amides (DP = 10) by automated and manual SPOS.[21] The manual SPOS generated oligomers in higher purity, but the reaction time was reduced to 33 hours, compared to 5 days for the manual approach. In general, SPOS is a time-efficient procedure, as purification is reduced compared to reactions in solution. However, reaction scales are rather limited on solid support and solution phase approaches were introduced to the synthesis of sequence-defined oligomers lately. Furthermore, characterization of the intermediate structures is clearly facilitated in comparison

to intermediates attached to the solid support.

Multicomponent reactions (MCRs) proved to be a valuable tool for the synthesis of sequence-defined oligomers in solution. MCRs implement more than two reagents in one pot and exhibit usually a very high atom efficiency.[22] A popular representative is the Passerini three-component reaction (P-3CR) based on components bearing, respectively, a carbonyl group, a carboxylic acid and an isocyanide, resulting in an α-acyloxy carboxamide.[23] Defined structures *via* P-3CR were already described in form of dendrimers, but only recently as a tool for generating sequence-defined oligomer chains.[24] When stearic acid, 10-undecenal and an optional isocyanide are applied, a subsequent thiol-ene reaction with 3-mercaptopropionic acid can be performed.[25] In this way, protecting groups can be completely avoided in this sub-monomer strategy. However, in comparison to a protection strategy based on an isocyanide component with a benzyl protected carboxylic acid, the overall yields were significantly lower.[26] The second mentioned strategy with the monoprotected AB monomer was performed with various aldehydes. After 20 steps, 2.4 grams of the monodisperse decamer were obtained with an overall yield of 44%. The P-3CR is therefore an excellent reaction for the synthesis of sequence-defined oligomers in high scales. Various side chains can be incorporated, as long as they are orthogonal to the P-3CR. For instance, a double bond was introduced enabling a final dimerization *via* self-metathesis of the decamer to a 20-mer.[26] Of course, other solution-based approaches exist, *e.g.* a photochemical approach joint with a Diels-Alder reaction to several isoindole-based decamers.[27] Interestingly, this approach was combined with the already mentioned P-3CR.[28]

The time scale for the preparation of sequence-defined oligomers is of course not comparable to the biological machinery. Approaches on solid support are clearly favored in this matter. However, when sequence-defined oligomers in high yields are required, the solution-based approaches are preferred. While in nature DNA assembles in a double helix or proteins exhibit a certain tertiary or even quaternary structure, the assembly of non-natural oligomers cannot be controlled yet.[7,29] One objective for sequence-defined oligomers in future will be to design them in a way that they arrange in a specific secondary structure, *e.g.* an α-helix. Apart from defined secondary or tertiary structures, sequence-defined oligomers and polymers are often mentioned in the context of data storage.[14] The read-out

can be performed with tandem mass spectrometry, which is comparably complex.[30]

In the context of conjugated structures, where this work builds upon, the focus might be a bit different. Mainly, organic chemists perform iterative reaction procedures to monodisperse or rarely sequence-defined conjugated oligomers and do not focus on high overall yields or scalability. Often, structure-activity or structure-property relationships are investigated, where small amounts of the products are sufficient.[31] For highly defined structures, where variations within the sequence shall be investigated, high scales and yields are still desirable. The purification is facilitated, and analytic procedures can be conducted without the need to regain the substance.

2. Theoretical Background

Consistent with chapter 1, chapter 2.1 focusses on monodisperse and sequence-defined conjugated oligomers: an important determination is the difference of monodisperse and sequence-defined oligomers, which was introduced before. For conjugated systems, mainly monodisperse oligomers were described: an iterative synthesis procedure was established, but the same building block was consistently incorporated.
Chapter 2.2 describes cross-coupling reactions, which are often used for the synthesis of monodisperse conjugated oligomers. The focus is on the Sonogashira reaction (chapter 2.2.1), which was applied in this work.
At last, the possible applications of conjugated polymers and oligomers are highlighted, describing organic light emitting diodes (OLEDs) and organic photovoltaics more thoroughly.

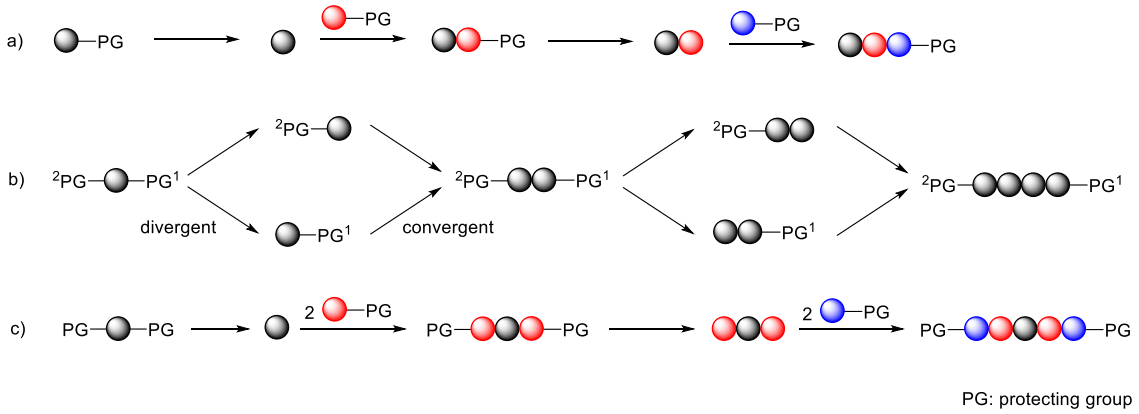
2.1 Monodisperse and Sequence-Defined Conjugated Oligomers

Conjugated oligomers are interesting model compounds to study the properties of their polymer analogues in more detail.[32] The definition of an oligomer does not exclude that it may be polydisperse, but when structure-property relationship investigations shall be performed it is inevitable.[33] Many procedures to monodisperse conjugated oligomers were published, which were not based on an iterative procedure as depicted in Scheme 1.[34,35] These syntheses are not applicable for the preparation of sequence-defined oligomers, while many iterative procedures to monodisperse oligomers could lead to sequence-definition. In Scheme 1, the three approaches to sequence-defined or monodisperse oligomers are depicted:

a) linear approach, which guarantees the highest control over the sequence;

b) divergent/convergent approach, which results in monodisperse oligomers, but the DP is doubled during each cycle;

c) bidirectional approach, where symmetric sequence-defined oligomers are obtained, and two units can be incorporated during each cycle.



Scheme 1: Different approaches to monodisperse conjugated oligomers: a) linear approach, b) divergent/convergent approach (also termed iterative exponential growth), which requires two orthogonal protecting groups (PG)s, and c) bidirectional approach.

Several reviews describe the synthesis to monodisperse conjugated oligomers, however, molecules obtained by non-iterative procedures are described as well.[32,36] Furthermore, mixtures of oligomers are often separated by preparative size exclusion chromatography (SEC) or HPLC leading to pure products. Here, the same problem occurs, since these procedures are not applicable for sequence-defined oligomers. Only iterative procedures as depicted in Scheme 1 are mentioned in the following chapters 2.1.1, 2.1.2. and 2.1.3.

2.1.1 Liquid Phase Approaches

This chapter is reproduced with permission from: S. C. Solleder, R. V. Schneider, K. S. Wetzel, A. C. Boukis, M. A. R. Meier, *Macromol. Rapid Commun.* **2017**, *38*.[37] Copyright © 2017, John Wiley and Sons. The termination of the scaffold structures is accomplished as **S1** *etc*.

Oligo(acetylene)s and derivatives

There are no iterative procedures for the synthesis of monodisperse oligo(acetylene)s (**S1**) with “ene-scaffold” published yet. However, several model compounds, such as oligo(diacetylene)s (**S2a-b**) with “enyne-scaffold”, oligo(triacetylene)s (**S3a-b**) with “enediyne-scaffold” or *iso*-oligo(diacetylene)s (**S4**) have been established (compare Figure 2). Furthermore, aromatic compounds were incorporated in oligo(triacetylene) scaffolds (**S5a-c**).

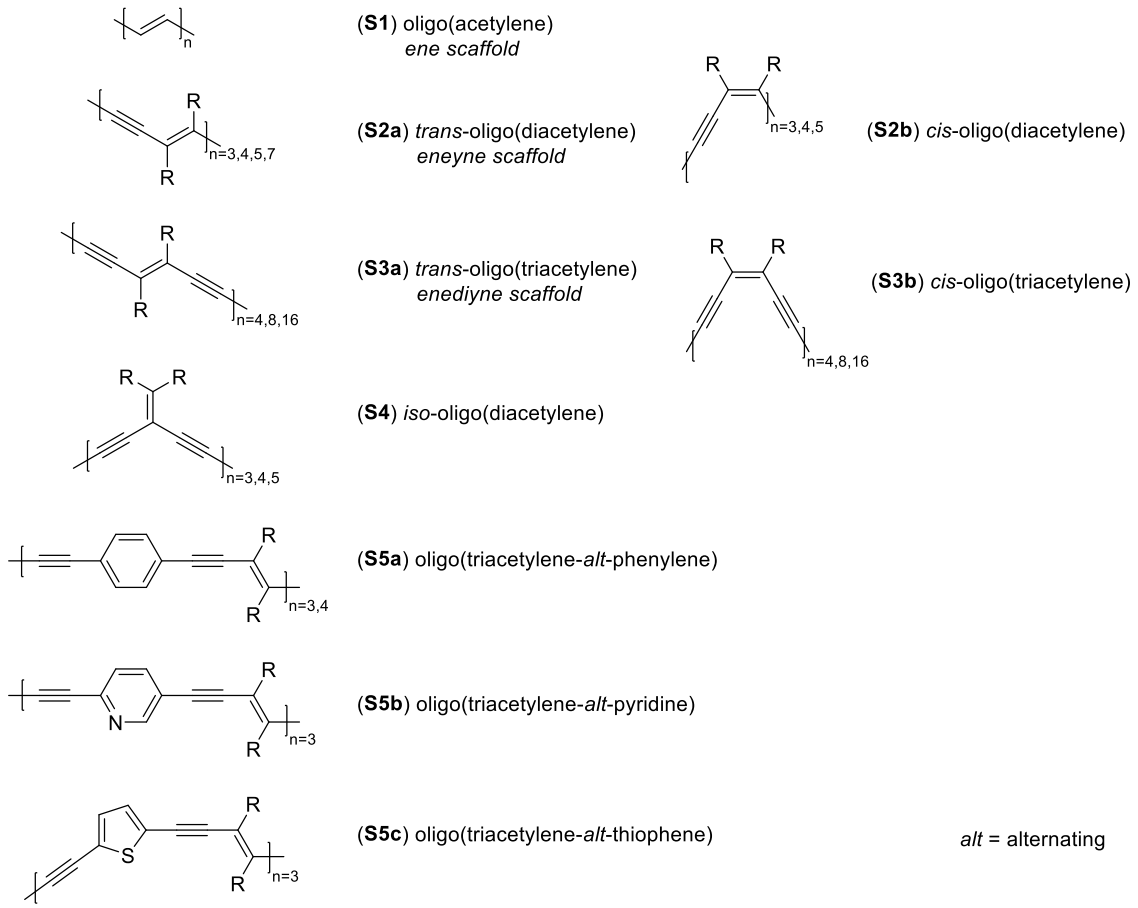


Figure 2: Overview of the different π-conjugated carbon scaffolds, based on oligo(acetylene) derivatives, described within this chapter. Each synthesized compound with three repeat units or more is depicted, but its synthesis might be also described on solid phase, *e.g.* **5a** n=4 (chapter 2.1.2). Adopted from S. C. Solleder, R. V. Schneider, K. S. Wetzel, A. C. Boukis, M. A. R. Meier, *Macromol. Rapid Commun.* **2017**, *38*.[37]

Diederich and coworkers performed pioneering work for the synthesis of oligo(triacetylene) (**S3a-b**) rod-like molecules. However, their work is often based on the synthesis of product mixtures, which are later purified by preparative SEC and therefore not further considered in this review.[38] In 1986, Wudl and Bitler reported an iterative strategy for synthesizing oligo(diacetylene)s (**S2a**).[39] The addition of one building block required four steps. First, a triple bond was activated with zinc chloride in order to form an alkynyl zinc, which was converted with (*E*)-1-chloro-2-iodoethylene *via* a Negishi coupling. In this way, a chlorine was introduced to the enyne-backbone. With trimethylsilyl (TMS) protected ethynylmagnesium bromide in hand, a Kumada coupling could then be performed. After the deprotection of the triple bond, the four-step iterative cycle can be repeated. Using 3,3-dimethylbut-1-yne as starting compound, a trimer

was obtained after three cycles (*i.e.* 12 steps).[40] Activation with zinc chloride and a final Negishi coupling with 0.5 equivalents of (*E*)-1,2-diiodoethylene yielded a heptamer composed of 30 conjugated carbon atoms. The heptamer exhibited solubility problems, so no nuclear magnetic resonance spectroscopy (NMR) data could be measured, but the respective mass was detected. Since no experimental section was provided, no yields, scales or purification methods were mentioned and thus, the comparison with other procedures synthesizing monodisperse oligo(diacetylene)s (**S2a**) is impossible. Wudl and Bitler also synthesized shorter molecules and analyzed them, as well as the heptamer, by ultraviolet-visible spectroscopy (UV/Vis), indicating the absorption maxima for the respective oligomers.

In 1994, Giesa and Schulz reported another route to oligo(diacetylene)s (**S2a**) based on Kumada couplings.[41] The starting molecule and building block, a bifunctional *trans*-vinylacetylene with a TMS protected triple bond and a chloro-functionalized double bond, were synthesized in yields of 60 to 75% and in a scale of 12.4-15.5 grams. For the monomer synthesis, the starting molecule was converted with a magnesium functionalized 3,3-dimethylbut-1-yne. After distillation, the hexenediyne product was obtained as a *Z*/*E*-mixture in a ratio of 1:4, which could be separated by recrystallization. Afterwards, the triple bond was activated with methyl magnesium bromide and another monomer unit could be added by Kumada coupling. After subsequent deprotection, the dimer was converted with (*E*)-1,2-diiodoethylene in a Sonogashira cross-coupling reaction to the final pentamer with 22 conjugated carbon atoms. Since the yields of each step are rather low and sometimes not reported, the overall yield was estimated to be less than 1%. Overall, 160 milligrams of the pentamer were synthesized and characterized by NMR as well as infrared (IR) spectroscopy, but the spectra were not displayed. As before, the oligomers were synthesized in a linear procedure with a final dimerization step. Giesa and Schulz used the obtained oligomers as model compounds for poly(diacetylene)s and emphasized the advantage of using exclusively all-*trans* oligo(enyne)s. In the manner of Wudl *et al.*, they also extrapolated the obtained data to infinite chain length.[39]

Zuilhof, Sudhölter *et al.* reported another synthesis of oligo(diacetylene)s (**S2a**) based on Sonogashira reactions.[42] One starting molecule was synthesized in 85% yield and the building block, described by Giesa *et al.*, was obtained in 82%

in a one-pot synthesis. The *trans*-vinylacetylene starting molecule first underwent a Sonogashira reaction with trimethylsilylacetylene (TMSA) to form the monomer. After deprotection and a further Sonogashira reaction with the respective building block, the dimer was obtained. Repeating the described cycle, the TMS-protected trimer could be obtained after five steps in an overall yield of 4%; a reaction scale was not reported. Column chromatography was necessary to purify the products after each Sonogashira reaction. Zuilhof, Sudhölter used this linear approach as alternative to the previously mentioned ones and recorded the absorption spectra of the respective oligomers. They also showed the synthesis of further compounds, but these were not performed in an iterative fashion.

In 2003, Sato and coworkers published an iterative synthesis procedure to obtain *trans*- (**S2a**) and *cis*-oligo(diacetylene)s (**S2b**), as well as oligo(triacetylene)s (**S3a-b**).[43] For the *trans*-oligo(diacetylene)s (**S2a**), the building block synthesis required two steps (41% overall yield; 1.05 gram scale). The synthesis of the starting material required one additional step, leading to an overall yield of 27% (474 milligrams). Here, an additional triple bond with an orthogonal 2-hydroxyisopropyl protecting group was introduced. As in the approaches described before, the building block resembles a bifunctional *trans*-vinylacetylene with a TMS protected triple bond and an iodo-functionalized double bond. However, additional propyl side chains improve the solubility of the obtained oligomers. The iterative synthesis is based on the deprotection of the respective TMS group and subsequent Sonogashira cross-coupling with another building block molecule. After eight steps, 170 milligrams of the protected pentamer were obtained in an overall yield of 25%. Further deprotection and Hay coupling of the respective pentamer yielded a molecule similar to the respective decamer (35 milligrams, 20%). As previously mentioned, Sato and coworkers also described the synthesis of *cis*-oligo(diacetylene)s (**S2b**), again based on iterative Sonogashira coupling. The "*cis*"-building block was obtained in one step in 1.80 gram scale and in a yield of 63%. The starting molecule requires an additional step and was received in a scale of 1.05 grams and in an overall yield of 54%. The synthesis procedure is consistent with the above described procedure for *trans*-oligo(diacetylene)s. The protected pentamer was isolated after eight steps in a lower overall yield of 8% but in a similar scale of 148 milligrams. Since the starting molecule exhibits an enediyne-scaffold with

two orthogonal protecting groups, Sato *et al.* utilized the respective "*trans*"- and "*cis*"-starting molecules for the synthesis of oligo(triacetylene)s (**S3a-b**). First, the TMS group was deprotected and subsequently a Hay coupling was applied. Then, both ends of the molecules exhibited terminal 2-hydroxyisopropyl protecting groups, where one of them was deprotected. This was performed in rather low yields ranging from 35 to 43%, but the starting material could be recovered by column chromatography. In this way, the cycle of Hay coupling and mono-deprotection can be repeated in a divergent/convergent approach, doubling the molecular weight. After eight steps, 74 milligrams of the respective "*trans*"-16mer (**S3a**) was obtained in 1% overall yield. The procedure to *cis*-oligo(triacetylene)s (**S3b**) required also eight steps, but the product was synthesized in an overall yield of 12%, although only 12 milligrams were isolated. Experimental data, such as NMR or matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectra, were provided in text form. The respective molecules were used for analyzing their electronic absorption properties.

In 2001, Hirsch and coworkers described another iterative linear approach, leading to *cis*-oligo(diacetylene)s (**S2b**).[44] The concept is based on two Sonogashira reactions with subsequent deprotection. Therefore, commercially available phenylacetylene served as starting material and 1,2-dibromocyclopentene as building block. A cyclic double bond was chosen in order to suppress *cis*/*trans*-isomerization. In the first step, the phenylacetylene was mono-coupled to the 1,2-dibromocyclopentene and a further Sonogashira reaction with the bromine residue and TMSA could be performed. Deprotection of the TMS group yielded the monomer. After eight steps, 70 milligrams of the protected trimer were obtained in an overall yield of 5%, since the mono-coupling of the dibromocyclopentene usually gave low yields. The products of the cross-coupling reactions were isolated by column chromatography and the products were fully characterized, but only UV/Vis spectra of the respective compounds are provided. Again, the oligomer was synthesized as model compound for *cis*-poly(diacetylene)s.

Tykwinski and coworkers reported routes leading to monodisperse *iso*-oligo(diacetylene)s (**S4**).[45,46] In 2002, they reported a linear and a bidirectional procedure to obtain the respective oligomers, based on Hay couplings.[46] The synthesis of the building block for the linear procedure, a

functionalized vinyl triflate with TMS-protected diethynylene unit, is described in literature.[47] The monomer was built by cross-coupling of the triflate building block and TIPS acetylene. Afterwards, the TMS protecting group was removed. In this way, another Sonogashira coupling with another building block can be performed and the cycle can be repeated. After seven steps, 61 milligrams of the protected tetramer were obtained in an overall yield of 37%. Column chromatography after the Sonogashira reactions afforded the pure products. A Hay coupling can be performed with the deprotected oligomers for a final dimerization. On the other hand, the bidirectional pathway is based on a bifunctional starting molecule, a vinyl tetrayne, which was synthesized in three steps in 60% overall yield and in a scale of 142 milligrams. Making use of the previously mentioned vinyl triflate building block, a trimer was produced and after subsequent deprotection as well as Hay coupling, the final protected pentamer was obtained in 82% overall yield (three steps, 62 milligrams). Every compound is characterized by NMR and the electronic absorption is also reported.

Takayama, Sato and coworkers published a synthesis procedure of alternating oligo(triacetylene)s with aromatic systems, such as benzene (**S5a**), pyridine (**S5b**) and thiophene (**S5c**) in 2004.[48] The building block consists of a TIPS protected tripled bond, fused to the respective aromatic compound with enyne-scaffold that is activated by an iodine moiety. Additionally, the double bond is substituted with alkyl groups in order to improve the solubility. The synthesis of the three respective building blocks was performed over five steps. Thereby, 428 milligrams of the benzene-containing molecule were obtained in 25% overall yield. The pyridine-analogue was obtained in 3.25 gram scale and 20% yield and the thiophene-representative in an overall yield of 21% (scale is not mentioned). The starting molecule, required for the synthesis of oligo(triacetylene-*alt*-phenylene)s, is a 1,4-diethynylbenzene with one 2-hydroxyisopropyl protecting group; it was synthesized in two steps (39 milligrams; 71% overall yield). The respective pyridine starting molecule required three synthesis steps and was obtained in an overall yield of 65% (scale not mentioned). This is the same for the thiophene starting molecule, which was obtained in an overall yield of 55%. Subsequent Sonogashira reaction and deprotection yielded the three different trimers after five steps. Column chromatography was required for the purification after each Sonogashira reaction. The tri(triacetylene-*alt*-phenylene) (**S5a**) was

obtained in 79 milligram scale and an overall yield of 51%, the tri(triacetylene-*alt*-pyridine) (**S5b**) in 28 milligram scale and in an overall yield of 34% and the tri(triacetylene-*alt*-thiophene) (**S5c**) in 40 milligram scale and 39% overall yield. The obtained trimers were fully characterized, fluorescence spectra of the obtained oligomers were provided and possible applications in OLEDs are envisioned for these conjugated macromolecules. In Table 1 the approaches to oligo(acetylene)s and its derivatives are summarized.

Table 1: Overview of the different approaches to oligo(acetylene)s and corresponding derivatives. Work-up was consistently performed by column chromatography after each cross-coupling reaction. The last column depicts the maximum DP. Adopted from Meier *et al*.[37]

	Authors, Reference	**Scale**	**Backbone structure**	**max. DP (overall yield)**
1	Wudl and Bitler[39]	not reported	(**S2a**)	7 (not reported)
2	Giesa and Schulz[41]	160 mg	(**S2a**)	5 (< 1%)
3	Zuilhof, Sudhölter *et al.*[42]	not reported	(**S2a**)	3 (4%)
4	Sato *et al.*[43]	170 mg 148 mg 74 mg 12 mg	(**S2a**) (**S2b**) (**S3a**) (**S3b**)	5 (25%) 5 (8%) 16 (1%) 16 (12%)
5	Hirsch *et al.*[44]	70 mg	(**S2b**)	3 (5%)
6	Tykwinski *et al.*[45,46]	62 mg	(**S4**)	5 (82%)
7	Takayama, Sato *et al.*[48]	79 mg 28 mg 40 mg	(**S5a**) (**S5b**) (**S5c**)	3 (51%) 3 (34%) 3 (39%)

Oligo(*para*-phenylene)s and Oligo(fluorene)s

Conjugated aromatic compounds with specific molecular weight have also been synthesized in an iterative fashion. Hereinafter, routes leading to monodisperse oligo(*para*-phenylene)s (**S6**) and oligo(fluorene)s (**S7**) (compare Figure 3) are described.

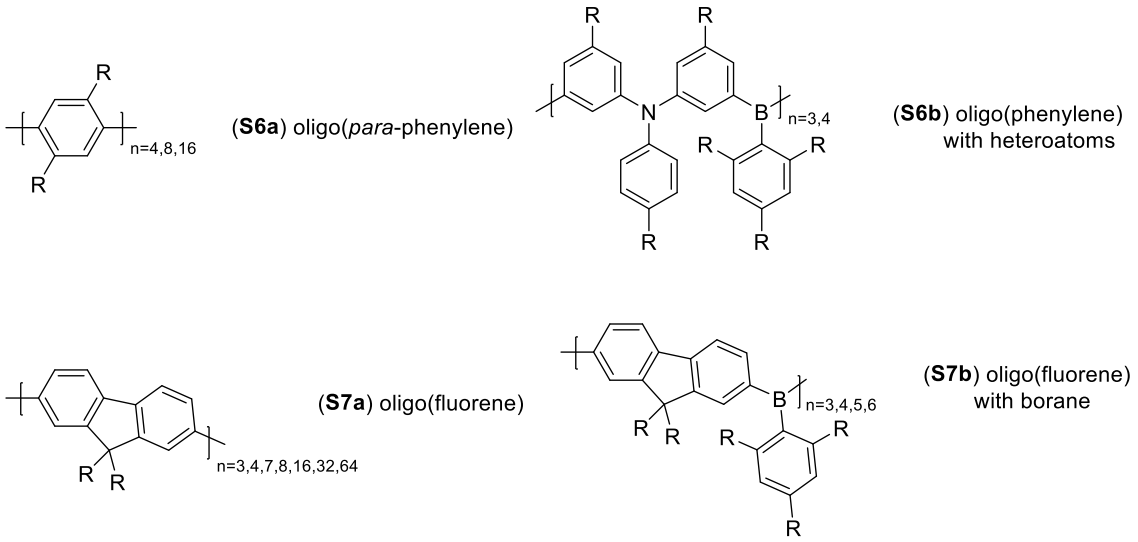
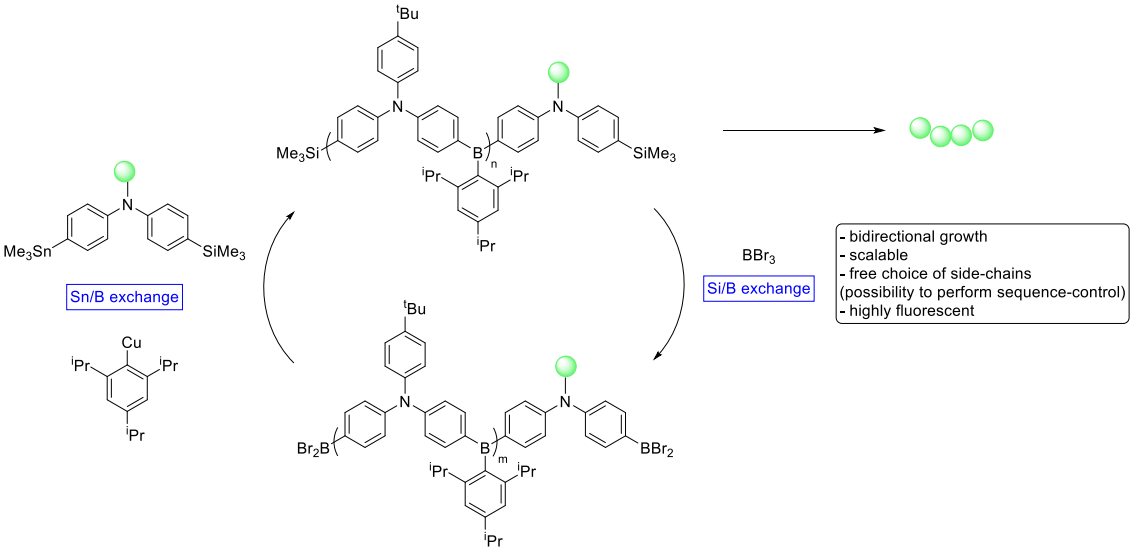


Figure 3: Overview of conjugated aromatic compounds, which can be synthesized monodisperse in an iterative fashion. Adopted from S. C. Solleder, R. V. Schneider, K. S. Wetzel, A. C. Boukis, M. A. R. Meier, *Macromol. Rapid Commun.* **2017**, *38*.[37]

Schlüter *et al.* published a divergent/convergent route towards oligo(*para*-phenylene)s (**S6a**) based on Suzuki couplings.[49] The starting molecule is a bifunctional biphenyl unit, equipped with a TMS group and a bromine residue. In one part of the starting molecule, the bromine residue is converted into a boronic acid and in the other, the TMS group is converted to iodine. Afterwards, the two resulting products are combined, and a Suzuki coupling can take place. The molecules are purified by column chromatography. This cycle can be repeated several times and after nine steps, the octamer with 16 aromatic rings exhibiting a TMS and a bromine residue was obtained. However, yields and scales are only reported until the tetramer stage. The tetramer is obtained in an overall yield of 19% after six steps in a scale of 3.3 grams. A SEC trace with minor impurities is depicted. Furthermore, Schlüter *et al.* mentioned the potential of these rigid rod molecules as reference standards for SEC measurements.

Oligo(phenylene)s with alternating heteroatoms (**S6b**) were published by Perry, Jäkle and coworkers in 2015.[50] They synthesized an alternating conjugated oligomer with electron-rich triarylamine and electron-deficient triarylborane derivatives by Sn/B exchange and subsequent activation to the boron dibromide by Si/B exchange. The starting materials and the building block are based on triphenylamine derivatives. The starting molecule for oligomers with an uneven number of repeat units, exhibiting a TMS group, a boron dibromide and a

tert-butyl group in *para*-position, was synthesized over two steps in an overall yield of 58% and a scale of 920 milligrams. The starting compound for molecules with an even number of repeat units had two boron dibromide residues and a *tert*-butyl group in *para*-position; it was prepared in two steps in 910 milligram scale and in an overall yield of 69%. The building block molecule features a TMS, a trimethylstannyl and a *tert*-butyl group in *para*-positions and is derived over two steps in 7.6 gram scale and in a yield of 51%. The starting molecules and the building block are connected by Sn/B-exchange and stabilization of the boron with 2,4,6-triisopropylphenyl copper (compare Scheme 2). The molecules were purified by preparative SEC. Subsequently, a Si/B exchange takes place and as two TMS groups are present, the procedure is thus bidirectional. After a further Sn/B exchange, the respective trimer and tetramer were obtained in overall yields of 30% (590 milligrams) and 25% (520 milligrams), respectively. The SEC traces of the oligomers are depicted and confirm their high purity. The oligomers were characterized thoroughly, indicating a potential use in non-linear optics applications.



Scheme 2: Synthesis approach of Perry, Jäkle and coworkers, leading to oligo(phenylene)s with alternating heteroatoms (**S6b**) by iterative Si/B and Sn/B exchange. This approach features bidirectional growth, scalability, free choice of side chains and highly fluorescent products. This scheme is reproduced with permission from: S. C. Solleder, R. V. Schneider, K. S. Wetzel, A. C. Boukis, M. A. R. Meier, *Macromol. Rapid Commun.* **2017**, *38*.[37] Copyright © 2017, John Wiley and Sons.

Monodisperse oligo(fluorene)s (**S7a**) have also been investigated, since they exhibit blue emission. In 2003, Chen and coworkers published several routes to monodisperse oligomers. However most of them were not built up in an iterative fashion.[51] A linear procedure was performed with 2-bromofluorene as starting molecule and 2-bromo-7-iodofluorene as building block, both equipped with alkyl side chains for improved solubility. The procedure is based on conversion of the bromine to boronic acid and subsequent Suzuki coupling with the iodine moiety. After two cycles, the trimer was obtained and reacted with a fluorene diboronic acid to lead to the final heptamer. The fluorene, exhibiting two diboronic acid moieties was synthesized in a yield of 52%. The heptamer was obtained after five steps in an overall yield of 17% (scale not mentioned). For each step, column chromatography was required for purification. For some oligomeric compounds, the respective MALDI spectra are depicted but not for the final heptamer. The obtained oligomers were easily processable and exhibit photoluminescence quantum yields of 43-60% for blue emission.

A similar approach was published by Geng and coworkers in 2011.[52] Two starting molecules are necessary: 2-Bromo-7-iodofluorene and a bifunctional fluorene, equipped with a TMS group and a boronic acid functionality. Both exhibit two octyl side chains for better solubility. After a Suzuki coupling of the two starting materials, the product is split up in two parts: in one part, the TMS group is converted into an iodine moiety and in the other the bromine is converted to a boronic acid. The Suzuki coupling of both batches yields the tetramer. After 13 steps, the 32-mer was obtained in an overall yield of 13% and a scale of 1.26 grams. The 32-mer can undergo a final Yamamoto coupling and can be deprotected afterwards, yielding a 64-mer in 15 steps in an overall yield of 8% and in a scale of 93 milligrams. For most of the reactions, work-up by column chromatography was essential. The respective SEC are slightly broadened. Since the photophysical and thermal properties are chain-length dependent, the larger representatives might be useful as model compounds for polyfluorenes.

As for oligo(phenylene)s, oligo(fluorene)s with alternating boranes as heteroatoms (**S7b**) were developed by Jäkle *et al.* in 2011.[53] Two starting materials for the synthesis of molecules of uneven and even DP were prepared, as well as one building block. The starting compound for the oligomers with uneven numbers of repeat units is a fluorene with a TMS protecting group and a

boron dibromide group. It was synthesized over two steps in 970 milligram scale and 50% overall yield. The starting molecule for oligomers with even numbers of repeat units exhibits two boron dibromide residues at the fluorene and was prepared over two steps in 1.68 gram scale and 48% overall yield. The fluorene-building block with a TMS and a trimethylstannyl group was obtained in one step in a yield of 66% (6.10 grams). The conjugated organoboranes were prepared by electrophilic substitution of the arylstannates of the building block with the boron halides of the starting materials. Subsequently, a Si/B exchange can take place by addition of boron tribromide and a further electrophilic substitution became possible and thus the iteration of the procedure (compare Scheme 2). The procedure is bidirectional and after five steps, 110 milligrams of the pentamer were obtained in an overall yield of 26%. A five-step synthesis leading to an odd DP afforded 180 milligrams of the hexamer in an overall yield of 21%. Column chromatography was required for the purification of the respective oligomers, however, the SEC traces still exhibit small shoulders. With the obtained oligomers in hand, the authors planned to investigate signal amplification effects.

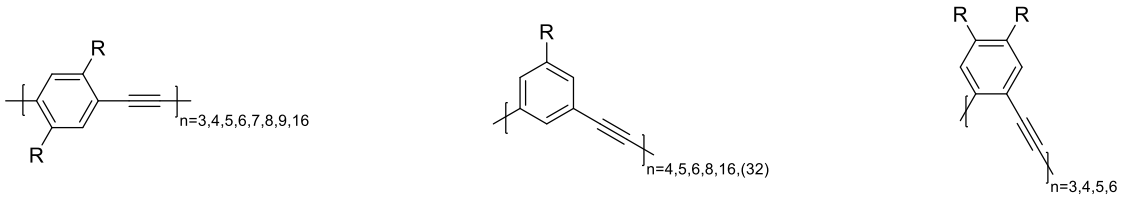
Table 2 summarizes the approaches to oligo(*para*-phenylene)s and oligo(fluorene)s.

Table 2: Overview of the different approaches to oligo(*para*-phenylene)s and oligo(fluorene)s. Work-up was consistently performed by column chromatography or preparative SEC after each step. Adopted from Meier *et al.*[37]

	Authors, Reference	**Scale (DP)**	**Backbone structure**	**Purity (method)**	**max. DP (overall yield)**
1	Schlüter *et al*.[49]	3.3 g (4)	(**S6a**)	not reported	4 (19%) 8 (not reported)
2	Perry, Jäkle *et al.*[50]	520 mg (4)	(**S6b**)	high (SEC)	4 (25%)
3	Chen *et al.*[51]	not reported	(**S7a**)	not reported	7 (17%)
4	Geng *et al.*[52]	93 mg (64)	(**S7a**)	high (SEC, slightly broadened)	64 (8%)
5	Jäkle *et al.*[53]	180 mg (6)	(**S7b**)	high (SEC, minor impurities)	6 (21%)

Oligo(phenylene ethynylene)s (OPEs) and Alternating Phenylene Ethynylenes

Oligo(phenylene ethynylene)s (OPEs) (**S8**) are a group of conjugated oligomers, which have been examined thoroughly starting from the late 20th century. Several routes to monodisperse *para*-OPEs (**S8a**) are described and divided into linear, bidirectional and divergent/convergent synthesis procedures. Afterwards *meta*-OPEs (**S8b**) and *ortho*-OPEs (**S8c**) are described (compare Figure 4). If not mentioned otherwise, the purification was performed by column chromatography for these molecules.



(**S8a**) oligo(*para*-phenylene ethynylene) *para*-OPE

(**S8b**) oligo(*meta*-phenylene ethynylene) *meta*-OPE

(**S8c**) oligo(*ortho*-phenylene ethynylene) *ortho*-OPE

Figure 4: Overview of the different OPEs that can be prepared in an iterative fashion. Adopted from S. C. Solleder, R. V. Schneider, K. S. Wetzel, A. C. Boukis, M. A. R. Meier, *Macromol. Rapid Commun.* **2017**, *38*.[37]

In 1996, Dixneuf and coworkers published a linear procedure leading to OPEs (**S8a**) based on Sonogashira cross-coupling and subsequent deprotection.[54] The TMS-protected iodo-phenylacetylene was synthesized from iodoaniline in two steps in a scale of 8.36 grams and an overall yield of 59%. It serves both as starting compound and as building block. First, a Sonogashira reaction with triisopropoyl silyl-protected acetylene was performed. After subsequent deprotection, another Sonogashira reaction with the respective building block can be conducted. Then, the cycle of deprotection and Sonogashira reactions can be repeated. After six steps, the deprotected trimer was obtained in milligram scale and in an overall yield of 26%. Only small cutouts of proton NMR spectra were reported, which are not unambiguously confirming the formation of the product. In principle, the trimer can be used for the synthesis of poly(yne)s.

In 2002, Hwang and Tour described a combinatorial approach towards OPEs (**S8a**), where also Sonogashira reactions were employed.[55] They synthesized five different TMS-protected iodo-phenylacetylene building blocks in two steps with overall yields ranging from 67 to 86% and scales of 8.6 to 13.2 grams. A first

Sonogashira reaction with phenylacetylene yielded the respective protected monomers, which were afterwards deprotected. Now, a further Sonogashira reaction with another building block could be performed. All in all, 24 trimers (note: in the respective literature, they are termed as tetramers, however in terms of repeat units, they should be called trimers) with four aromatic rings were synthesized in overall yields ranging from 12 to 39% and in scales of 14 to 125 milligrams. Interestingly, these molecules were also prepared by a solid phase approach, facilitating the purification (compare chapter 2.1.2). Apart from proton and carbon NMR and high resolution mass spectrometry (HRMS) in text form, no further analytical data were provided. This is the only publication for the synthesis of sequence-defined hetero-OPEs. These OPEs are discussed for application as molecular wires.

In 2005, Zhao and Bo performed a synthesis procedure towards homo-OPEs, which was based on Tour's previously mentioned work.[55,56] The building block was again a TMS-protected iodophenylacetylene, prepared in one step in 1.1 gram scale and in a yield of 47%. The starting material, a phenylacetylene with an ester substituent, was prepared in three steps (520 milligrams; 90% yield). Apart from the last step, i.e. the incorporation of an iododiphenylethyne (one step, 36 milligrams, 40% yield), the procedure is linear and consistent with the one of Tour described before. Zhao and Bo synthesized 15 milligrams of a tetramer with six aromatic rings over seven steps in an overall yield of 11%. Absorption and emission spectra of the respective compounds were shown. Apart from the linear procedures leading to monodisperse *para*-OPEs (**S8a**), many other divergent/convergent procedures were published, especially by the Tour group. In 1994, they published a route to a system with 16 aromatic rings.[57] Since they published the same approach with improved results three years later, where they also applied solid phase synthesis (compare chapter 2.1.2), we confine to the more recent publication.[58] They synthesized three potential starting materials differing in the side chains (ethyl, 3-ethyl-heptyl, dodecyl). The starting materials are based on bifunctional phenylacetylenes and exhibit a diethyltriazene moiety as well as a TMS protected triple bond. All compounds were synthesized starting from the corresponding nitro compounds. The phenylacetylene, bearing an ethyl side chain, was obtained after four steps in an overall yield of 10.8 grams (25%). The starting molecule with a 3-ethylheptyl side

chain was synthesized in ten steps (1.90 grams, 7%) and the respective molecule with a dodecyl side chain in six steps (1.17 grams, 42%). The starting molecules are split up in two parts; the triazene is either converted with methyl iodide to the iodine moiety or the TMS group is deprotected. After recombining the two resulting products, a Sonogashira reaction can take place. By repeating the splitting up with subsequent activation and deprotection, as well as recombination and coupling, the DP is doubled in each step. Due to solubility problems, the oligomer with the ethyl side chain was only synthesized until the tetramer stage (1.17 grams in an overall yield of 81%). The other oligomers could be synthesized up to the 16-mer in twelve steps. The 16-mer with 3-ethylheptyl side chains was isolated in an overall yield of 6% and the one with dodecyl side chains in 1.20 gram scale and a remarkable overall yield of 27%. Especially the purification of the 3-ethylheptyl 16-mer proved to be difficult, as the octamer and the 16-mer could not be separated by column chromatography. It took several washing steps and centrifugation to obtain a pure product (yield was not mentioned). The yield before purification was estimated to 15 milligrams. For all other steps, column chromatography was sufficient to obtain products of high purity. ^{1}H NMR spectra are provided but suffer from poor resolution. As mentioned before, the procedure was also established for solid phase synthesis and therefore the superior dodecyl starting material was chosen, due to higher overall yields and improved solubility (compare chapter 2.1.2). Furthermore, the oligomers can be end-functionalized to obtain thiols, enabling the adhesion to gold surfaces, which is interesting in terms of conduction studies.

In 1997, another divergent/convergent synthesis procedure was published by Ziener and Godt.[59] This procedure is also based on Sonogashira cross-coupling reactions, playing with the different selectivity between iodine and bromine moieties. Instead of the triazene moiety, the phenylacetylenes thus exhibit a bromine residue and again a TMS protecting group. Ziener and Godt synthesized two different starting molecules bearing two hexyl side chains and two 3-methylbutyl side chains. The starting molecules were synthesized from the 1,4-dibromobenzenes with the respective moieties and the synthesis thereof being mentioned in literature.[60,61] The starting molecule with 3-methylbutyl side chains was obtained after two steps in 4.0 gram scale and 80% overall yield. The analogue with hexyl side chains was obtained after two steps in 16.1 gram scale

and a yield of 84%. As before, the starting molecules are split up in two parts; in one part, the triple bond is deprotected and in the other part, the bromine residue is converted to an iodine moiety with *n*-butyllithium and 1,2-diiodoethane. The combination of the two parts and the addition of catalyst yields the Sonogashira product. For the conversion of the bromine into the iodine moiety, the formation of side products in the range of 1-5% was mentioned, which were detected by ^{1}H NMR analysis. Still, only cutouts of some ^{1}H NMR spectra are provided. *Via* the procedure mentioned before, eight repeat units could be combined and an end-functionalization with methyl 4-iodobenzoate was performed. 170 Milligrams of the end-functionalized octamer with 3-methylbutyl side chains was obtained in eleven steps in 9% overall yield (before end-functionalization: ten steps, 540 milligrams, 13%). The end-functionalized octamer with hexyl side chains was obtained in 265 milligram scale and in an overall yield of 19% (before end-group functionalization: 570 milligrams, 28%). The absorption spectra of some of the obtained compounds are provided and the potential use as building blocks for nanoarchitectures was mentioned.

Another synthesis procedure towards monodisperse oligomers, built up in an iterative fashion, is based on bidirectional growth. In 1999, Huang and Tour published a procedure based on Sonogashira cross-coupling.[62] 1,4-Didodecyl-2,5-diiodobenzene served as bifunctional core molecule and is formed in two steps in 86% overall yield. As a first step, the symmetric core molecule was modified with TMSA on both sides. Subsequent deprotection of the TMS protecting groups and a further Sonogashira reaction with 2 equivalents 1-bromo-4-iodobenzene yields a structure with three aromatic rings. This cycle was repeated two times, yielding a symmetric hexamer with seven aromatic rings (termed heptamer in the publication, although in terms of repeat units it is a hexamer). The overall yield accounted to 4%, but scales were not mentioned. Since only the core molecule exhibited side chains, solubility issues were a problem of this strategy. Moreover, the authors reported the formation of insoluble by-products, mainly resulting of bromine/alkyne coupling, resulting in larger oligomers. Proton and carbon NMR data were provided in text form and UV/Vis absorbance spectra were depicted.

In 2003, Chen and coworkers reported a bidirectional strategy towards *para*-OPEs (**S8a**) with building blocks exhibiting higher solubility.[63] The building

block is a bifunctional phenylacetylene with an iodine moiety and a TMS protected triple bond. Additionally, two hexyloxy (OHex) side chains are implemented for better solubility behavior of the oligomers. The building block was synthesized starting from hydroquinone in three steps and obtained in 3.3 gram scale and an overall yield of 20%. The core molecule was a benzene with two TMS protected triple bonds and two OHex side chains. It is also based on hydroquinone and was obtained after three steps in 6.3 gram scale in an overall yield of 41%. The iterative procedure begins with the deprotection of the triple bonds and subsequent Sonogashira reaction with the building block. After eight steps, 120 milligrams of the TMS protected nonamer were obtained in an overall yield of 7%. Apart from the UV/Vis absorption spectra, only the ^{1}H NMR spectrum of the protected pentamer was illustrated. End-functionalization with 1-iodo-4-thioacetylbenzene was depicted but not for the nonamer. The authors also investigated the morphology of solid-state films of the protected pentamer and mentioned its possible application as a high mobility field effective transistor through solution processing.

In 2005, Martín, Guldi *et al.* used a similar procedure to Chen's in order to connect two fullerene units for structure property relationship investigation.[64] The synthesis of the required building block is given in additional literature.[34,65] 1,4-Diethynylbenzene with two OHex side chains was used as core unit and a protected phenylacetylene with an iodine moiety and two OHex side chains as building block. Through subsequent Sonogashira reactions and deprotections, 139 milligrams of the pentamer were obtained after three steps in an overall yield of 51%. Further conversion with 2 equivalents of 4-iodobenzaldehyde enabled a 1,3-dipolar cycloaddition with *N*-octylglycine and C_{60}. In this way, a triad of a C_{60} with an OPE-bridge and a further C_{60} was obtained. The obtained products were fully characterized and fluorescence spectra as well as cyclic voltammetry data were provided, revealing that electronic interaction does not take place between the fullerene units.

Also, *meta*-OPEs (**S8b**) have been investigated, which are not rod-like molecules but rigid molecules with a predefined architecture. Moore and coworkers published a divergent/convergent approach leading to *meta*-OPEs in 1992.[66] Moore *et al.* started with a compound exhibiting two phenyl rings and two triple bonds. One of the phenylene units is equipped with a diethyltriazene moiety in

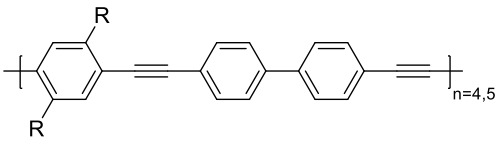
para-position. The other is equipped with a *tert*-butyl group and a TMS protected triple bond in *meta*-position. The synthesis of the starting molecule is fully depicted over eight steps, but the yields are not mentioned. The divergent/convergent approach is similar to Tour's route towards *para* OPEs.[57] Thus, the concept of converting a triazene group into an iodine moiety, whilst the triple bond is deprotected in another pot and subsequent Sonogashira reaction, was first published by Moore and coworkers.[66] After nine steps, the octamer, exhibiting 16 phenylene units, was obtained in an overall yield of 46%. The scale was not mentioned, and analytical data were only provided in text form (^{1}H, ^{13}C, HRMS). These molecules exhibit a structure, which might be useful as building blocks for nanoarchitectures.

In 2003, the group of Tew published a linear procedure leading to *ortho*-OPEs (**S8c**).[67] The starting molecule corresponds to a TMS protected phenylacetylene with a diethyltriazene moiety in *ortho*-position and an alkoxy group in *para*-position. 315 Milligrams of the starting molecule were synthesized from 4-iodo-3-nitrophenol over four steps in an overall yield of 48%. The building block can be synthesized by further conversion of the triazene moiety to an iodine, reducing the overall yield to 34%. The *ortho*-OPE (**S8c**) was built by subsequent deprotection of the triple bond and following Sonogashira reaction with the building block. 11 Milligrams of the TMS protected tetramer could be obtained after six steps in 12% overall yield. Furthermore, Tew *et al.* described the activation of the protected trimer with methyl iodide, which can then be reacted with the deprotected trimer to yield the corresponding hexamer. Over seven steps, 17 milligrams of the hexamer could be isolated with an overall yield of 12%. Analytical data, besides the UV and fluorescence spectra, were only provided in text form. The *ortho*-OPEs (**S8c**) might adopt helical structures and are therefore interesting in the context of foldamers. Table 3 displays the summary of the approaches towards monodisperse OPEs.

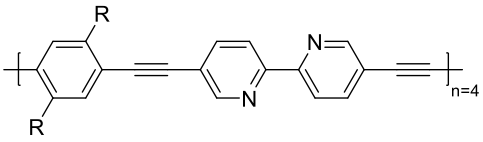
Table 3: Overview of the different approaches towards monodisperse OPEs. Work-up was consistently performed by column chromatography after each cross-coupling reaction. Adopted from Meier *et al*.[37]

	Authors, Reference	Scale	Backbone structure	max. DP (overall yield)
1	Dixneuf *et al.*[54]	not reported	(**S8a**)	3 (26%)
2	Hwang and Tour[55]	125 mg	(**S8a**)	3.5 (39%)
3	Zhao and Bo[56]	15 mg	(**S8a**)	4 (11%)
4	Tour *et al.*[58]	1.20 g	(**S8a**)	16 (27%)
5	Ziener and Godt[59]	570 mg	(**S8a**)	8 (28%)
6	Huang and Tour[62]	not reported	(**S8a**)	6.5 (4%)
7	Chen *et al.*[63]	120 mg	(**S8a**)	9 (7%)
8	Martín, Guldi *et al.*[64]	139 mg	(**S8a**)	5 (51%)
9	Moore *et al.*[66]	not reported	(**S8b**)	8 (46%)
10	Tew *et al*.[67]	17 mg	(**S8c**)	6 (12%)

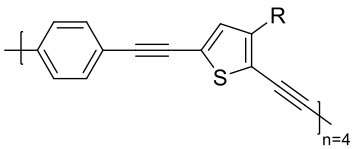
Some routes towards alternating monodisperse oligomers containing phenylene ethynylene units were also published (Figure 5).



(**S9a**) oligo(phenylene ethynylene-*alt*-biphenylene ethynylene)



(**S9b**) oligo(phenylene ethynylene-*alt*-bipyridine ethynylene)



(**S9c**) oligo(phenylene ethynylene-*alt*-thiophene ethynylene)

Figure 5: Alternating structures with phenylene ethynylene units and other aromatic compounds with triple bonds. Adopted from S. C. Solleder, R. V. Schneider, K. S. Wetzel, A. C. Boukis, M. A. R. Meier, *Macromol. Rapid Commun.* **2017**, *38*.[37]

Oligo(phenylene ethynylene-*alt*-biphenylene ethynylene)s (**S9a**) were synthesized by Schanze and coworkers in 1999.[68] The synthesis is based on the bifunctional core molecule 5,5'-diethynyl-2,2'-bipyridine and a building block of a 2-hydroxyisopropyl mono-protected diethynylbiphenyl connected to an alkoxy modified iodobenzene.[69] This building block was synthesized in four steps in 1.07 gram scale and an overall yield of 7%. After five consecutive Sonogashira reactions and subsequent deprotection, 319 milligrams of an end-functionalized tetramer could be obtained in an overall yield of 41%. After each Sonogashira reaction, the product was purified by column chromatography. Complexation of the obtained oligomers could be performed with ruthenium or rhenium and their absorption spectra were compared with the oligomers itself. The complexed oligomers exhibited a red-shift in their absorption spectra compared to the pure oligomers.

In 2005, Bryce and coworkers published a similar molecule, based on iterative Sonogashira reactions, deprotections and final dimerization.[70] Here, the ethynylbenzene and the ethynylbiphenyl unit, both exhibiting a 2-hydroxyisopropyl protecting group and an iodine moiety, were incorporated separately. The ethynylbenzene is modified with two OHex side chains for better solubility and was obtained in a one-step reaction in 12.2 gram scale and a yield of 50%. The ethynylbiphenyl unit was synthesized in one step as well and 3.08 grams of the desired product were obtained in a yield of 43%. A Sonogashira reaction with TMSA and the ethynylbenzene was performed as first step. Then, the 2-hydroxyisopropyl group was removed and a further Sonogashira reaction with the ethynylbiphenyl unit could be performed. This cycle was repeated two times and a thiophenol end-group was incorporated (pentamer, twelve steps, 170 milligrams, 11%).[71] Subsequently, the TMS group could be deprotected and a final Sonogashira reaction with a fluorene, exhibiting two iodine moieties, was performed. After 13 steps, 11 milligrams of an undecamer were thus obtained in an overall yield of 2%. The Glaser coupling side product was obtained in 3% overall yield and a scale of 14 milligrams. A further bidirectional approach was also established with a fluorenone core unit (one step, 3.66 grams, 63%). The pentamer was obtained after six steps in an overall yield of 47% and 380 milligram scale. The molecules were purified by column chromatography and their optical and electrochemical properties were analyzed. Further analytical

data (NMR, MS and elemental analysis) were provided in text form. The group of Bryce published also two more monodisperse oligomers based on oligo(phenylene ethynylene-*alt*-fluorenone)s, however these are not performed in an iterative fashion and are therefore not described in detail.[71,72]

Khatyr and Ziessel published the synthesis of monodisperse oligo(phenylene ethynylene-*alt*-bipyridine ethynylene)s (**S9b**) in 2000.[73] The synthesis of the required starting materials and building blocks was performed according to published procedures.[69,74] 5-Bromo-2,2'-bipyridine served as starting material and a diethynylbenzene with one 2-hydroxyisopropyl protected triple bond and two dodecyloxy solubilizing side chains served as one of the building blocks. A further building block was 5,5'-dibromo-2,2'-bipyridine. Subsequent Sonogashira reaction and deprotection yields a tetramer after five steps (24 milligrams, 42% overall yield). As a last step, the 5,5'-dibromo-2,2'-bipyridine was introduced by using 0.5 equivalents of it as core unit. In this way, 18 milligrams of an octamer could be obtained after six steps in an overall yield of 31%. Chromatography on alumina was performed for purification of the monodisperse oligomers. Complete analytical data are provided in text form and the absorption and emission spectra for some oligomers were shown. The oligomers can serve as polytopic ligands when complexed with a metal and could be used as an artificial photon-harvesting system. In the same publication, a route to oligo(bipyridine ethynylene)s was described, but since this procedure to a tetramer is not performed in an iterative fashion, it is not described in detail.[73] Wang and coworkers published a divergent/convergent route towards oligo(phenylene ethynylene-*alt*-thiophene ethynylene)s (**S9c**) in 2006.[75] Two starting molecules are synthesized: an ethynylthiophene with an iodine moiety, a TMS protecting group, as well as a butyl side chain and a phenyl unit with a triple bond and a diethyltriazene moiety. The thiophene unit was prepared over four steps in 5.22 gram scale and an overall yield of 49%, whereas the phenyl unit was prepared over three steps in 300 milligram scale and in an overall yield of 94%. The units are connected by Sonogashira cross-couplings, which require column chromatography as purification method after each step. The product is split up; one part is deprotected, and in the other part, the triazene moiety is converted to an iodine moiety. This procedure can be iterated and after seven steps 470 milligrams of the octamer were obtained in an overall yield of 76%. The solution phase

approach was compared with one on a solid support (compare chapter 2.1.2). Furthermore, the potential use of the obtained oligomers as molecular wires is mentioned. Table 4 summarizes approaches generating alternating structures with phenylene ethynylenes and other aromatic compounds connected to a triple bond.

Table 4: Overview of the different approaches towards monodisperse alternating structures with phenylene ethynylenes and other aromatic compounds fused to a triple bond. Work-up was consistently performed by column chromatography after each cross-coupling reaction. Adopted from Meier *et al*.[37]

	Authors, Reference	Scale	Backbone structure	max. DP (overall yield)
1	Schanze *et al.*[68]	319 mg	(**S9a**)	4 (41%)
2	Bryce *et al.*[70]	380 mg	(**S9a**)	5 (47%)
3	Khatyr and Ziessel[73]	18 mg	(**S9b**)	8 (31%)
4	Wang *et al.*[75]	470 mg	(**S9c**)	8 (76%)

Conjugated Aromatic Compounds Connected by Ethynylenes

This section describes synthesis routes leading to conjugated macromolecules, where aromatic compounds are connected by ethynylene units (Figure 6).

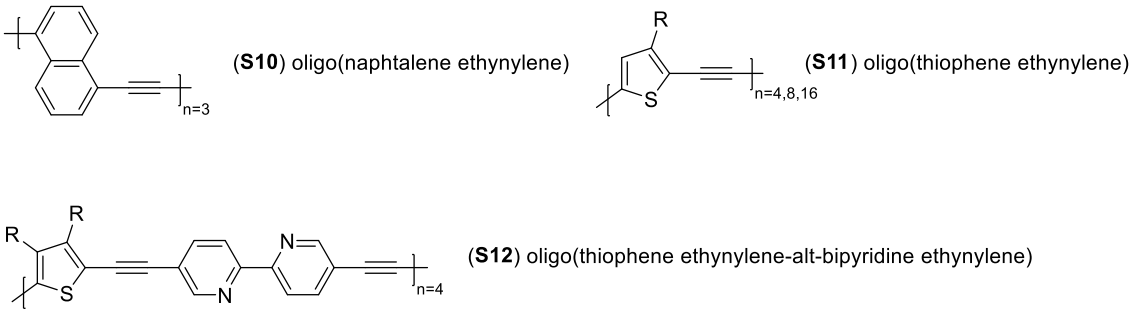


Figure 6: Monodisperse aromatic compounds connected by ethynylenes. Adopted from S. C. Solleder, R. V. Schneider, K. S. Wetzel, A. C. Boukis, M. A. R. Meier, *Macromol. Rapid Commun.* **2017**, *38*.[37]

In 2002, Rodríguez and Tejedor connected naphthalenes with ethynylenes, to yield monodisperse oligo(naphthalene ethynylene)s (**S10**).[76] The linear concept is based on Sonogashira reactions and subsequent deprotection, making use of 1-ethynyl-5-nitronaphthalene as starting molecule. It is derived in four steps in 258 milligram scale and in an overall yield of 33%. 470 Milligrams of the building

block, 1-ethynyl-5-iodonaphthalene equipped with a 2-hydroxyisopropyl protecting group, were obtained after three steps in an overall yield of 14%. Two cycles of Sonogashira reaction and deprotection (four steps) yielded the deprotected trimer in a scale of 177 milligrams and an overall yield of 32%. After the Sonogashira reactions, the dimer and trimer were purified by flash column chromatography. Furthermore, the trimer can be dimerized by a final Glaser coupling to yield the symmetric hexamer (five steps, 50 milligrams, 26% overall yield) or another end-group functionalization is possible. Complete analytical data are provided in text form and charge-transfer absorption and fluorescence emission spectra were reported for the end-functionalized representatives. Another aromatic system connected to triple bonds are oligo(thiophene ethynylene)s (**S11**), published by the group of Tour in 1997.[77] The starting molecule, a TMS-protected 3-ethyl-2-ethynylthiophene, was synthesized starting from 3-bromothiophene in three steps in an overall yield of 70% and in a scale of 12.7 grams. The molecule is on the one hand activated with iodine and on the other hand deprotected to finally be recombined in a Sonogashira reaction. This cycle was repeated three times. By this, the 16-mer was obtained after twelve steps. The overall yield adds up to 600 milligrams and 20%. As usual for Sonogashira reactions, column chromatography was necessary for purifying the obtained oligomers. Analytical data (^{1}H NMR and IR spectroscopy) were provided in text form in this publication, however, in a continuative publication, rather poorly resolved ^{1}H NMR spectra are provided.[77] In the continuative publication, the synthesis of additional potential starting molecules and an end-functionalization of the derived oligomers was described. However, the same 16-mer with identical yield was published. The products were also discussed in the context of molecular wires.

Monodisperse oligo(thiophene ethynylene-*alt*- bipyridine ethynylene)s (**S12**) were published in 2005 by Ziessel and coworkers.[78] The concept is based on bidirectional Sonogashira reaction and deprotection. The synthesis of the bifunctional core molecule 5,5'-diethynyl-2,2'-bipyridine is not depicted. The building block is a triethylsilyl protected diethynylbipyridine fused to a thiophene, exhibiting two butyl solubilizing groups and an iodine moiety. The synthesis starts from 5,5'-dibromo-2,2'-bipyridine and after four steps, the building block is obtained in a yield of 175 milligrams and 21%. After four steps, the tetramer

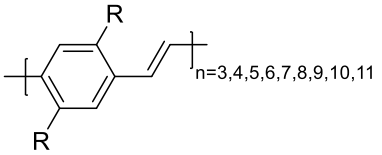
(termed as pentamer, however four repeat units are present) was obtained in an overall yield of 54% and a scale of 108 milligrams. This molecule can be end-functionalized with iodothiophene. Alternatively, a route starting from a thiophene core molecule was established, but this is not strictly iterative. Once more, column chromatography was performed for the purification after the Sonogashira reactions. The products were fully characterized, absorption and emission spectra were provided, as well as cyclic voltammograms. Moreover, the synthesized oligomers can be used as ligands for metal complexes. Table 5 illustrates the summary of the synthesis routes to monodisperse conjugated aromatic compounds connected by ethynylene units.

Table 5: Overview of the different approaches towards conjugated aromatic compounds connected by ethynylenes. The abbreviation CC refers to column chromatography. Adopted from Meier *et al*.[37]

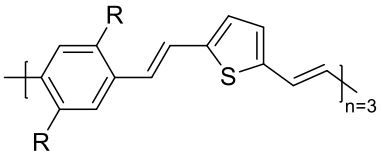
	Authors, Reference	**Scale (DP)**	**Backbone structure**	**Work-up**	**max. DP (overall yield)**
1	Rodríguez and Tejedor[76]	50 mg	(**S10**)	flash CC	6 (26%)
2	Pearson and Tour[77]	600 mg	(**S11**)	CC	16 (20%)
3	Ziessel *et al*.[78]	108 mg	(**S12**)	CC	4.5 (54%)

Oligo(phenylene vinylene)s (OPVs)

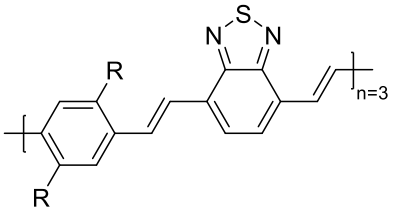
A further important class of conjugated oligomers are oligo(phenylene vinylene)s (OPVs). Several linear iterative routes towards monodisperse OPVs have been described. First, four procedures, where starting materials with two benzene rings were employed, are depicted. Afterwards, approaches based on a single benzene building block, enabling a higher degree of control are described. Additionally, phenylene vinylenes alternating with other aromatic compounds have been described in the literature (Figure 7).



(**S13**) oligo(phenylene vinylene)
oligo(PV)



(**S14a**) oligo(PV-*alt*-thiohene vinylene)



(**S14b**) oligo(PV-*alt*-benzothiadiazole vinylene)

Figure 7: Overview of the structures of potential monodisperse oligo(phenylene vinylene)s. Adopted from S. C. Solleder, R. V. Schneider, K. S. Wetzel, A. C. Boukis, M. A. R. Meier, *Macromol. Rapid Commun.* **2017**, *38*.[37]

The first approach towards monodisperse OPVs (**S13**) was published by Yu and coworkers in 1996.[79] They synthesized two building blocks and one starting compound. One building block is a vinyl-styryl-benzaldehyde and the other an iodo-styryl-benzylphosphonate. They both exhibit two octyloxy side chains on one aromatic ring for better solubility. The vinyl-styryl-benzaldehyde is synthesized in two steps in 525 milligram scale and an overall yield of 41%; the synthesis of iodo-styryl-benzylphosphonate requires five steps and is obtained in 1.02 grams and an overall yield of 12%. The starting molecule is a styrylbenzene with an iodine moiety; it is formed in one step, but yields are not mentioned. With the starting molecule and the building block carrying both a vinyl and an aldehyde end group in hand, a Heck reaction can be performed. Subsequently, the formed monomer can undergo a Horner-Wadsworth-Emmons (HWE) reaction with the other building block, exhibiting a phosphonate and an iodine moiety. After five steps, the pentamer with twelve aromatic rings was obtained, but yields and scales are not provided. The proton NMR spectrum confirms the purity of the compounds. The authors reported also the formation of the *cis*-product in the HWE reaction and the generation of regioisomers by the Heck reaction, but these impurities could be separated by column chromatography. Later, Yu *et al.* used

the formed oligomers for the synthesis of OPV-polyisoprene diblock copolymers.[80] By transmission electron microscopy, they could verify microphase separation and the formation of bilayer lamella phases.

In 2004, Jørgensen and Krebs published another procedure towards monodisperse OPVs (**S13**) by HWE reactions and subsequent acetal deprotections.[81] In this way, the only required building block is a diphenylethene core with two propyl groups, an acetyl protected aldehyde and a methylphosphonate. It was obtained after two steps in 42.9 gram scale and in an overall yield of 71%. The building block was prepared according to literature.[60,82] First, the building block was converted with 4-methoxybenzaldehyde or 4-(dimethylamino)benzaldehyde in a HWE reaction. Then, the aldehyde was deprotected and further cycles of HWE reactions with the building block and subsequent deprotection could be performed. The approach with the dimethylamino moiety was conducted until the trimer stage in an overall yield of 71%, the other with the methoxy side chain until the pentamer stage in an overall yield of 27%. The scale was not mentioned. The compounds were purified by precipitation and washing, but the SEC traces are slightly broadened and indicate the presence of traces of starting material. Additionally, Jørgensen and Krebs performed an end-group functionalization and applied the synthesized oligomers in photovoltaic cells. In 2005, Jørgensen and Krebs extended their concept for further building blocks, enabling the synthesis of oligo(PV-*alt*-thiophene vinylene)s (**S14a**) and oligo(PV-*alt*-benzothiadiazole vinylene)s (**S14b**) as well as a sequence-defined trimer based on both of the aforementioned oligomers.[83] Furthermore, a further building block with propoxy chains groups, instead of propyl, was synthesized in two steps in 99% yield and in a scale of 47.8 grams. The styrylthiophene building block with an acetal fused to the benzene and a methylphosphonate fused to the thiophene (propyl side chains) was synthesized over five steps in 3.2 gram scale and 6% overall yield. An analogue with isopropoxy side chains was obtained in 9% overall yield. The styrylbenzothiadiazole is built up in the same way but with propyl residues only. It was obtained in a ten-step synthesis in 6.5 gram scale and an overall yield of 4%. Again, 4-methoxybenzaldehyde was introduced in the first HWE reaction. With the concept described above, four different homo-trimers with the described building blocks were synthesized over three steps. 1.2 Grams of the tri-(PV) (**S13**)

with propoxy groups was obtained in a yield of 52%. The tri-(PV-*alt*-thiophene vinylene) (**S14a**) with propyl side chains in a yield of 19%, the analogue with propoxy side chains in 45% overall yield and the tri-(PV-*alt*-benzothiadiazole vinylene) (**S14b**) could not be evaluated, since the scale only allowed mass spectrometry and absorption spectroscopy. Making use of the three different building blocks and piperonal as starting compound a sequence-defined hetero-trimer was synthesized over three steps in an overall yield of 15%. The hetero-trimer is the first described sequence-defined conjugated OPV. Again, purification by washing was sufficient, but this time only proton NMR and HRMS data were provided in text form. SEC traces were not provided, but absorption spectra were depicted. The materials were again tested in photovoltaic cells with efficiencies ranging from 0.5 to 1%.

Several publications focus on the synthesis of monodisperse OPVs (**S13**) based on single benzene building blocks. In 2001, Detert and coworkers published a procedure based on HWE reaction and subsequent acetal deprotection or ester reduction.[84] A bifunctional benzene exhibits a methylphosphonate and an acetal protected aldehyde or ester. The protected acetal was synthesized in three steps in an overall yield of 20%. The synthesis of the ester is neither illustrated nor is the respective literature mentioned. The starting compound, exhibiting a methylphosphonate and two octyloxy side chains for better solubility, was synthesized in three steps in an overall yield of 49%. With this compound in hand, a first HWE with the acetal building block, which is immediately deprotected, is performed. The concept itself is inconsistent, as sometimes the acetal and other times the ester form is used to mask the aldehyde. After four steps, 3.9 grams of the trimer were obtained in an overall yield of 35%. Column chromatography was chosen for the purification of the oligomers. The aldehydes can be further converted into halogens, enabling a Heck reaction with alkoxysilanes, exhibiting a double bond, which is interesting for electronic applications. Analytical data (NMR, MS, IR, elemental analysis) were only provided in text form.

Iwadate and Suginome published a linear procedure towards OPVs based on Suzuki couplings in 2009.[85] Through hydroboration of bromine-substituted phenylacetylenes with an iridium-catalyst and the 1,8-naphtalene-diaminatoboran ((dan)BH) protecting group, several building blocks were synthesized. In this way, six different B(dan)-protected styrene derivatives were

obtained in reaction scales between 53 and 700 milligrams and overall yields between 41 and 81%. The monomers are formed by Suzuki reaction with *para*-tolylboronic acid, but the iterative procedure was only pursued with one specific monomer. When applying hydrochloric acid, the boronic acid is obtained and a further Suzuki coupling with another building block can be performed. By repeating this cycle, a protected trimer in a scale of 42 milligrams and an overall yield of 72% was obtained after five steps. The ^{1}H and ^{13}C NMR spectra of the obtained compounds are provided, presenting oligomers of high purity, which were obtained after column chromatography.

The group of Tara Meyer developed several routes to OPVs (**S13**). The first one, published in 2010, is based on cross-metathesis with subsequent Wittig reaction.[86] Therefore, one starting molecule and two building blocks were required. The starting molecule, 2,5-*bis*(hexyloxy)-4-iodobenzaldehyde, was synthesized in four steps in an overall yield of 67% and in a scale of 45.2 grams. One step further provided the building block molecule 2,5-*bis*(hexyloxy)-4-vinylbenzaldehyde, diminishing the overall yield to 51%. It was obtained in a 5.97 gram scale. The synthesis of the other building block, 4-vinylbenzaldehyde, was referred to literature.[87] With the starting material in hand, a cross-metathesis with 4-vinylbenzaldehyde can be performed. By a subsequent Wittig olefination of the implemented carbonyl with $Ph_3P{=}CH_2$, a new vinyl group is created. Now, the other building block can be incorporated, leading to 93 milligrams of an alternating pentamer in an overall yield of 21% over eight steps. The ^{1}H and ^{13}C NMR spectra are provided and confirm a high purity of the obtained products, which were obtained after column chromatography. Furthermore, the iodine moiety permits orthogonal functionalization by Suzuki coupling with a chromophore. Additionally, the pentamer was functionalized with a further vinyl group and subsequently polymerized in an acyclic diene metathesis (ADMET) polymerization using the second generation Grubbs catalyst. In 2013, Hutchison, Meyer and coworkers published a procedure leading to OPVs *via* HWE reaction and subsequent diisobutyl aluminium hydride (DIBAL-H) reduction of implemented cyanide residues.[88] Two different starting compounds and two different building blocks were used; one starting compounds is 4-bromobenzaldehyde, which is commercially available. Its analogue with two OHex chains was synthesized over two steps in 40.5 gram scale and 50% overall

yield. As building blocks, 4-cyanobenzylphosphonate was synthesized over two steps in a 16.7 gram scale in an overall yield of 35% and the analogue with two OHex side chains over six steps in 11.7 gram scale and in an overall yield of 29%. In cycles of HWE reaction and DIBAL-H reduction, three different pentamers with six aromatic rings were obtained after nine steps. The scales differ from 147 to 280 milligrams and the overall yields from 21 to 48%. The authors reported the formation of *Z*-stereoisomers, demanding a purification by column chromatography. NMR and MS data were provided in text form and absorption and emission spectra, as well as cyclic voltammograms were depicted. These data indicated an important coherence of sequence and electronic properties.

Further investigations in this field were published by Hutchison, Meyer and coworkers in 2016.[89] Here, the concept is also based on HWE reaction and subsequent DIBAL-H reduction. A newly designed building block, based on benzothiadiazole with a methylphosphonate and a cyanide group, was prepared over five steps in a 120 milligram scale. The yields are not mentioned. The synthesis of the respective benzothiadiazole starting block with a bromine moiety instead of the cyanide, was published by Jørgensen and coworkers.[83] The starting molecule with two OHex chains and the respective building block of the formerly described publication were reused.[88] Hutchison and Meyer compared the optical properties of two dimers with three aromatic rings and their polydisperse polymers. The dimer with the benzothiadiazole in the center was obtained after three steps in an overall yield of 61% and a scale of 38.0 milligrams. The dimer with the benzothiadiazole at the end was obtained in 49.0 milligram scale and 54% yield. The ^{1}H NMR spectra are provided and exhibit a high purity, which was obtained after column chromatography. Interestingly, the electrochemical properties of the dimers are similar to the polymer-analogues. Table 6 summarizes the synthetic procedures towards OPVs.

Table 6: Overview of the different approaches towards monodisperse OPVs. Adopted from Meier *et al*.[37]

	Authors, Reference	Scale	Backbone structure	Purity	Work-up	max. DP (overall yield)
1	Yu *et al.*[79]	not reported	(**S13**)	high (NMR)	CC	5.5 (not reported)
2	Jørgensen and Krebs[81]	not reported	(**S13**)	high (SEC, minor impurities)	precipitation and washing	5 (26%)
3	Jørgensen and Krebs[83]	1.20 g (**13**)	(**S13**) (**S14a**) (**S14b**)	not reported	washing	3 (52%) 3 (19%) 3 (45%)
4	Detert *et al.*[84]	3.9 g	(**S13**)	not reported	CC	3 (35%)
5	Iwadate and Suginome[85]	42 mg	(**S13**)	high (NMR)	mostly CC	3 (72%)
6	Meyer *et al.*[86]	93 mg	(**S13**)	high (NMR)	CC	5 (21%)
7	Hutchison, Meyer *et al.*[88]	280 mg	(**S13**)	not reported	CC	5.5 (48%)
8	Hutchison, Meyer *et al.*[89]	38 mg	(**S14b**)	high (NMR)	CC	2.5 (61%)

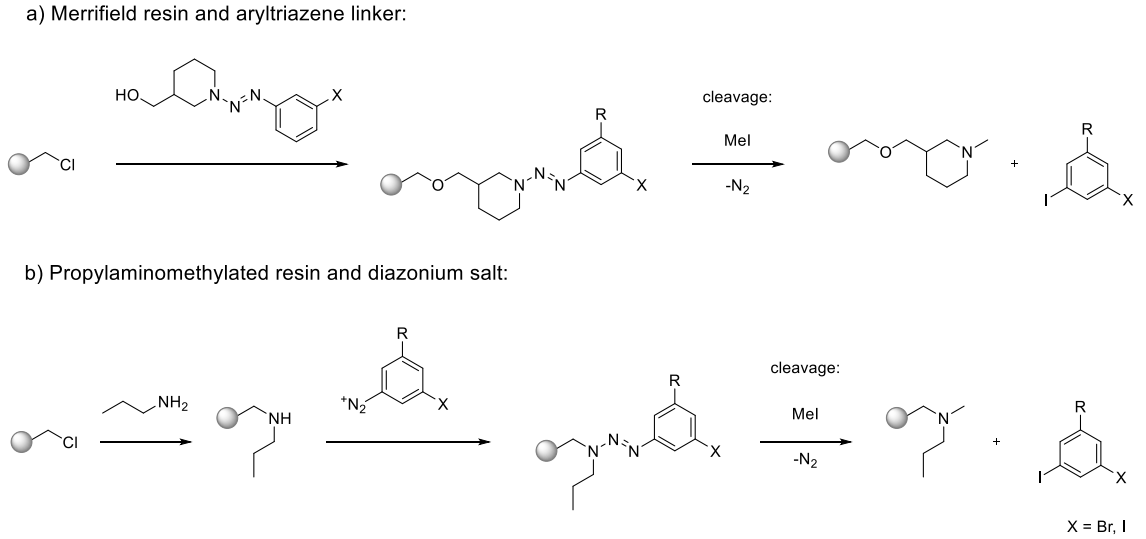
All in all, manifold approaches for the synthesis of conjugated monodisperse macromolecules in solution are reported, leading to diverse backbone structures and different side chain substitutions. The liquid-phase approaches thereby benefit from simple characterization, scalability and liquid-phase kinetics. The next chapter describes synthesis approaches on solid supports.

2.1.2 Solid Phase Approaches

Apart from the solution-based synthesis of monodisperse conjugated oligomers, some procedures have been established on a solid support. Purification is often time-consuming, and procedures based on SPOS require mostly only one purification step after cleavage.

Oligo(acetylene)s and Derivatives

Diederich and coworkers published a route to monodisperse oligo(triacetylene-*alt*-phenylene)s (**S5a**) in 2003.[90] The synthesis of the hexenediyne/diethynylethene starting molecule, with one triple bond protected with a TMS group, has been reported earlier.[91] A triazene linker was chosen for the attachment to the Merrifield resin, since it is compatible with Pd(0)-catalyzed reactions (Scheme 3a).[58,92–95]



Scheme 3: Two synthesis procedures towards a polymer resin with triazene linker as published by Moore *et al*.[93] Either a triazene linker is prepared and connected to chloromethylated polystyrene (Merrifield resin) as in a) or the Merrifield resin is treated with *n*-propylamine generating propylaminomethylated polystyrene, which can then react with a diazonium salt creating the triazene linkage (b). Cleavage is performed with methyl iodide and results in the respective aryl iodide, nitrogen and the methylated resin residue.[96] This scheme is reproduced with permission from: S. C. Solleder, R. V. Schneider, K. S. Wetzel, A. C. Boukis, M. A. R. Meier, *Macromol. Rapid Commun.* **2017**, *38*.[37] Copyright © 2017, John Wiley and Sons.

The 1-aryltriazene linker of Diederich also exhibits an iodine moiety and can undergo a Sonogashira reaction with the formerly described starting molecule. The building block, required for oligomer synthesis, was synthesized on a solid support and obtained after cleavage from the resin using methyl iodide (two steps, 83%). With this phenyl containing diethynylethene- building block in hand, subsequent TMS deprotection and Sonogashira coupling can be performed. After six reaction steps, the cleaved tetramer could be obtained in a yield of 36%. The scale of the oligomers amounted to 100-200 milligrams. The purification is

facilitated due to the solid support, compared with the solution phase approaches. Therefore, only one column chromatography after the final cleavage was necessary to obtain the pure oligomers. Apart from UV/Vis spectra, where a high fluorescence emission was reported, analytical data in text form were only provided for the dimer. Compared to the solution-based publication of Takayama, Sato and coworkers, where a trimer was synthesized over five steps in 51% overall yield and a scale of 79 milligrams, the solid-phase approach offers minor advantages, allowing an overall yield of 56%.[48] The approach is summarized in Table 7.

Oligo(thiophene)s

Oligo(thiophene)s are another class of monodisperse conjugated oligomers. The synthesis of homo-oligo(thiophene)s was only investigated on solid supports so far. In solution, different co-oligomers alternating with thiophenes have been prepared in an iterative fashion.[75,77] The first approach towards oligo-(thiophene)s was published by Malenfant and Fréchet in 1998.[97] The linkage to the Merrifield resin is achieved using [2,2'-bithiophene]-5-carboxylic acid in 84% yield (measured by yield after cleavage). A bromination was performed with *N*-bromosuccinimide and subsequently a Stille coupling can be performed with 4 equivalents of 2-(trimethylstannyl)-4-octylthiophene. The synthesis of the employed building block has been described before.[98] By repeating brominations and Stille couplings, a pentamer was obtained after seven steps, including cleavage (the linker molecule already displays a dimer). Before performing analytical HPLC, the oligomers were filtered through silica gel. For the pentamer, a purity of 89% (HPLC) was detected. The pentamer was obtained in a scale of 67 milligrams and the overall yield was calculated to 90%, assuming full conversion in each step and considering the loading of the uncleaved pentamer (the respective reverse phase HPLC chromatograms were not depicted). Analytical data (NMR, HRMS, IR, elemental analysis) of the pentamer were provided in text form.

Another approach, leading to monodisperse oligo(arylthiophene)s was described by Bäuerle and coworkers.[99] The 3-arylthiophene starting molecules, exhibiting a traceless silyl linker and different moieties on the phenyl residue, were synthesized in one-step procedures. Overall, four different linker molecules as

well as four 3-arylthiophene building blocks with dioxaborolanes were prepared. The residue on the *para*-position of the phenyl ring is either a trifluoromethyl group (73%, 71%; yield linker molecule and building block, respectively), a hydrogen (65%, 69%), a methyl (60%, 74%) or a methoxy (79%, 85%) group.[100] The described molecules enabled the synthesis of a library of 256 tetramers with the linkers anchored to a hydroxymethylated cross-linked polystyrene. The procedure is based on iterative iodination with lithium diisopropylamide and iodine and subsequent Suzuki coupling of the building blocks. The silyl linker is cleaved from the polystyrene resin upon treatment with trifluoroacetic acid and purified by automated preparative HPLC. After eight steps, the tetramers could be isolated in yields ranging from 2 to 51%. Most of them exhibited a purity higher than 98%. The conversion for every step ranges between 89 and 93%, with an overall conversion of 40 to 55% as detected by ^{1}H NMR of selected raw products. Cyclic voltammetry was performed for every tetramer in a 256 well plate. Apart from the cyclic voltammetry, NMR data of four selected tetramers were provided in text form. The concept of performing combinatorial chemistry with subsequent screening for their electronical or optical properties could be implemented successfully. In an additional publication of Briehn and Bäuerle, this library was analyzed in a more detailed way and some HPLC and NMR data were depicted.[101] The mentioned scale amounts to 5 to 15 milligrams. Table 7 summarizes the solid phase approaches to monodisperse oligo(triacetylene-*alt*-phenylene)s and oligo(thiophene)s.

Table 7: Overview of the depicted approaches to oligo(triacetylene-*alt*-phenylene)s and oligo(thiophene)s on solid phase. Adopted from Meier *et al*.[37]

	Authors, Reference	**Scale (isolated)**	**Backbone structure**	**Purity**	**Work-up**	**max. DP (overall yield)**
1	Utesch and Diederich[90]	200 mg	(**S5a**)	not reported	CC	4 (36%)
2	Malenfant and Fréchet[97]	67 mg	thiophene	89% (HPLC)	filtration	5 (90%)
3	Bäuerle *et al.*[99]	15 mg	thiophene	mostly ≥98% (HPLC)	HPLC	4 (51%)

Oligo(phenylene ethynylene)s (OPEs) and alternating Phenylene Ethynylenes

For OPEs, the *para*-OPEs (**S8a**) established by Tour and coworkers are herein described first.[55] Therefore, the same set of building blocks as in the liquid phase approach was used, but additionally a diazonium linker exhibiting a TMS protected triple bond was synthesized in one step from the aniline derivative in an overall yield of 85%. The Merrifield resin was treated with *n*-propylamine displaying a secondary amine function, which can react with the diazonium linker under basic conditions (compare Scheme 3b). By subsequent deprotection and Sonogashira coupling, various sequence-defined trimers with three aromatic repeat units were synthesized. Note that in the solution phase approach trimers, exhibiting four aromatic compounds with a thioester terminus, were prepared. The thioester termini were not compatible with the cleavage, which was performed with 10% hydrochloric acid in tetrahydrofuran (THF) and sonication. After five steps, including the formation of the triazene linkage, 25 trimers were obtained after one final column chromatography in overall yields ranging from 18 to 34% and in scales of 23 to 48 milligrams. Both yields and scales are comparable with the solution phase approach, but the end-group functionalization with thioester termini was only possible in the solution phase approach, which diminishes the overall yield of the oligomers obtained in solution. Before the last Sonogashira reaction, the TMS protected trimers were obtained in yields between 38 and 81% in the solution phase approach (136 to 310 milligrams). Apart from the complicated purification, the solution phase approach is thus favored when yields, scale and possible end-group functionalization are considered.

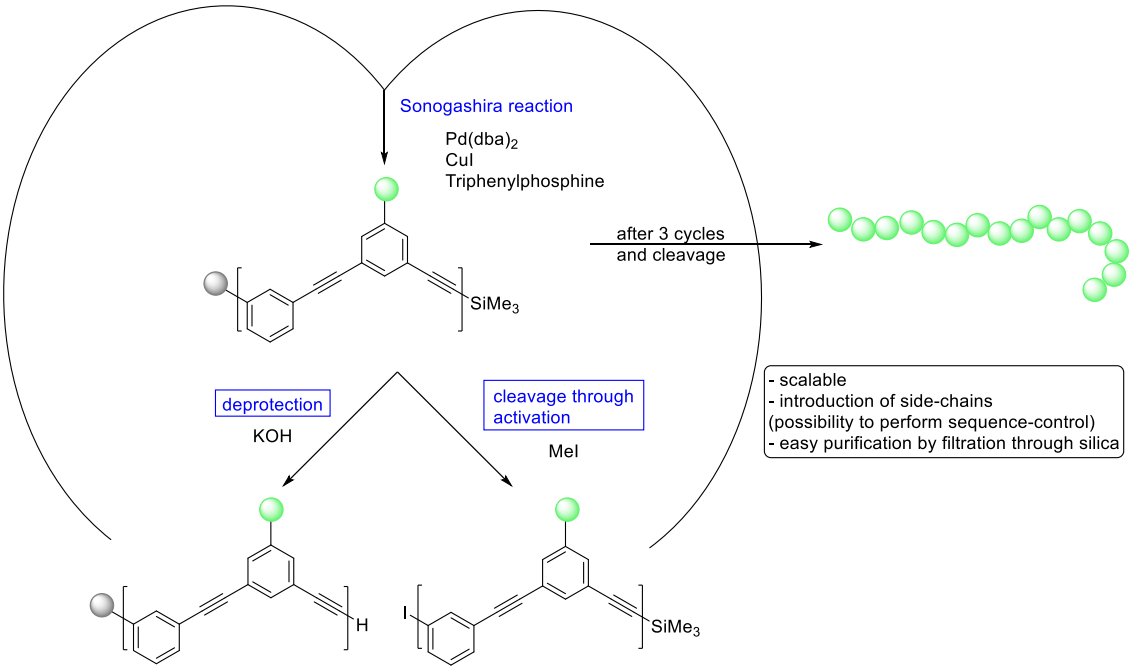
As for the linear approach, the divergent/convergent approach towards *para*-OPEs (**S8a**) was described for solution and solid phases synthesis in the same publication of Tour and coworkers in 1997.[58] For the solid support, a triazene linker was synthesized from 1-iodo-3-nitrobenzene (compare Scheme 3). After seven steps, a TMS-protected phenylacetylene, exhibiting a dodecyl solubilizing group and the triazene with a primary hydroxy group for attachment to the Merrifield resin, was obtained. This molecule can either be treated with potassium carbonate, generating the unprotected linker molecule (36%, 940 milligrams) or with methyl iodide, cleaving the TMS-protected 1-ethynyl-4-iodobenzene with one dodecyl side chain (39%, 2.83 grams) as

starting molecule. The attachment of the linker to the resin had an efficiency of 77%, which was detected by elemental analysis. Then, a Sonogashira reaction with the starting molecule was performed. The resulting molecule was either cleaved with methyl iodide or deprotected with Tetra-*n*-butylammonium fluoride (TBAF). Recombining the two products, a Sonogashira reaction can be performed. After twelve steps, including the attachment to the linker, 840 milligrams of the cleaved 16-mer was obtained in an overall yield of 32% after final workup by column chromatography. When excluding the attachment to the resin, the overall yield is 42%. This value was calculated by elemental analysis and not confirmed by other experiments. Comparing the solution and the solid phase synthesis, the yield is better in the solid phase approach (42% vs. 27%), but 1.2 grams (vs. 840 milligrams) were obtained in solution. Also, here, end-group functionalization of the oligomers is possible enabling the adhesion to a surface for conduction studies.

Bidirectional procedures combined with a divergent/convergent strategy towards *para*-OPEs have been also performed with solid phase syntheses by the Tour group.[95,102] For this approach, 1.28 grams of a core molecule were synthesized from 1,4-dichlorobenzene over four steps in an overall yield of 32%. The core molecule is a 1,4-diiodobenzene with two hydroxypentyl ($C_5H_{10}OH$) groups. Two building block molecules, a 1,4-diethynylbenzene with one TMS protected triple bond (one step, 92%, 3.14 grams) and a 1,4-diiodobenzene with two dodecyl side chains (two steps, 86%, 10.9 grams), are required for the synthesis. 3,4-Dihydro-*2H*-pyran-2-methanol, a typical linker to the Merrifield resin, was used, where the hydroxy group of the core molecule could be easily attached. A Sonogashira reaction with the 1,4-diethynylbenzene building block can be performed with subsequent TBAF deprotection. Then, another Sonogashira reaction can be conducted and this molecule is split up in two parts. On the one hand, a further Sonogashira reaction with the 1,4-diethynylbenzene building block was performed, and on the other hand, the tetramer (exhibiting five aromatic rings) was cleaved with pyridinium *para*-toluenesulfonate. With a further Sonogashira reaction of the recombined parts, a 16-mer with 17 aromatic rings was obtained. After cleavage, 1.30 grams of the respective 16-mer were obtained in a seven-step procedure in an overall yield of 20%, which was determined by comparing the loading of the core molecule on the resin with the yield of the final

oligomers.[95] Only flash column chromatography was necessary to obtain the pure 16-mer after cleavage from the resin. In one of the publications, the formation of alternating block co-oligomers with thiophene was described, but the oligo(thiophene ethynylene)s were incorporated as whole tetramers.[102] The respective ^{1}H NMR spectra are shown but suffer from poor resolution. A comparison with the corresponding bidirectional approach in solution is not useful, since it is not combined with a divergent/convergent step.[62]

Furthermore, monodisperse *meta*-OPEs (**S8b**) have been synthesized on the solid support. The group of Moore established not only the solution phase approach but also published a route based on solid support synthesis.[66,93,94] As shown in Scheme 3, the group of Moore published both routes towards triazene linkage systems for solid supports in 1994.[93] With both strategies, a bromine-substituted benzene is incorporated, which can be reacted to a phenylacetylene. Then, the phenylacetylene coupled to the solid support is converted with TMS-protected 1-(*tert*-butyl)-3-ethynyl-5-iodobenzene. The synthesis of 1-(*tert*-butyl)-3-ethynyl-5-iodobenzene is not depicted. The resin-bound dimer is split up in two parts and either deprotected with potassium hydroxide or cleaved with methyl iodide. Recombining the two products under Sonogashira conditions afforded the resin-bound tetramer (Scheme 4). After eleven steps, the 16-mer is obtained in an overall yield of 50%. When applying a further cycle towards the 32-mer, solubility problems and diminished swelling behavior appeared. The 32-mer did not fully convert and 5% of unreacted 16-mer were still present. The cleaved oligomers were purified by filtration through silica gel. Nevertheless, the SEC traces of the respective oligomers, even for the 32-mer, confirm a high purity. Compared to the solution phase approach (46% for octamer), the synthesis on a solid support leads to a higher overall yield (50% for 16-mer) and is therefore not only easier to perform but synthetically more favored.[66]



Scheme 4: Solid phase synthesis approach by Moore et al. towards meta-OPEs (**S8b**). Therefore, Sonogashira reactions are performed to couple the deprotected part and a part, which was previously cleaved from the resin. This divergent/convergent approach features scalability, the introduction of side chains along with simple synthesis and purification procedures. This scheme is reproduced with permission from: S. C. Solleder, R. V. Schneider, K. S. Wetzel, A. C. Boukis, M. A. R. Meier, *Macromol. Rapid Commun.* **2017**, *38*.[37] Copyright © 2017, John Wiley and Sons.

A linear concept leading to *meta*-OPEs (**S8b**) on solid support was also published by Moore and coworkers in 1996.[94] The triazene linkage to the polymer support was obtained *via* the pathway illustrated in Scheme 3b). Overall, three different diazonium salts were prepared, exhibiting a bromine and a further side chain, *i.e.* OHex (six steps, 18%, 5.62 grams), hexanoate ($COOC_6H_{13}$) (two steps, 72%, 6.35 grams) or cyano (five steps, 29%, 7.23 grams). The synthesis of the mentioned diazonium salts was conducted according to literature.[103] After attachment to the solid support, a Sonogashira reaction with TMSA was performed and monitored by gas chromatography (GC). Therefore, an aliquot of the solution was removed and quenched with diethylamine, releasing the diethyltriazene and conversion can easily be followed by GC. Cleavage with methyl iodide resulted in the necessary building blocks exhibiting an iodine moiety, a protected triple bond, and an OHex or a hexanoate side chain. The OHex derivative was obtained in 94% yield and a purity of 97%, the hexanoate-derivative in 98% and a purity of 94%. The oligomers were prepared by TBAF

deprotection and subsequent Sonogashira reaction with the building blocks. In this way, after ten steps including cleavage and flash column chromatography, 1.59 grams of a hexamer were obtained in 48% overall yield and a purity of 92%. Moore *et al.* synthesized also a further hexamer (58% yield, 460 milligrams, 98% purity) with cyano and *tert*-butyl side chains, but the monomer synthesis was not described. The authors reported the execution of the same hexamer syntheses in solution with 39% and 40% yield, but the experimental part is not depicted. Small impurities are present, which were detected by HPLC.

Anderson described a further solid supported synthesis leading to mixed *ortho*-, *meta*- and *para*-OPEs (**S8**).[92] Starting from 2-, 3- and 4-iodoaniline, the respective TMS protected *ortho*-, *meta*- and *para*-ethynylbenzenediazonium salts were prepared over two steps and a further treatment with potassium iodide yielded the respective building blocks. The *ortho*, *meta* and *para* building blocks were obtained in 6.3 gram scale (52%), 700 milligram scale (47%) and 700 milligram scale (48%), respectively. Furthermore, a *para* building block exhibiting a TIPS protecting group instead of TMS, was synthesized in an additional step in 6.2 gram scale and 38% overall yield. As before, the Merrifield resin was treated with *n*-propylamine and the respective diazonium salts were attached, forming a triazene linkage. TBAF deprotection and Sonogashira reaction with the building blocks was used for chain elongation. Anderson used a so called tea bag synthesis, where the different approaches are locally divided, but the reactions are performed in one pot. After cleavage and flash column chromatography, 18 pentamers exhibiting various geometries were obtained in yields ranging from 16 to 47% and scales ranging from 70 to 210 milligrams. The yields were calculated from elemental analysis data. NMR and MS data were provided in text form and selected absorption and emission spectra are depicted. One of the pentamers was incorporated into a single-layer light emitting diode.

The synthesis of oligo(PE-*alt*-thiophene ethynylene) (**S9c**) was not only performed in solution, but the group of Wang performed this procedure also on a solid support.[75] Also here, the triazene linkage system with diazonium salts, which was synthesized from 4-iodoaniline in 97% yield, was used. After a Sonogashira reaction with TMSA and a subsequent deprotection, the aforementioned thiophene building block was incorporated. Now, the same divergent/convergent synthesis procedure as for the solution phase approach

was applied. The same octamer is obtained after cleavage and washing in a scale of 190 milligrams. The authors reported that the yields presented are only roughly estimated, based on the weight changes of the resins before and after a reaction. With the declared yields of each step, an overall yield of 25% can be calculated. Compared to the solution phase approach, where 470 milligrams of the octamer were obtained in an overall yield of 75%, the solid supported synthesis cannot compete. In Table 8 the approaches towards OPEs and alternating phenylene ethynylenes are summarized.

Table 8: Overview of the approaches to OPEs and alternating phenylene ethynylenes on solid support. Adopted from Meier *et al*.[37]

	Authors, Reference	**Scale (isolate)**	**Backbone structure**	**Purity**	**Work-up**	**max. DP (overall yield)**
1	Hwang and Tour[55]	48 mg	(**S8a**)	not reported	CC	3 (34%)
2	Tour *et al.*[58]	840 mg	(**S8a**)	high (NMR)	CC	16 (42%)
3	Huang and Tour[102]	1.30 g	(**S8a**)	high (NMR)	CC	16.5 (20%)
4	Moore *et al.*[93]	not reported	(**S8b**)	high (SEC)	filtration	16 (50%)
5	Moore *et al.*[94]	460 mg	(**S8b**)	98% (HPLC)	flash CC	6 (58%)
6	Anderson[92]	210 mg	(**S8**)	not reported	CC	5 (47%)
7	Wang *et al.*[75]	190 mg	(**S9c**)	not reported	washing	8 (25%)

In summary, a large variety of approaches for the synthesis of non-conjugated sequence-defined macromolecules on solid supports, leading to diverse backbone structures and different side chain substitutions, are reported. The solid phase approaches thereby benefit from simple purification by filtration and washing.

2.1.3 Fluorous-Supported Synthesis and Polymer-Tethered Approach

Fluorous-supported and polymer-tethered approaches are more recent techniques, which are an alternative to classical SPOS. Fluorous-tagged (F-tag) compounds can be purified more easily, since they interact specifically with other fluorous substrates, such as fluorous silica gel.[104] Through fluorous solid phase extraction (FSPE) impurities can be separated easily. Polymer-tethered

approaches use a soluble polymer support and can be purified by simple precipitation.[105]

Oligo(phenylene vinylene)s (OPVs)

One example using FSPE in the synthesis of oligo(phenylene vinylene)s was published in 2005 by Jian and Tour.[106] Ten sequence-defined trimers were obtained by subsequent Heck and HWE reaction. Purification was performed with a FSPE HPLC system. Overall yields ranged from 22-64%, scales were not reported. The trimers were analyzed by NMR, MS and UV/Vis, confirming a high purity. The F-tag was only cleaved for one example, where a trimer with 9 milligrams and an overall yield of 30% was obtained.

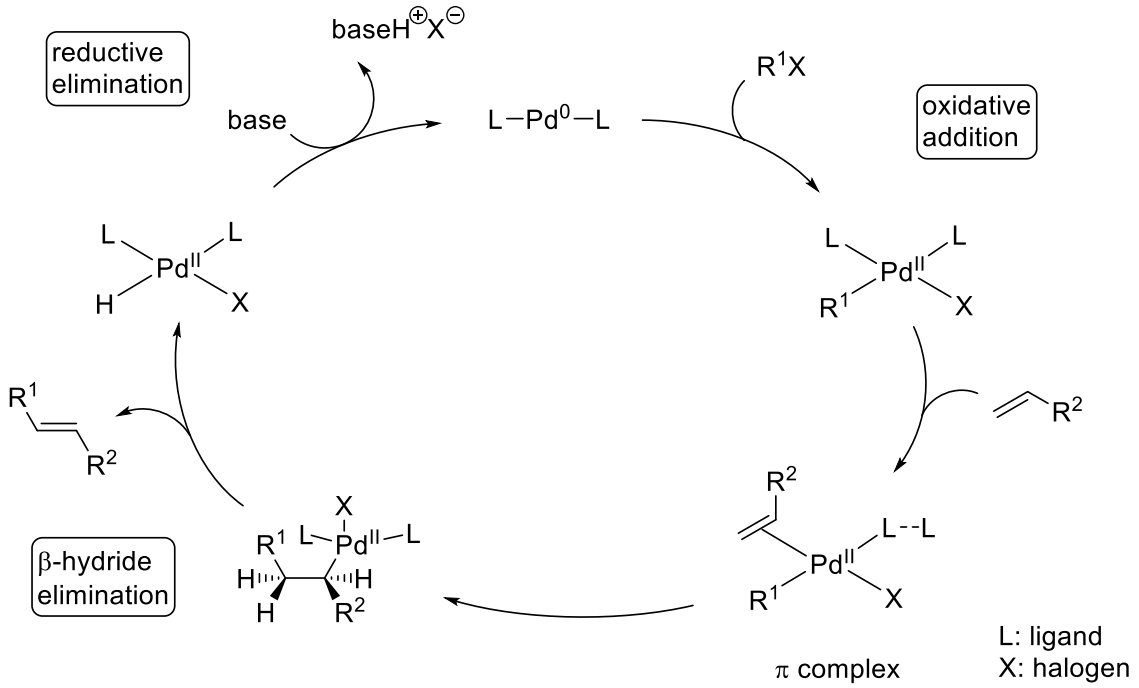
Oligo(arylene ethynylene)s (OAEs)

In 2017, Lutz *et al*. published a procedure to a defined sequence of oligo(arylene ethynylene)s (OAEs) with a soluble polystyrene support.[107] The polystyrene was synthesized *via* atom transfer radical polymerization and end-functionalized, in a way that a free triple-bond was accessible. As a result, Sonogashira reactions can be conducted with either a TMS-protected iodo-phenylacetylene or a TMS-protected bromo-pyridinylacetylene as building block. The synthesis of the building blocks was described in literature.[108] Through Sonogashira cross-coupling with subsequent TMS deprotection, four tetrameric sequences were attached to the soluble polymer. Since Glaser side product was obtained during the Sonogashira reaction, a simple purification by precipitation was not possible and column chromatography was performed after the reaction. The polymers were analyzed with ^{1}H NMR including correlated spectroscopy (COSY), electrospray ionization- (ESI-) or MALDI-TOF-MS, IR spectroscopy and SEC. Additionally, UV/Vis analysis was performed. Only theoretical yields were represented, exhibiting 2-11% when full conversion for the deprotection is assumed. One of the four tetrameric sequences was cleaved from the soluble support and characterized by ^{1}H NMR and ESI-MS in text form, but information about scale and yield was not provided. Apart from the cleaved tetramer, the polymers do not represent monodisperse representatives, since the soluble support exhibits a dispersity.

A lot of monodisperse conjugated oligomers with various scaffold structures have been published and were summarized in the literature.[37] Only a few examples base on sequence-defined conjugated oligomers, including the previous mentioned FSPE approach by Jian and Tour.[106] Hwang and Tour also directly compared solution and solid phase approaches, where the solution approach exhibited higher overall yields and scales.[55] Also, Jørgensen, Krebs and Meyer *et al.* published procedures to sequence-defined conjugated oligomers.[83][88] The investigation of sequence-defined conjugated oligomers for structure-property relationships is therefore still topical.

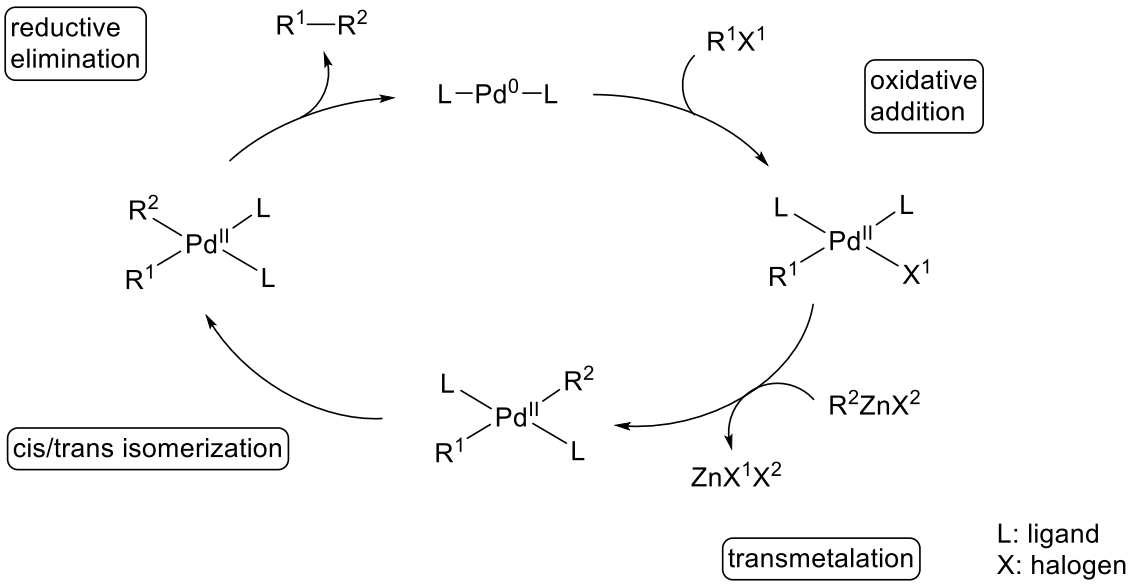
2.2 Cross-Coupling Reactions

According to Stephen L. Buchwald, cross-coupling reactions are defined as follows: "*The substitution of an aryl, vinyl, or alkyl halide or pseudohalide by a nucleophile that takes place with catalysis by a transition-metal complex is generally referred to as a cross-coupling reaction if it follows the mechanistic course of oxidative addition, transmetalation, and reductive elimination*."[109] Within this chapter, the Glaser coupling is described as well; however, it is a homocoupling and therefore only a coupling and not a cross-coupling reaction (compare chapter 2.2.2). Furthermore, the mechanism differs fundamentally. The most known representatives are palladium catalyzed cross-coupling reactions. In 2010, the Nobel prize was awarded to Richard Heck, Ei-ichi Negishi and Akira Suzuki for their work in this field.[110] Many cross-coupling reactions create carbon-carbon (C-C) bonds; one exception is the Buchwald-Hartwig amination leading to a formation of a carbon-nitrogen bond.[111] The Heck reaction describes the reaction of an alkene with an organohalogen or triflate to form a substituted alkene.[112] Mechanistically, the Heck reactions differs from the definition above, since a π-complex is formed during the catalytic cycle and a transmetalation does not take place.[113] The mechanism is depicted in Scheme 5: First, the catalyst attaches the organohalogen in an oxidative addition. Subsequently, the alkene and the palladium complex form a π-complex and the alkene is inserted afterwards. The β-hydride elimination yields the respective Heck product. The palladium is recovered *via* reductive elimination by a base.



Scheme 5: Catalytic cycle of the Heck reaction *via* oxidative addition, migratory insertion, β-hydride elimination and the recovery of the catalyst.[114]

The Negishi reaction utilizes organozinc compounds and organohalogen compounds or triflates.[115] This reaction is not restricted to palladium catalysis, also more cost-effective nickel catalysts provide good yields.[116] The catalytic cycle coincides with the definition given above incorporating an oxidative addition, a transmetalation, a cis/trans isomerization and a reductive elimination and is depicted in Scheme 6.[109,117] Consequently, the mechanism is consistent with other cross-coupling reactions, such as the Suzuki reaction.[118] The Suzuki reaction describes the coupling of a boronic acid – usually an organoboron species – with the usual organohalogen compound.[119] Apart from the described cross-coupling reactions, where the inventors were awarded with the Nobel prize, further cross-coupling reactions exist, *e.g.* Stille (organotin compounds) or Kumada (Grignard reagents) reaction.[120] Often, the palladium catalyst is activated *in situ*: *bis*(triphenylphosphine)palladium(II) dichloride [$PdCl_2(PPh_3)_2$] is a common catalyst and reduced to a Pd(0) complex.[121]

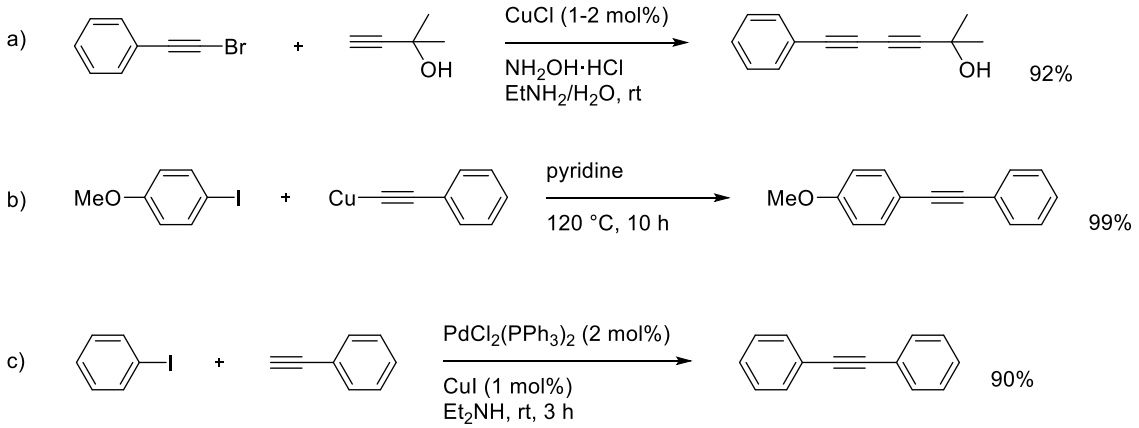


Scheme 6: Catalytic cycle of the Negishi reaction. The process of oxidative addition, transmetalation, cis/trans isomerization and reductive elimination is similar in other palladium catalyzed cross-coupling reactions.[118]

The applications of cross-couplings are diverse but are not discussed further herein. Since the Sonogashira reaction was used for the synthesis to sequence-defined oligomers within this thesis, it is presented in more detail in the following chapter.

2.2.1 The Sonogashira Reaction – A Cross-Coupling Reaction

The Sonogashira reaction (also termed Sonogashira-Hagihara reaction) describes the coupling of an alkyne with an organohalogen compound and was first published in 1975.[122] Before, the Cadiot-Chodkiewicz reaction was published in 1957.[123] The Cadiot-Chodkiewicz reaction is depicted in Scheme 7a): a bromoalkyne and an alkyne react under the catalysis of copper to a dialkyne. It was the first report of a selective cross-coupling reaction.[110] The Castro-Stephens coupling illustrated in Scheme 7b) describes the reaction of aryl or vinyl halides with copper acetylides to diphenylacetylene or phenylvinylacetylene derivatives and was published in 1963.[124] The Cadiot-Chodkiewicz coupling forms a C-C bond between two sp-carbon centers, while the Castro-Stephens coupling forms a C-C bond between sp- and sp^2-carbon centers. The Sonogashira reaction is shown in Scheme 7c). As in the Castro-Stephens coupling the C-C bond is formed between sp- and sp^2-carbon centers.



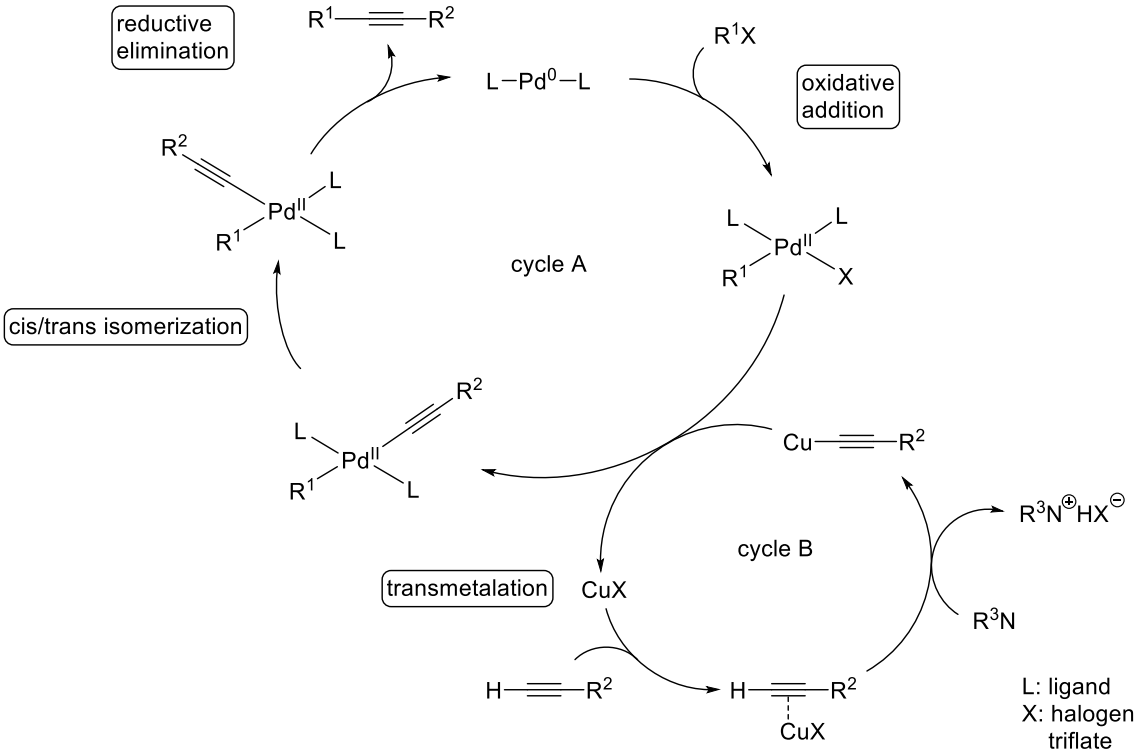
Scheme 7: Overview of the reactions related to the Sonogashira reaction: a) Cadiot-Chodkiewicz coupling, b) Castro-Stephens coupling and c) the Sonogashira reaction itself.[110]

In the Sonogashira reaction, the organocopper compound is created *in situ* and the reaction is catalyzed by palladium. Whilst stoichiometric amounts of copper are applied in the Castro-Stephens coupling, the Sonogashira cross-coupling requires only catalytic amounts. A further advantage is the possibility to perform the Sonogashira reaction at room temperature.

The mechanism of the Sonogashira reaction is not completely elucidated, yet and it is more complicated compared to other cross-coupling reactions, since two catalytic cycles are involved (compare Scheme 8).[125] The palladium *cycle A* is similar to the Negishi mechanism depicted in Scheme 6. As the other cross-coupling reactions, the Sonogashira reaction requires a Pd(0) complex. However, mainly $PdCl_2(PPh_3)_2$ – a Pd(II) complex – is applied as catalyst. The inactive catalyst forms a $Pd(II)(PPh_3)_2(C{\equiv}CR^2)_2$ intermediate with the aid of the amine base. Reductive elimination provides the activated $Pd(0)(PPh_3)_2$ catalyst and the dialkyne ($R^2C{\equiv}C\text{-}C{\equiv}CR^2$) as side product. The mechanism in Scheme 8 is therefore simplified, since the activation of the palladium catalyst is not depicted.[125,126]

First, a π-complex of the Pd(0) complex and the arylated species is formed. Then, the oxidative addition, which is also considered as the rate-limiting step, takes place. The reactivity depends both on the type of halogen, as well as the type of R^1 (*e.g.* aromatic, vinylic or the presence of electron-withdrawing groups). In the next step, the transmetalation connects *cycle A* and the copper *cycle B*. The copper cycle was less investigated so far and is at least partially based on assumptions. Within the copper *cycle B*, a copper acetylide is formed with the

help of an amine base deprotonating the terminal alkyne (C-H acidity increases upon Cu-complexation, thus facilitating the deprotonation step). The copper acetylide is a far better nucleophile as the free acetylene and undergoes the earlier mentioned transmetalation. Thereby, a ligand exchange on the palladium takes place and a palladium acetylide is formed. The reductive elimination yields again a π-complex, decomposing into the respective coupling product and the Pd(0) complex.[126]



Scheme 8: Mechanism of the Sonogashira reaction involving two catalytic cycles.[127]

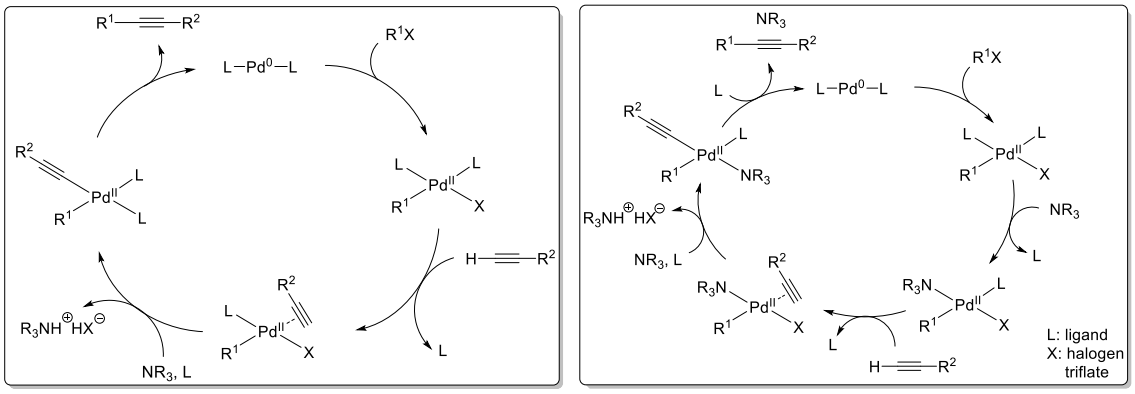
The overall reactivity of the Sonogashira reaction depends heavily on the introduced reactants and reagents. Disubstituted reagents, such as 2-bromo-4-iodo-quinoline were introduced to test the reactivity of the respective moieties.[128] In a Sonogashira reaction with one equivalent of TMSA, the iodide was substituted exclusively. In general, the reactivity can be depicted as follows: vinyl iodide ≥ vinyl triflate > vinyl bromide > vinyl chloride > aryl iodide > aryl triflate ≥ aryl bromide >> aryl chloride.[127] However, the reaction of triflates with acetylenes is also termed Cacchi cross-coupling and the respective mechanism might proceed slightly different.[126,129] If there is the same substituent at two positions within the reagent, the more electrophilic position is attacked first.[130] In an elaborate screening, the influence of substituents was tested for aryl bromides,

acetylenes and phosphines.[131] The acetylene hinders the reactivity most if it is sterically demanding; the bromide, however, requires more catalyst when it is sterically demanding. Electron-withdrawing groups accelerate the reaction but are more efficient if attached to the acetylene. Furthermore, the steric bulk of the acetylene should be considered when choosing the Pd/phosphine catalyst: more bulky side groups demand a less sterically demanding ligand, such as tricyclohexylphosphine rather than a tri-*tert*-butylphosphine ligand.[131]
A lot effort has been made on accessing unreactive substrates; alkyl bromides or iodides with sp^3 centers can be applied in Sonogashira reactions as well.[132] This development was also possible due to new ligands, such as *N*-heterocyclic carbenes, which were applied for the conversion of alkyl bromides and iodides. Apart from the triphenylphosphine related palladium-complexes, myriads of other catalytic systems exist.[133] Triphenylphosphines can be substituted with electron-rich phosphine ligands to facilitate the reaction with deactivated bromo- or chloroarenes. Supported palladium-phosphorus complexes might be recovered and reused and palladium-nitrogen complexes are used for low reactive vinyl chlorides. Moreover, palladacycles, ligand-free palladium species or palladium nanoparticles are applied as catalytic species.

The Sonogashira reaction with copper as cocatalyst exhibits a crucial disadvantage: Traces of oxygen enable the formation of dialkynes, which is also known as Glaser coupling (chapter 2.2.2).[134] It is noteworthy that the activation of the Pd catalyst usually generates the dialkyne as side product; small traces are therefore inevitable (see discussion above).[125]
In order to suppress Glaser couplings within the Sonogashira reaction several methods were established. A reducing atmosphere of hydrogen gas diluted with nitrogen or argon resulted in a significantly lower Glaser product formation of ≤ 2% (compared to ≥ 20% in the original publications).[135] Hydrogen itself had the same effect; due to safety reasons, only 10-40% hydrogen were applied along with the inert nitrogen or argon. However, a simple setup with a balloon filled with hydrogen was not possible and complicates the reaction setup accordingly. Glaser coupling can be further suppressed by adding the acetylene solved in THF dropwise, yielding less than 5% of diacetylene.[136] Nevertheless, Glaser product was still obtained in the described procedures and a promising approach is the complete avoidance of copper. Already parallel to Sonogashira in 1975, Cassar

and Heck published two versions of the Sonogashira reaction without copper cocatalysis.[137,138] Both alternatives required more drastic conditions: elevated temperatures up to 100 °C and also a higher catalyst loading. Often, copper-free alternatives require a large excess of amine or it is even used as solvent, which is also the case for the Heck modification.[138] Nevertheless, copper-free Sonogashira reactions are usually not termed after Cassar or Heck.

The mechanism of the copper-free Sonogashira reaction is still not completely understood. In Scheme 9, two possible pathways for the copper-free Sonogashira reaction are depicted: the mechanism on the left was proposed first.[127] As usual, an oxidative addition takes place as the first step. A reversible π-coordination yields an alkyne-palladium complex, which facilitates the deprotonation of the alkyne. As a last step, the reductive elimination forms the product and provides the catalyst for a further cycle. The mechanism depicted on the right suggests that the amine is preferred as ligand compared to the alkyne.[139] The amine supports the oxidative addition by generating more active amine-palladium complexes. Here, a π-coordination takes also place and the rest of the catalytic cycle is in accordance with the earlier mentioned proposition. Possibly, both mechanisms proceed depending on the choice of ligand and amine. Triphenylphosphine ligands are more likely substituted by the alkyne (left cycle, Scheme 9); triphenylarsine ligands are preferably substituted by piperidine (right cycle).[139]



Scheme 9: Two possible catalytic cycles for the copper-free Sonogashira reaction.[127,139]

However, traces of copper are also present in the palladium catalyst raising doubts about the complete avoidance of copper.[140]

Cacchi investigated the reaction of triflates and acetylenes with *N*,*N*-dimethylformamide (DMF) as solvent, $Pd(OAc)_2(PPh_3)_2$

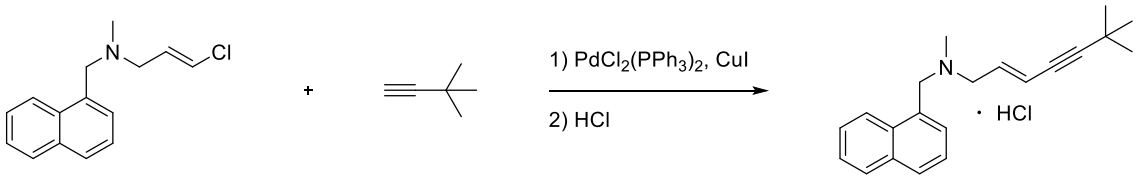
(*bis*(triphenylphosphine) palladium(II) diacetate) as catalyst and various amines. Without the addition of copper salts, the reaction required an elevated temperature of 60 °C; when adding copper iodide, the reaction proceeded already at room temperature.[141] The results coincide with the previously mentioned results of Heck and Cassar.[137,138] The $PdCl_2(PPh_3)_2$ catalyst was used in a Sonogashira reaction with 3 equivalents of TBAF without the necessity of further solvents or copper.[142] In this way, an amine is avoided; however, elevated temperatures of 80 °C were necessary. The classical Sonogashira reaction with palladium-phosphorus complexes as catalysts are optimized for the use with copper cocatalysts and other systems were developed for copper-free Sonogashira reactions.

A procedure without copper, amine and ligand-free palladium as nanoparticle was published in 2005.[143] As solvent, ethanol was applied; potassium carbonate served as base. The palladium nanoparticle was attached to a solid support to enable the recovery of the catalyst. Further unconventional reaction procedures were described, *e.g.* a Sonogashira reaction in water.[144] The reaction proceeds at room temperature and small amounts of an amphiphilic vitamin E derivative were added as surfactant. Various catalysts were tested, *e.g.* a palladacycle. The system of $PdCl_2(MeCN)_2$ (*bis*(acetonitrile) dichloropalladium(II)) with XPhos (2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl) as ligand was created *in situ* and turned out to be the most efficient.

The Sonogashira reaction has been used for the alkynylation of arenes and heterocycles, as well as in the formation of enynes, enediynes, ynones, carboxylic and heterocyclic systems, other natural products and the molecules with electron properties or for nanostructure.[127] However, only few palladium catalyzed reactions find their way to large scale applications.[145] The cost for palladium is one of the limiting factors, but also the reagents (aryl bromides and iodides in comparison to less reactive aryl chlorides) are comparably expensive. For pharmaceutical applications, the palladium and the copper pose a problem, since they cannot be removed completely and contaminate the product. Furthermore, at least 1 equivalent of inorganic salt is formed, which has to be removed as well.

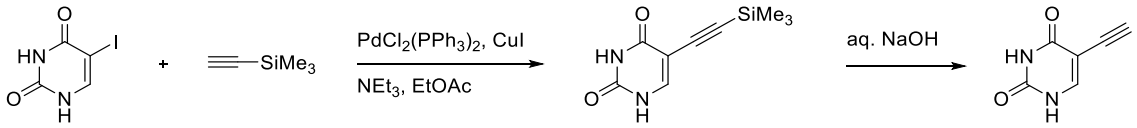
Terbinafine – also known as Lamisil – is an example of an antifungal agent, where the Sonogashira reaction is applied in a multi-ton scale synthesis.[146] It is usually

applied topically as cream or powder on skin infections. The coupling of the tertiary amine with *tert*-butylacetylene is depicted in Scheme 10 and was developed by researchers at Sandoz. Less than 0.05 mol% palladium catalyst are necessary to convert the vinyl chloride.



Scheme 10: Sonogashira reaction in the synthesis of antimycotic terbinafine.[146]

Further pharmaceuticals involving a Sonogashira reaction in its synthesis are being investigated, *e.g.* eniluracil, which entered Phase II clinical trials.[147,148] Eniluracil inactivates an enzyme (dihydropyrimidine dehydrogenase), which itself deactivates 5-fluoroacil, an anti-cancer drug. Therefore, eniluracil might complement 5-fluoroacil in anti-cancer treatments.[149] Eniluracil (also termed 5-ethynyluracil) is synthesized from 5-iodouracil (compare Scheme 11). First, a Sonogashira reaction with TMSA is performed and subsequently the TMS group is deprotected under basic conditions. The catalyst and the copper iodide were applied with low loadings of 0.5 mol% in a 1,500 liter plant yielding 30 kilograms of eniluracil.



Scheme 11: Synthesis of eniluracil *via* Sonogashira coupling with TMSA and subsequent deprotection.[147]

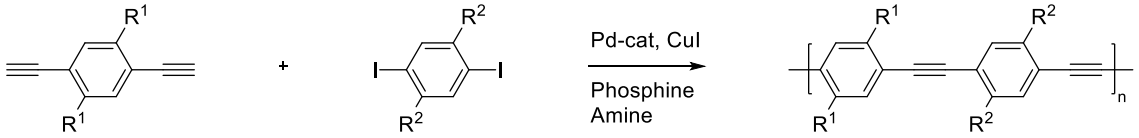
Further potential pharmaceutical syntheses comprise a Sonogashira cross-coupling, but apart from terbinafine, none of these products are commercially available so far.[150]

Apart from pharmaceuticals and natural products, the Sonogashira reaction is used in the design of new materials, such as molecular wires or three-dimensional nanostructures.[127] In this way, conjugated systems can be generated, which could be used as organic semiconductors. Sonogashira cross-coupling gives access to OAEs and poly(arylene ethynylene)s (PAE) (compare chapter 2.1.3). The monodisperse oligo(di- and triacetylene)s, OPEs and further

ethynylene-based structures described in chapter 2.1.1 and 2.1.2 are examples of OAEs derived by Sonogashira reaction. As mentioned before, further monodisperse oligomers were derived by non-iterative procedures. For instance, OPEs derived by Sonogashira reaction were incorporated as spacers into acceptor-donor conjugates.[151] The length of the spacer was adjusted between 18 and 38 Å, depending on the amount of phenylene ethynylene units. In this way, the energy transfer within the donor-spacer-acceptor triads could be investigated by spectroscopic analysis and the influence of the spacer length was detected.

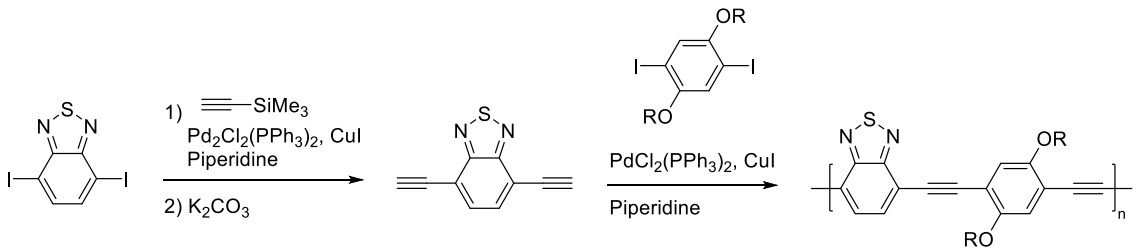
A similar system for investigating Förster resonance energy transfer was also realized *via* Sonogashira cross coupling, among others.[152] Consequently, the Sonogashira reaction can be used to design sophisticated structures for the investigation of energy transfer.

The Sonogashira reaction was also applied in polymerizations, for instance, to poly(phenylene ethynylene)s as depicted in Scheme 12.[153]



Scheme 12: Polymerization to poly(phenylene ethynylene)s *via* Sonogashira reaction.[154]

PAE are generally synthesized *via* Sonogashira reactions and can be applied as sensor cores.[155] Donor-acceptor copolymers can be obtained *via* Sonogashira reaction, too. In Scheme 13, the synthesis of a 2,1,3-benzothiadiazole with a benzene derivative is depicted.[156]



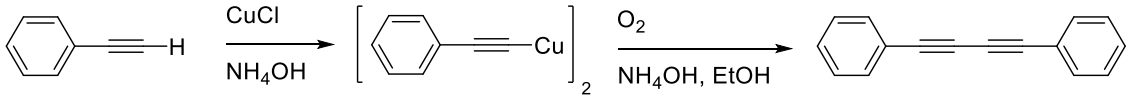
Scheme 13: Polymerization *via* Sonogashira cross-coupling to a donor-acceptor copolymer.[156]

The applications of the Sonogashira reaction are manifold and only a few examples were illustrated in this chapter. Copper as cocatalyst, however, is a

limiting factor, as it favors Glaser coupling. The next chapter addresses this side reaction.

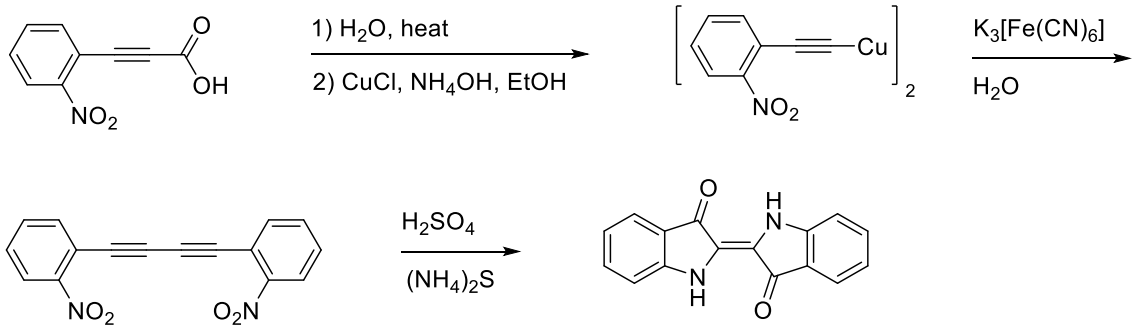
2.2.2 The Glaser Coupling – A Coupling Reaction

The copper-induced homocoupling of phenylacetylene was described by Glaser in 1869.[134] The copper complex is initially formed (compare Scheme 14) and can be isolated. The oxygen in the air promotes the homocoupling of the phenylacetylene to 1,4-diphenylbuta-1,3-diyne and copper(I) oxide.



Scheme 14: The Glaser coupling of two acetylenes *via* a copper-mediated process.[134]

Apart from phenylacetylene, Glaser converted also phenylpropiolic acid *via* copper- and silver-mediated homocoupling.[157] A derivative thereof was later applied in the synthesis of the indigo dye of Baeyer in 1882. In Scheme 15, the indigo synthesis is depicted, where a Glaser coupling was performed as first step.[158]



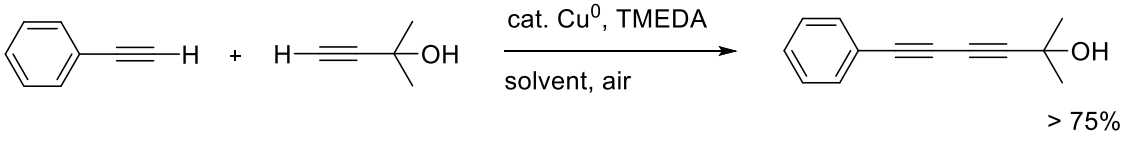
Scheme 15: Synthesis of indigo containing a Glaser coupling as first step.[158]

The indigo synthesis was later modified and the Glaser coupling was no longer applied in its synthetic pathway.[159]

Two main modifications were developed for the Glaser coupling: the Eglinton reaction requires stoichiometric amounts of copper but no oxygen and was first used for the synthesis of macrocycles.[160] Here, copper(II) salts and, more precisely, copper(II) acetate was utilized instead of copper(I) chloride. In the Hay reaction, *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) is applied as base.[161] TMEDA forms a complex with copper(I) chloride and accelerates the reaction.

Additionally, the TMEDA-copper complex is soluble in more organic solvents and there is no restriction to water and alcohols as solvents.

More recently, a Glaser-Hay cross-coupling was reported (compare Scheme 16).[162] The conversions under different conditions proved that the heterocoupling is favored compared to the homocoupling. With a chloroform/dioxane mixture, a yield of 83% of the cross-coupled product was obtained.



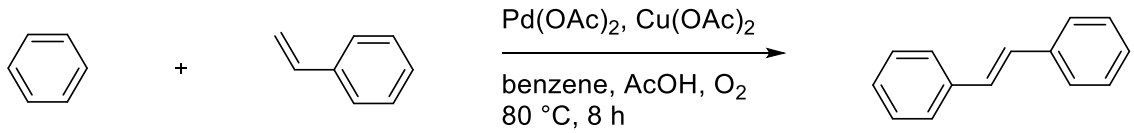
Scheme 16: Heterocoupling of terminal alkynes under Glaser-Hay conditions.[162]

Furthermore, different substituted phenylacetylenes were coupled as well. This variation of the Glaser-Hay coupling is therefore an alternative to the Cadiot-Chodkiewicz coupling mentioned before (compare Scheme 7).
As for the Sonogashira reaction, modifications concerning the catalyst and the solvent were developed.[163] Amongst others, cobalt can be applied as catalyst under reductive conditions.[164]
The applications are similar to the Sonogashira reaction: oligomers and other two- or three-dimensional structures are accessible. Shape persistent macrocycles were synthesized *via* Glaser-Hay coupling.[165] Besides, interlocked compounds, such as rotaxanes or catenanes, can be obtained by Glaser coupling.[166] Glaser-Hay coupling enabled the synthesis of oligoynes with four and five repeating units.[167] On the contrary, polyynes are instable or at least not reproducible in a reliable fashion and cannot be obtained by Glaser coupling.[32]

Since heterocoupling was discovered only recently, the Glaser coupling, and its modifications were not as attractive as other cross-coupling reactions so far. However, the Glaser coupling plays a crucial role when an alkyne and copper salts are present in a reaction mixture. This is relevant for the Castro-Stephens reaction, where elevated temperatures and stoichiometric amount of copper is required but also for the Sonogashira cross-coupling and the azide-alkyne Huisgen cycloaddition.[168] Copper-free reactions with alkynes are therefore favored, not only with respect to pharmaceutical applications.

2.2.3 Outlook: Direct Heteroarylation

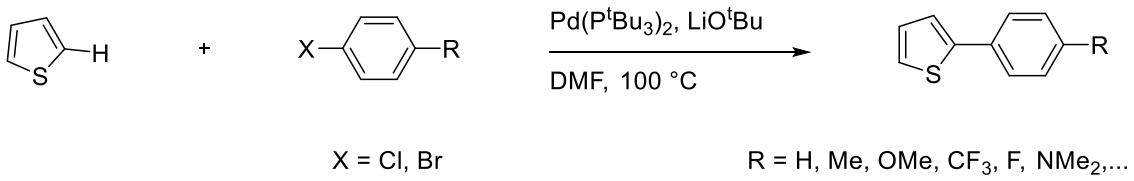
A desirable development would be the direct C-H activation without any prefunctionalization of the respective starting materials. Obviously, this reaction is no longer a cross-coupling as defined in chapter 2.2, since any alkyl or aryl group can be converted with a nucleophile.[109,169] Also the mechanism is not comparable to conventional cross-coupling reactions. In 1969, an oxidative Heck reaction was described before the actual reaction was published in 1972.[170] Scheme 17 illustrates this C-H alkenylation.



Scheme 17: Early example of a Heck-type direct C-H activation reaction.[170]

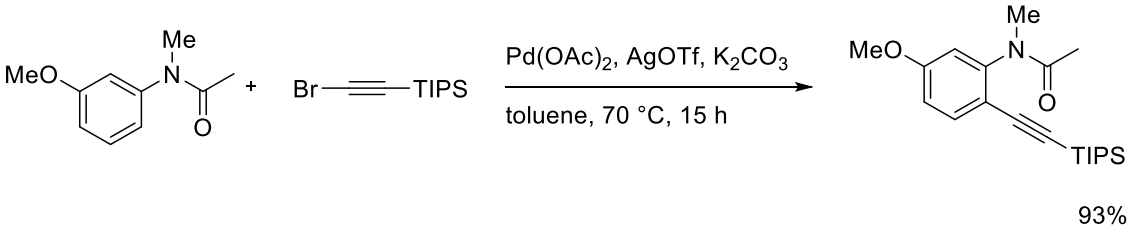
Cyclopalladations are one mechanistic pathway of C-H activations. Usually, a nitrogen-directing group is required and the substrate scope is rather limited.[171] Further complex-induced proximity effects enable C-H activation, *e.g*. through direct metalation in *ortho*-position of carboxylic acid groups.[172] Carbonate or carboxylate additives support the direct heteroarylation of heteroarenes.[173,174]

Several examples for C-H activation have been published, but the different mechanisms require rather exotic reagents under quite specific conditions.[175] In this way, C-H activation reactions are not comparable to conventional cross-coupling reactions. Often, high catalyst loadings of 10 mol% are necessary, which restricts any industrial application.[170,176] With the formerly mentioned tri-*tert*-butylphosphine ligand, a significantly lower catalyst loading of 2 mol% was sufficient.[177] As depicted in Scheme 18, an electron-rich heteroarene such as thiophene could be coupled with aryl bromides or chlorides.

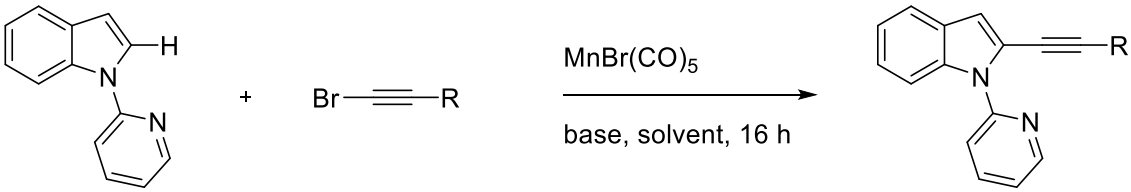


Scheme 18: C-H activation with a low catalyst loading of 2 mol%.[177]

Furthermore, a rather specific example of C-H alkynylation was published, but the catalyst loading of 10 mol% was rather high (Scheme 19).[178] A further C-H alkynylation was described with a manganese catalyst and pyrrole or indole derivatives as reagent along with substituted haloalkynes (Scheme 20).[179] The catalyst loading could be reduced to 5 mol% and the haloalkanes are not restricted to the TIPS protecting group but alkynes, alkenes and aryl groups. In the publication the synthesis of peptides was illustrated as well.

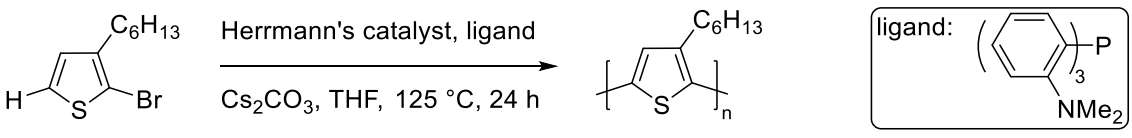


Scheme 19: A Sonogashira-type C-H alkynylation.[178]



Scheme 20: A Sonogashira -type C-H alkynylation with a manganese catalyst.[179]

More recently, conjugated polymers have been synthesized by direct heteroarylation as well.[174] Often, conventional cross-coupling reactions are not efficient enough for polymerizations, since structural defects cannot be removed by purification and high conversions area prerequisite to obtain suitable molecular weights in this step-growth polymerizations. Among others, the polymerization to poly(3-hexylthiophene-2,5-diyl) (P3HT) can be performed *via* direct heteroarylation as depicted in Scheme 21.[180] In this way, a number average molecular weight of 30,600 Da and a dispersity of 1.60 could be achieved. However, the reaction was performed in supercritical THF, which might not be realizable easily.



Scheme 21: Polymerization to P3HT *via* direct heteroarylation.[180]

Direct heteroarylation is an alternative to cross-coupling reactions, as it reduces organometallic byproducts and requires less prefunctionalized starting materials. In the field of sequence-defined conjugated oligomers, iterative procedures are required complicating the application of such reactions. However, for the applications mentioned in the next chapter, polymers obtained by direct heteroarylation might be sufficient.

2.3 Applications of Conjugated Polymers and Oligomers

Conjugated species were originally defined as molecules with alternating single and multiple bonds.[181] However, their π-bonding is described as delocalized and is therefore not alternating classically.[182] Conjugated polymers are interesting materials, since they are organic semiconductors. Organic semiconductors have been known since the 19th century, but their breakthrough was the detection of doped polymers in 1977.[183] Alan Heeger, Alan MacDiarmid and Hideki Shirakawa discovered that polyacetylene doped with arsenic pentafluoride is more than a millionfold more conductive as polyacetylene itself. They were awarded with the Nobel prize in 2000.[184] Dopants serve as charge carriers along the π-bonded polymer; two types exist: n-type (reduced) and p-type (oxidized) dopants.[185] Although polyacetylene itself was not commercially applied, the synthesis of further conjugated polymers was initiated. Compared to metalloids – the semiconductors of choice – polymers can be processed more easily and with lower cost and offer different mechanical properties (*e.g.* flexibility). They have the big advantage that they are transparent and lightweight, and tuning of the monomers or precursors enables the adjustment of the electronic properties. Furthermore, side chains can be incorporated or adapted for better solubility. Solution-processing, such as spin-casting or ink-jet printing, give access to thin-film devices and conjugated polymers were incorporated into devices, such as light-emitting diodes, thin-film transistors and photovoltaic cells.[184] OLEDs and organic photovoltaic cells are depicted with more detail in the following chapters.

2.3.1 Organic and Polymer Light Emitting Diodes

Nowadays, OLEDs are produced for all kinds of displays, especially for mobile phones. Various companies develop novel devices for specific applications, *e.g.* BMW plans to incorporate OLEDs as tail and interior light.[186]

The first OLED was reported in 1987 as double-layer device.[187] The device is depicted in Figure 8 and consists of a transparent indium tin oxide (ITO) anode on a glass substrate. Two organic films are located between the ITO anode and an alloyed magnesium silver (10:1) cathode: *N*,*N*′-*bis*(3-methylphenyl)-*N*,*N*′-diphenylbenzidine as hole-transporting layer (750 Å) and an emissive layer containing of 8-hydroxyquinoline aluminium (600 Å).[188] The organic layers were laid on *via* vapor deposition.

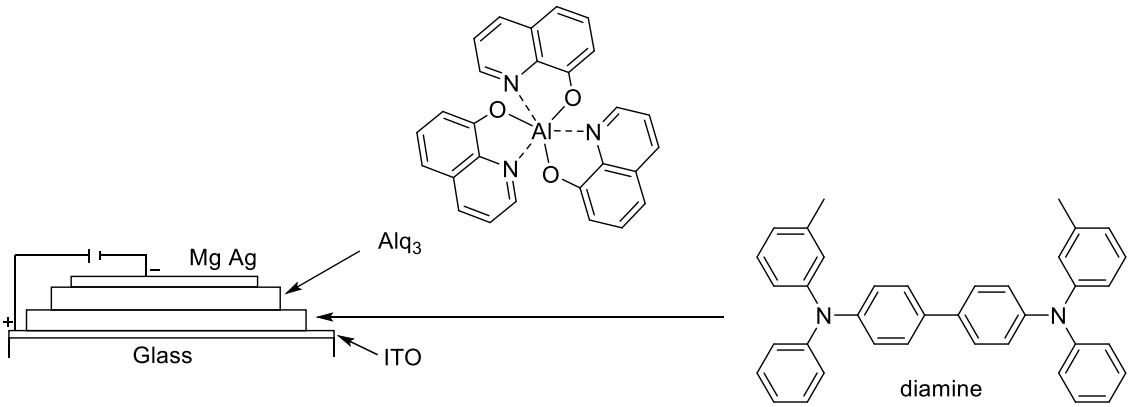
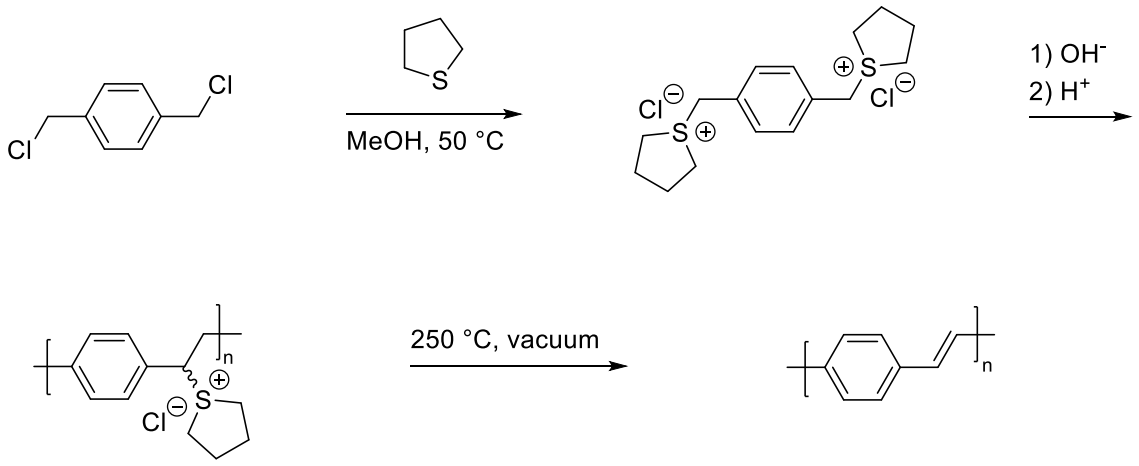


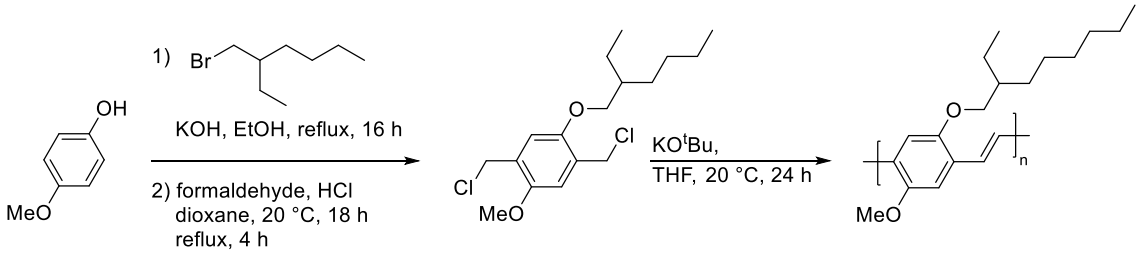
Figure 8: The first OLED, a double layer device.[187]

One year later, an OLED with a three-layer structure was published. It contained an additional electron transporting layer between emissive layer and cathode.[189] In 1990, a light emitting diode based on a conjugated polymer was described.[190] Poly(*para*-phenylene vinylene)s (PPV) were obtained *via* a solution-processable precursor polymer as depicted in Scheme 22. The emissive layer based on PPV exhibited a thickness of ~1,000 Å and was directly positioned between cathode and anode generating a single-layer device.

PPV with side groups exhibits a better solubility and also better external efficiencies.[191,192] The most prominent representative is poly(2-methoxy-5-(2'-ethylhexyloxy)-*para*-phenylene vinylene) (MEH-PPV), where the polymer is soluble itself and a precursor is not necessary (compare Scheme 23).[191] However, multi-layer devices are difficult to obtain by solution-processing, especially when the polymers are easily soluble.



Scheme 22: Synthetic route to PPV *via* a solution-processable precursor. PPV serves as emissive layer in an OLED based on polymers.[190]



Scheme 23: Synthetic route to MEH-PPV. Since MEH-PPV is soluble in organic solvents no precursor was necessary.[193]

Further polymer classes have been investigated for OLEDs based on polymers, *e.g.* poly(phenylene ethynylene)s (PPE). Usually, PPEs are obtained by Sonogashira reactions as depicted in chapter 2.2.1. In a combinatorial approach, several monomers were synthesized and new materials could be screened.[194] However, the Sonogashira reaction leads to the previous mentioned diyne defects, which promote photoinduced cross-linking.[195]

The recombination of the induced electron and holes in the emissive layer is supposed to be spin-independent. Thus, the excitons are generated in the singlet and in the triplet configuration in a ratio of 1:3. The triplet state excitons decay in form of phosphorescence and not with the required radiative emission. The large energy difference between singlet and triplet state hinder a cross-over from triplet to singlet.[196] Harvesting triplet excitons is therefore desirable and can be achieved by adding phosphorescent dyes, such as platinum octaethylporphyrin.[197] High efficiencies of 90% could be achieved compared to the 25% available through singlet excitons, heavy metal complexes as dopants

are required though. The same platinum-complex used in phosphorescent OLEDs was also applied as dopant in a polymer blend emissive layer.[198]

A more recent development avoiding the use of heavy metal complexes are molecules enabling reverse intersystem crossing (RISC).[199] Intersystem crossing (ISC) describes the “radiationless transition between two electronic states”.[200] Normally, the transition from the singlet excited state (S_1) to the triplet excited (T_1) state is described; thus, RISC describes the opposite as depicted in Figure 9. Through RISC, a delayed fluorescence is possible resulting in a fluorescence efficiency of 90%.[199] Since heat usually accelerates RISC, this phenomenon is described as thermally activated delayed fluorescence (TADF).[201] Molecules with TADF function require a low energy gap ($\Delta E_{ST} \leq 100$ meV) between the S_1 and T_1 excited state, which can be realized by incorporating spatially separated and sterically hindered electron donating and accepting groups within one molecule. In this way, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are located on the donor and acceptor moieties. Carbazolyl dicyanobenzenes (Figure 9, right) exhibit donor moieties through the carbazoles and the acceptor dicyanobenzene and were therefore published as TADF materials.[199] In OLEDs, the external electroluminescence efficiency amounted to approximately 20%.

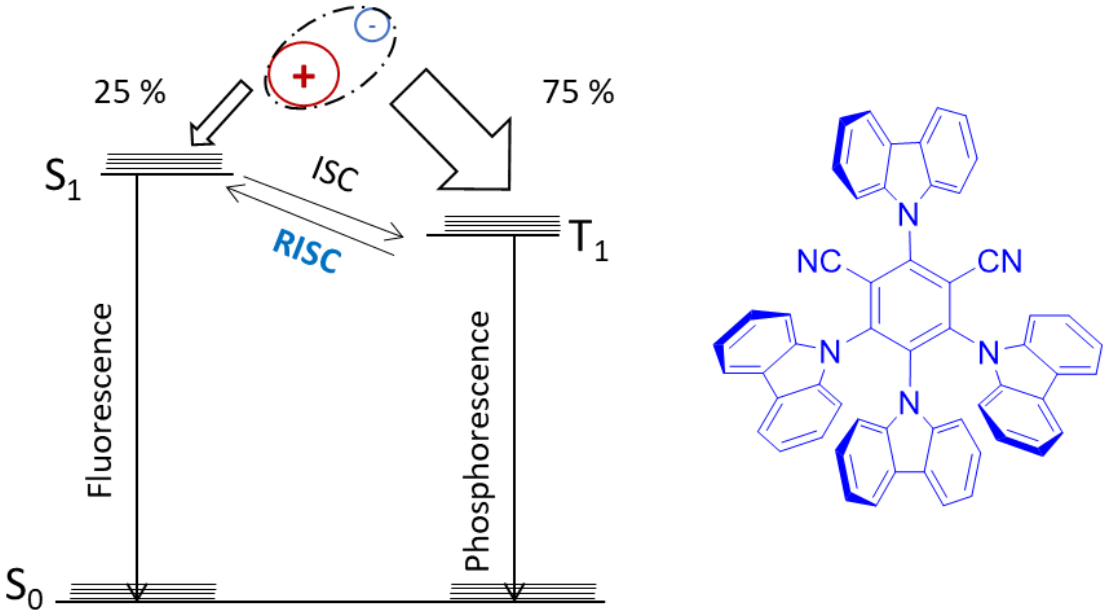


Figure 9: Jablonski diagram (left) illustrating the ground state (S_0), S_1 and T_1 excited state and the respective ISC and RISC.[201] A carbazolyl dicyanobenzene in blue is enabling RISC and TADF is depicted on the right.[199]

Many molecular classes qualify for TADF materials, such as phenoxazine-triphenyltriazines, heptazine derivatives, as well as oxadiazole and oxatriazole-based molecules.[202] Furthermore, a blue OLED with an external quantum efficiency of more than 25% based on TADF could be produced.[203] Blue OLEDs are comparably less efficient and only few examples of external quantum efficiencies over 20% exist in general.

The herein described molecules with TADF function are small molecules, however, TADF polymers, which can be solution-processed, were published as well.[204] Interestingly, many polymers with TADF function are not conjugated but are based on a non-conjugated backbone.[205]

The preferential solution-processing for polymeric emitters resulted in the development of organic photovoltaic cells based on polymers as well.

2.3.2 Organic and Plastic Photovoltaic Cells

The term “photovoltaic” describes the conversion of light into electricity with a semiconducting material.[206] A single layer device is the simplest form of an organic solar cell and was realized in 1958 with magnesium phthalocyanine and *N*,*N*,*N′*,*N′*-tetramethyl-*para*-phenylenediamine, but the electrodes were not further specified.[207] Polyacetylene was incorporated into a single layer plastic solar cell in 1982.[208] In 1993, PPV was applied in a photovoltaic cell and an efficiency of 0.1% was reached.[209] However, in these single layer cells, photogenerated excitons are not dissociated easily. Therefore, organic solar cells are realized as bulk heterojunction, where electron donating and electron accepting materials are combined in a single composite.[210] In this way, the excitons overcome the Coulomb attraction more easily at the interfaces and the electrons can be conveyed to the cathode (and the holes to the anode). As electron donor, polymers (*e.g*. MEH-PPV, polythiophenes) are usually applied, and fullerenes proved to be good electron acceptors.[211] Essential for bulk heterojunctions is the control of the morphology: a high charge collection is only possible when the donor and acceptor interfaces are maximal.[212] The morphology depends highly on the solvent applied during spin coating. A bulk heterojunction film based on P3HT and the fullerene derivative [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) was spin coated with chloroform, toluene, chlorobenzene and xylene.[213] The morphology of the film was investigated *via*

various techniques, *e.g.* atomic force microscopy. The vertical distribution and the lateral phase separation fitting to the exciton diffusion length have a relevant impact on the device efficiency. Films from chloroform were less efficient compared to the other solvents as cluster formation of PCBM occurred. PCBM is better soluble in toluene, chlorobenzene and xylene and is therefore interpenetrating more with P3HT. Lateral structure size is not important, however, the range of the exciton diffusion length should be reached.[213] Moreover, the perfect donor acceptor ratio was investigated with P3HT and PCBM. The optimal efficiency was reached with a PCBM loading of 40%.[214]

A bulk heterojunction can also exist exclusively of two semiconducting polymers, such as MEH-PPV as donor and CN-PPV – a cyano containing PPV – as acceptor.[215] The mixture of the two polymers can be spin coated, subsequently phase separation occurs and an interpenetrating network is formed. A schematic illustration of this plastic solar cell is depicted in Figure 10.

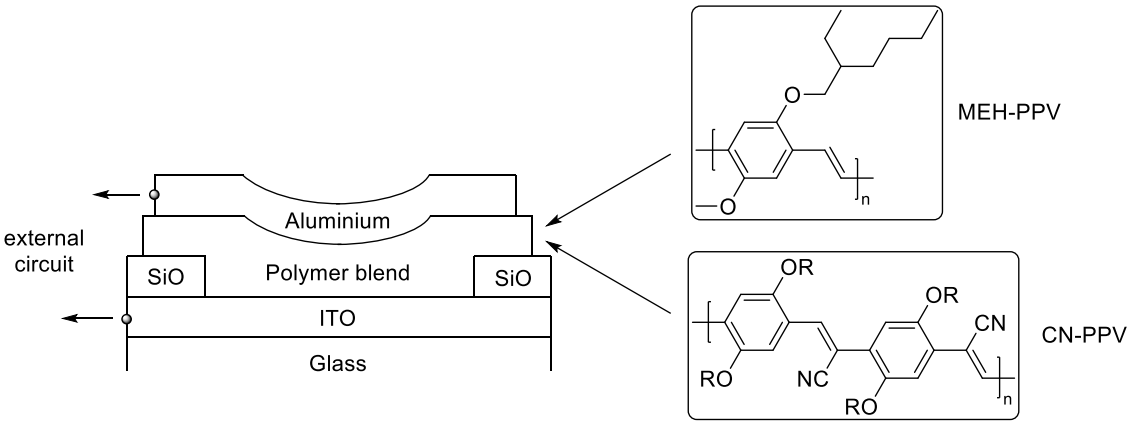


Figure 10: Plastic solar cell with ITO and aluminium electrodes. The polymer blend consists of MEH-PPV as donor and CN-PPV as acceptor.[215]

Apart from the photoactive layer, a hole transport layer such as PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) is usually applied in recent bulk heterojunction solar cells.[216]

Plastic and organic solar cells cannot compete with conventional silicon-based solar cells with regard to efficiency; so far, more than 10% can be reached (compared to approximately 30% for conventional silicon-based solar cells).[217] On the other hand, as for OLEDs, organic and plastic solar cells are easy to produce and very cost efficient. Furthermore, plastic solar cells can be fabricated on flexible substrates, show transparency and exhibit little weight and are

therefore applicable more diverse.[218] Challenges remain to understand the fundamental processes taking place in plastic solar cells, *e.g*. the exciton dynamics. Tailor-made sequence-defined oligomers might be useful to shed light on these processes, as depicted in the next chapter.

3. Motivation

This PhD thesis is part of the project A4 within the Cooperative Research Centre 1176 “Molecular Structuring of Soft Matter”. In this project, “Tailor-made sequence-controlled polymer-dye conjugates for controlling exciton dynamics” shall be investigated.[219] For the project, sequence-defined rod-like macromolecules should be connected with dyes with TADF function. A schematic depiction of these polymer-dye conjugates is illustrated in Figure 11. Apart from the synthetic requirement, these macromolecules are interesting systems for investigating exciton dynamics: Molecules with TADF function could separate excitons into hole and electron, which is a considerable process in the formerly mentioned plastic solar cells as well. Therefore, the sequence-defined oligomers shall be varied, units with electron accepting (A, Figure 11) and electron donating (D, Figure 11) properties can be specifically positioned within the oligomer chain. Initially, a “donor” and an “acceptor” chain are sufficient (upper part of Figure 11). Later, the influence of a varied position within these chains with regard to the exciton dynamics should be investigated (lower two molecules of Figure 11).

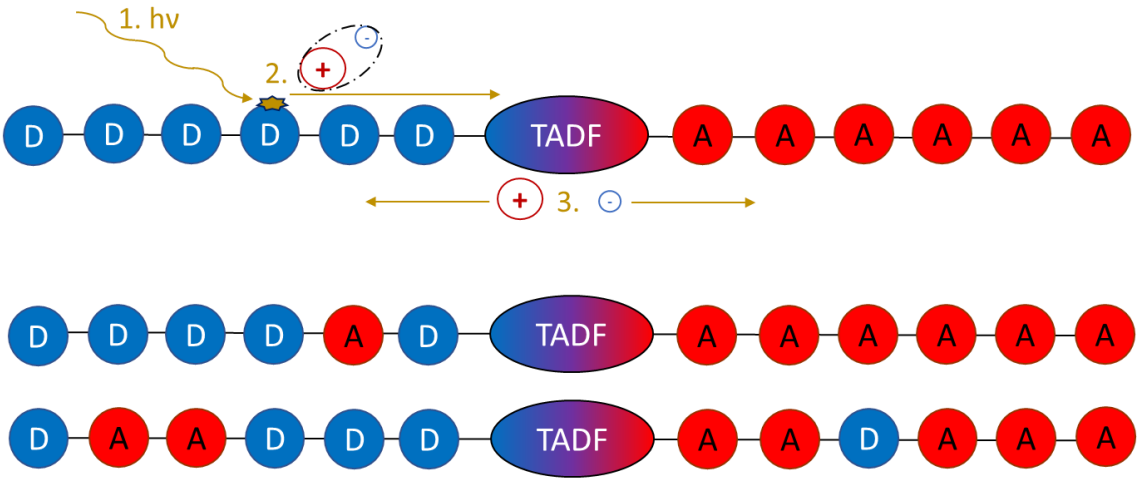
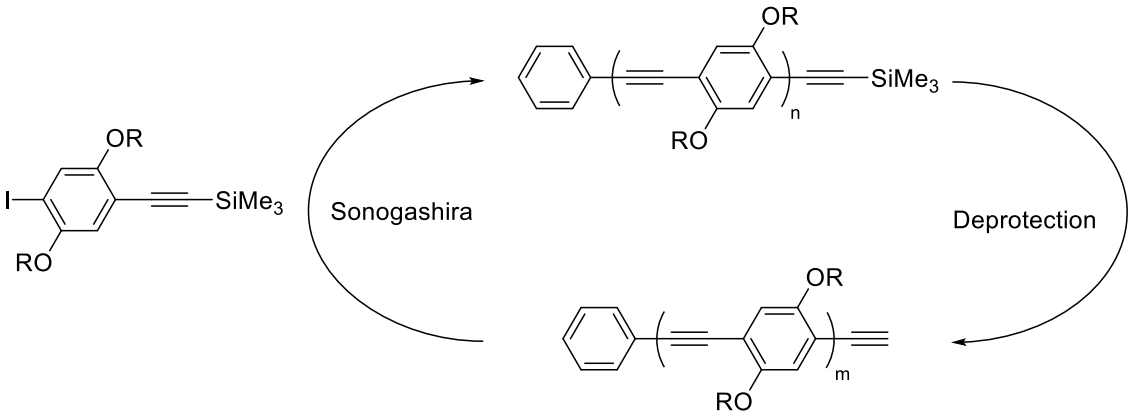


Figure 11: Schematic overview over the planned polymer-dye conjugates and their function in investigating exciton dynamics. The blue circles constitute units with electron donating properties, the red circles with electron accepting properties.

In order to achieve these highly complex systems, a synthesis strategy towards these oligomers has to be established. Only a few examples of sequence-defined conjugated oligomers have been published so far.[55,83,88] Most of the structures exhibit the same precursor and are therefore monodisperse but not sequence-

defined. In the field of rod-like oligomers based on oligo(1,4-phenylene ethynylene)s, one linear procedure towards sequence-defined oligomers was described.[55] Thus, a synthesis strategy towards rod-like molecules in solution should be investigated. Therefore, several precursor molecules are generated and an iterative (step-by-step) procedure based on Sonogashira reactions and subsequent deprotection is established (Scheme 24).



Scheme 24: Procedure to sequence-defined rod-like oligomers through Sonogashira reaction and subsequent deprotection.

The individual reaction steps require optimizations to enable full or almost full conversion. Only in this way, high yields can be obtained. However, the reaction scale should be chosen as high as possible, as well. Apart from the reaction itself, suitable purification methods are essential. During the optimization, appropriate characterization methods for the relevant molecules are developed. Since building blocks based on dialkoxybenzenes were investigated for establishing a synthesis procedure, rod-like molecules with electron donating properties were obtained first. However, other precursors with electron accepting properties should also be designed, which enable the adjustment of photophysical properties. Precursors with electron accepting properties might be benzothiadiazole derivatives or benzonitriles.

Within this work, rod-like oligomers were synthesized and connected with dyes with TADF-function synthesized in the group of S. Bräse (KIT).

4. Results and Discussion

This work is divided into the synthesis of building blocks (chapter 4.1), the oligomer formation (chapter 4.2) and the connection of the oligomers to the molecules with TADF function (chapter 4.3). The respective molecules are termed according to their function (**B** for building block, **P** for precursor, **T** for TADF-conjugate) or their degree of polymerization (**1**-**5** for monomer to pentamer). Every obtained compound was fully characterized by proton and carbon NMR, mass spectrometry (*i.e.* either fast atom bombardment (FAB)- or ESI-MS) and IR spectroscopy. Respective oligomers and TADF-conjugates were further characterized by SEC.

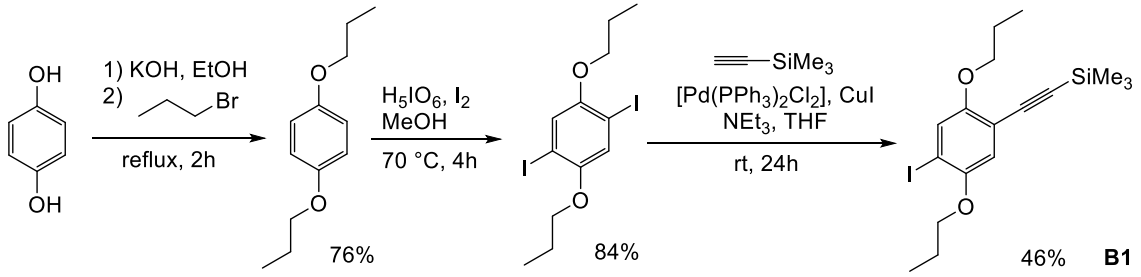
4.1 Syntheses of Building Blocks

The synthesis of building blocks is divided in two subchapters: building blocks with electron donating properties are described in chapter 4.1.1, building blocks with electron accepting properties in chapter 4.1.2. As mentioned before, building blocks are termed **B1**-**B8**. The respective precursors for the building blocks are denoted according to the final building block, *e.g.* **P1a** and **P1b** for **B1**. For the building blocks with electron accepting properties, several precursors exist, although the synthesis of the respective building blocks are not completed yet. Therefore, chapter 4.1.2 gives also an outlook.

4.1.1 Building Blocks with Electron Donating Properties

The building blocks for the synthesis procedure to oligo(1,4-phenylene ethynylene)s require an orthogonally addressable benzene derivative with a halogen and a protected triple bond. For better solubilization, alkoxy side groups were incorporated. Most of the building blocks are based on hydroquinone, including the first building block **B1** with dipropoxy solubilizing side groups. The reaction procedure towards building block **B1** is depicted in Scheme 25. As a first step, a Williamson ether synthesis with 1-bromopropane was performed according to a procedure published by H. Meier *et al.*[34] The product, 1,4-dipropoxybenzene **P1a**, was obtained in 76% yield by recrystallization. The yield is less than the yield in the original publication of 85%, however 40.0 grams of the product were obtained, and optimization was not further pursued. For the

incorporation of a halogen, an iodination to 1,4-diiodo-2,5-dirpopoxybenzene **P1b** seemed promising. H. Meier *et al.* performed also a subsequent iodination; however, tetrachloromethane was applied. Therefore, a procedure avoiding the toxic tetrachloromethane was chosen: a publication of Park *et al.*[220] uses periodic acid, iodine and methanol as solvent. Again, recrystallization was performed, and the product **P1b** was obtained in 84% yield. In the original publication by Park *et al.*, 92% yield were obtained. The last and crucial step is a Sonogashira reaction, as published by the group of Tour.[221] Two iodine moieties are present, but a monofunctionalization with TMSA is required. Usually, a tenfold excess of 1,4-diiodo-2,5-dirpopoxybenzene in comparison to TMSA is utilized. In this way, mainly monofunctionalized product is obtained, but a huge excess of starting material remains. Moreover, purification by column chromatography cannot be avoided. In order to force the formation of product **B1**, we chose almost similar equivalents for both reagents. Apart from the starting material and **B1**, the difunctionalized side product is generated as well. Figure 12 depicts a chromatogram of the crude mixture obtained by GC.



Scheme 25: Synthesis of the first building block **B1** based on hydroquinone. First, a Williamson ether synthesis with 1-bromopropane was performed to precursor **P1a**. In the iodination, periodic acid was used as oxidizing agent to form **P1b** and finally, a Sonogashira monocoupling with TMSA was performed. The overall yield of **B1** amounted to 29%.

For the Sonogashira monocoupling, generating **B1**, several test reactions in 500 milligram scale were performed and compared (Table 9). The initial approach (entry 1) was similar to the publication by Tour *et al.*: 1 equivalent TMSA, 2.5 mol% $PdCl_2(PPh_3)_2$ and 5 mol% copper iodide (CuI) resulting in 41% yield.[221] The screening revealed that elevated temperature (entry 2 and 3) did not have a positive effect on the yield, as a clear trend towards lower yields was observed with increasing temperature. Further optimizations were performed with increased as well as decreased equivalents of the respective reactants. For the

reagent TMSA, only more equivalents were screened, since less reagent necessarily yields less **B1**. Interestingly, a higher catalyst loading of 5 mol% was not beneficial (entry 5), and the lower catalyst loading of 1 mol% (entry 4) resulted in a lower yield. A lower amount of copper iodide was not beneficial (entry 6), but a higher amount seemed promising (entry 7). Since copper promotes the Glaser coupling (compare chapter 2.2.1 and 2.2.2), a further increase of copper iodide was not pursued. Altered amounts of triethylamine or THF (entries 8-11) resulted in lower or similar yields. The amount of THF did not have a significant influence in general, although a low concentration is often associated with less side product formation. Different amounts of TMSA, however, had quite an impact (entry 12 and 13). A positive effect on the yield was detected when 1.2 equivalents were applied, which resulted in an increase in yield of more than 20% (entry 12). When increasing the TMSA further to 1.5 equivalents (entry 13), the yield decreased again. Therefore, the conditions of entry 12 were chosen for further reactions.

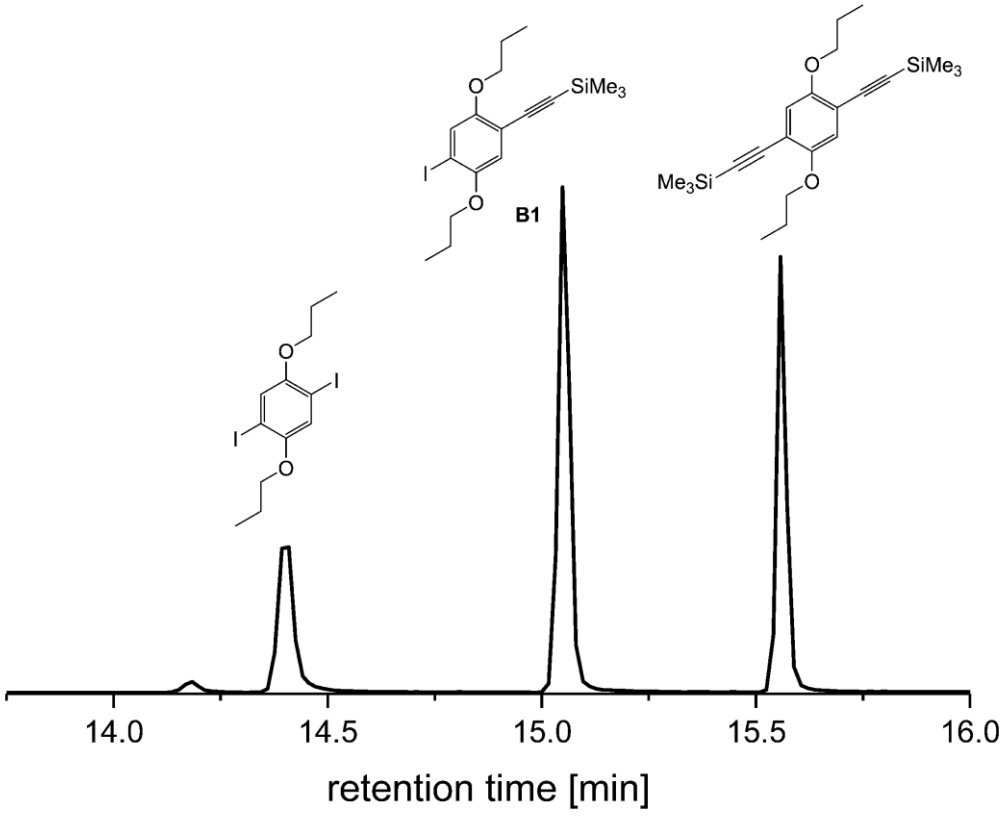


Figure 12: Chromatogram of the crude reaction mixture of **B1** obtained by GC. First, the starting material elutes (**P1b**), then the product **B1** followed by the difunctionalized side product.

Table 9: Overview of the optimization approaches. The first entry represents the initial approach. The further variations are marked in bold. Room temperature is abbreviated as RT.

	Temperature	$PdCl_2(PPh_3)_2$	CuI	NEt_3	THF	TMSA	Yield
1	RT	2.5 mol%	5.0 mol%	10.0 eq.	45 mM	1.0 eq.	41%
2	**40 °C**	2.5 mol%	5.0 mol%	10.0 eq.	45 mM	1.0 eq.	37%
3	**60 °C**	2.5 mol%	5.0 mol%	10.0 eq.	45 mM	1.0 eq.	27%
4	RT	**1.0 mol%**	5.0 mol%	10.0 eq.	45 mM	1.0 eq.	32%
5	RT	**5.0 mol%**	5.0 mol%	10.0 eq.	45 mM	1.0 eq.	41%
6	RT	2.5 mol%	**2.5 mol%**	10.0 eq.	45 mM	1.0 eq.	34%
7	RT	2.5 mol%	**10.0 mol%**	10.0 eq.	45 mM	1.0 eq.	44%
8	RT	2.5 mol%	5.0 mol%	**5.0 eq.**	45 mM	1.0 eq.	31%
9	RT	2.5 mol%	5.0 mol%	**20.0 eq.**	45 mM	1.0 eq.	33%
10	RT	2.5 mol%	5.0 mol%	10.0 eq.	**22.5 mM**	1.0 eq.	40%
11	RT	2.5 mol%	5.0 mol%	10.0 eq.	**90 mM**	1.0 eq.	38%
12	RT	2.5 mol%	5.0 mol%	10.0 eq.	45 mM	**1.2 eq.**	62%
13	RT	2.5 mol%	5.0 mol%	10.0 eq.	45 mM	**1.5 eq.**	46%

The optimized conditions (Table 9, entry 12) were transformed to a larger scale for the synthesis of **B1** of 10.0 grams 1,4-diiodo-2,5-dipropoxybenzene. The yield of 62% for the optimized 500 milligram scale reaction could not be achieved. However, a scale of 4.26 grams and a yield of 46% were satisfactory. Tour *et al.* obtained 56% but only 1.77 grams of product.[221] Additionally, by silica column chromatography, the starting material (**P1b**) was recovered with 3.06 grams. Exactly as shown in Figure 12, the starting material (**P1b**) elutes before the product **B1** and the side product, which was not collected. Furthermore, traces of Glaser side product – the "TMSA-diyne" – was collected before **P1b**. The ^{1}H NMR spectrum with assigned signals of the purified product **B1** and its chromatogram is depicted in Figure 13. The ratio of the integral of aromatic signal *b* (1.01) with the integral of trimethylsilyl signal *f* (9.03) and the chromatogram confirm the purity of building block **B1**. Its overall yield over three steps amounted to 29%.

For the synthesis of a sequence-defined pentamer, further building blocks are necessary. Therefore, other bromoalkanes such as 2-bromopropane, bromocyclohexane and 1-bromooctane were incorporated in the Williamson ether synthesis. A further building block is based on 1,4-dimethoxybenzene, which is commercially available. An overview over the synthesized building blocks **B2**-**B5** is illustrated in Figure 14.

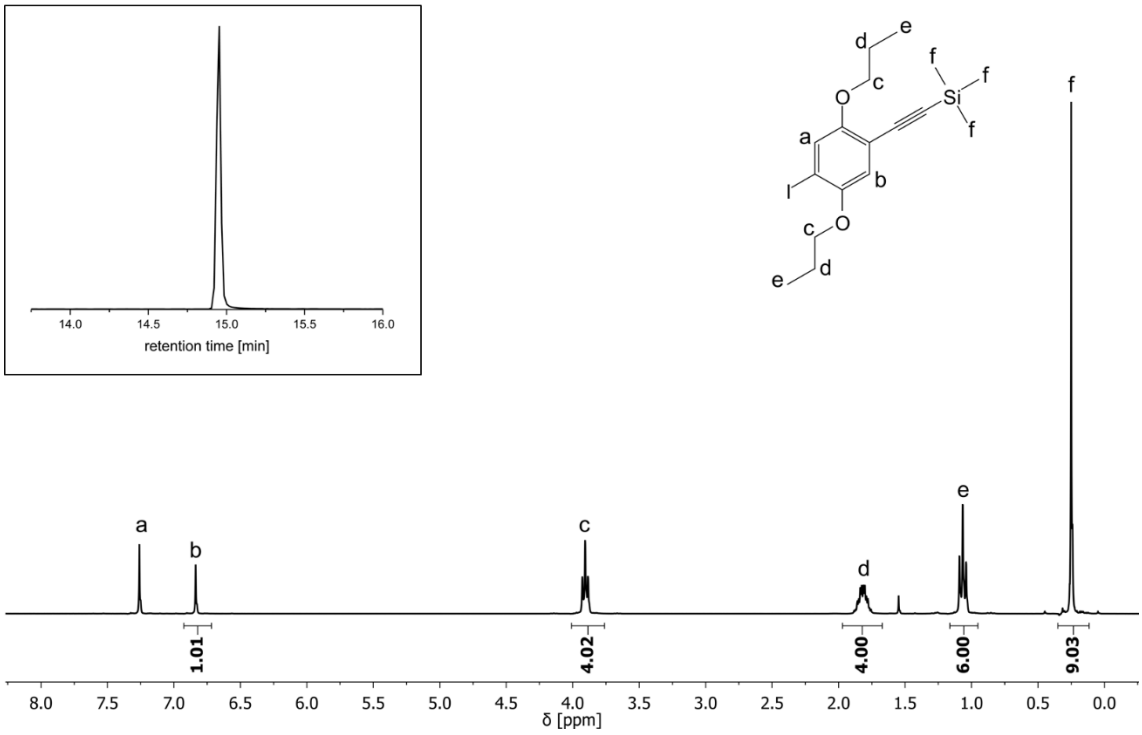


Figure 13: ^{1}H NMR spectrum of building block **B1** with assigned signals. Signal *a* overlaps with the chloroform in $CDCl_3$ (7.26 ppm) and the signal was not integrated. The signal at 1.55 ppm is water present in the $CDCl_3$. Additionally, the chromatogram is depicted, confirming the purity.

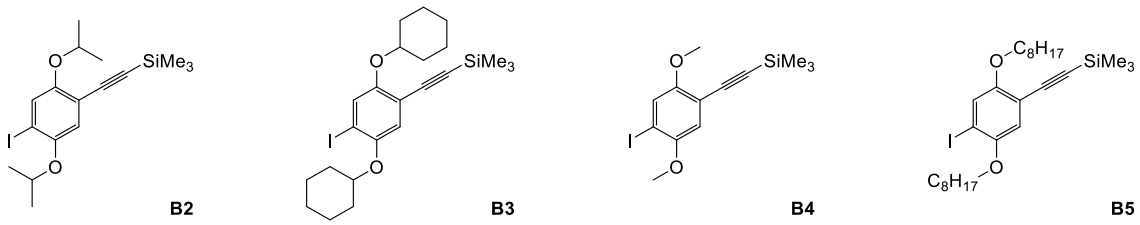


Figure 14: Further synthesized building blocks: **B2** with isopropoxy, **B3** with cyclohexyloxy, **B4** with methoxy and **B5** with octyloxy side chains.

The synthesis of building block **B2** proceeded smoothly and the product was obtained in an overall yield of 17%. The Williamson ether synthesis with bromocyclohexane was challenging. Since the Williamson ether synthesis proceeds *via* a s_N2 mechanism (second order nucleophile substitution), primary carbon atoms are favored. However, 2-bromopropane was converted easily, because it is less sterically hindered. The reaction to 1,4-*bis*(cyclohexyloxy)benzene **P3a** was therefore monitored by GC-MS; fresh bromocyclohexane was added when it was no longer detected. Although full conversion was detected by GC-MS, only 28% **P3a** were obtained. The overall

yield of **B3** thus only amounted to 8.7%. A further Williamson ether synthesis with *tert*-butyl bromide did not lead to the desired product, since a tertiary carbon cannot undergo a s_N2 reaction.

As mentioned before, 1,4-dimethoxybenzene was commercially available and the final building block **B4** was obtained in two steps and an overall yield of 31%. Building block **B5** is based on hydroquinone and exhibits octyloxy side chains. The purification of the last step by silica column chromatography was more challenging, since a further spot was apparent, which was not detected by UV detection of the thin-layer chromatography (TLC) (but by Seebach staining solution). After a second silica column chromatography, the product was obtained in an overall yield of 12%. A comparison of the ^{1}H NMR spectra of building blocks **B2**-**B5** is given in Figure 15.

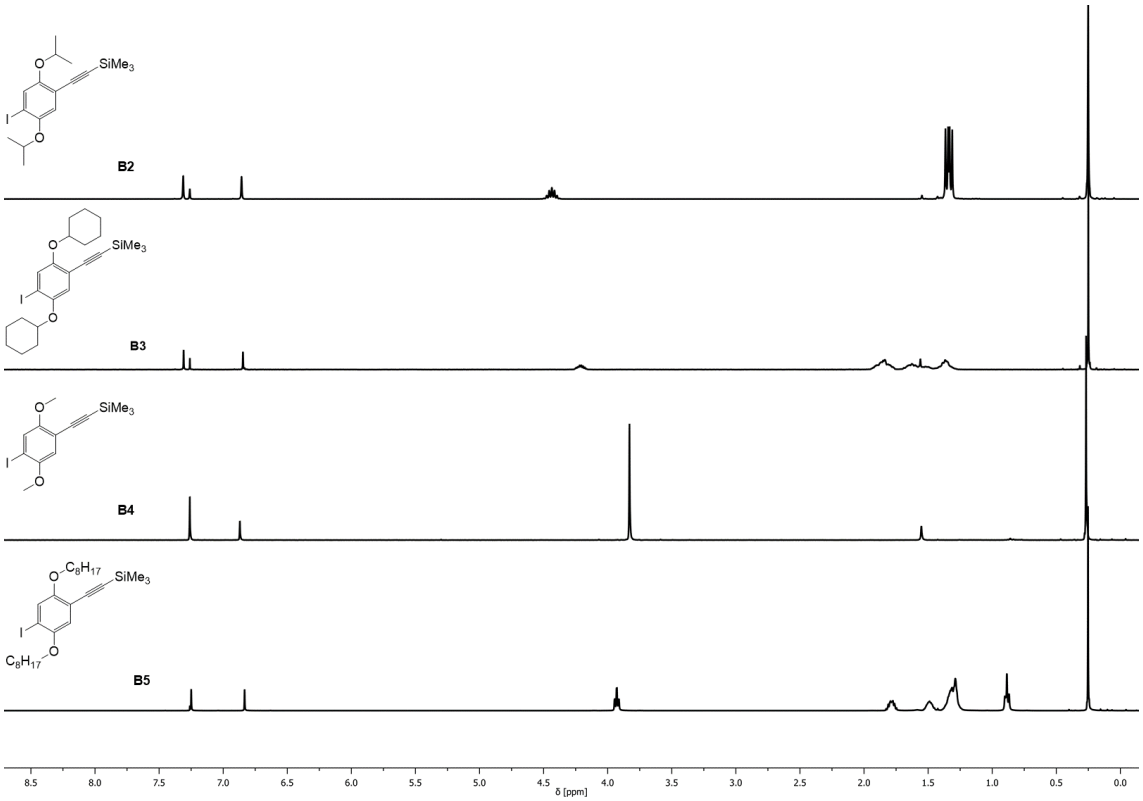


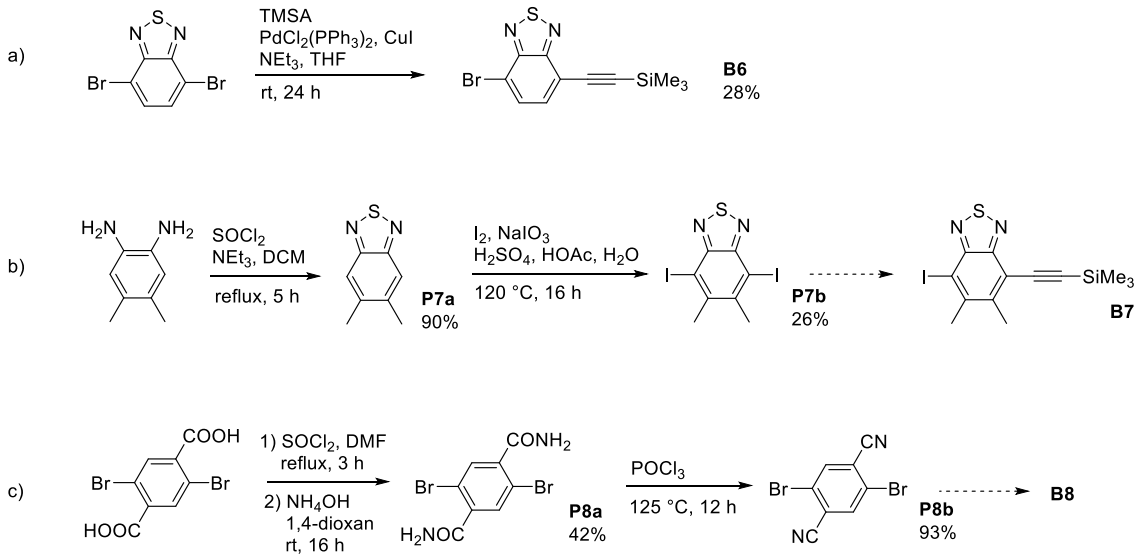
Figure 15: ^{1}H NMR spectra of the building blocks **B2**-**B5**. The aromatic signals differ slightly, the respective alkyl signals can be distinguished according to the different moieties.

The building blocks **B1**, **B2**, **B3** and **B5** were obtained in three steps in overall yields ranging from 8.7-29%. The methoxy building block **B4** was obtained in two steps and an overall yield of 31%. Larger amounts (more than 3 grams each) were obtained for **B1** (4.26 grams), **B4** (3.10 grams) and **B5** (3.17 grams). Since

the building blocks are incorporated with high excess during the formation of rod-like macromolecules (chapter 4.2), multiple grams of building blocks were necessary.

4.1.2 Building Blocks with Electron Accepting Properties

For the polymer-dye conjugates (compare chapter 3), building blocks with electron accepting properties are required as well. 4,7-Dibromobenzo[*c*][1,2,5]thiadiazole is commercially available and can be transformed with TMSA in a Sonogashira monocoupling to building block **B6**. Scheme 26a) depicts the synthesis of building block **B6**. Here, the optimized conditions for **B1** were not ideal. According to GC, the disubstituted side product is favorably formed and appeared insoluble in the reaction mixture. Therefore, less TMSA might be a solution for a more efficient formation of **B6.** In Figure 16, the high purity of **B6** is depicted by a ^{13}C NMR spectrum with assigned signals. Since **B6** does not exhibit any groups for solubilization, oligomer formation could be significantly aggravated. Therefore, another benzothiadiazole building block **B7** with two methyl side chains was designed, which is also illustrated in Scheme 26b). However, only the respective precursor **P7b** with a few impurities was obtained so far. The synthesis starts with 4,5-dimethyl-1,2-phenyldiamine, which is converted with thionyl chloride to the respective 5,6-dimethylbenzo[*c*][1,2,5]thiadiazole **P7a**.[222] The iodination to **P7b** was performed with sodium iodate as described in the same patent.[222] While the yield of **P7a** was significantly higher as in the patent specification, the yield of **P7b** was lower, but a further Sonogashira monocoupling should be possible. For the “acceptor chain”, further building blocks with electron accepting properties should be synthesized for a possible variation: the synthesis of cyanobenzene building block **B8** was investigated. Here, the final Sonogashira monocoupling could not be performed so far, but precursor **P8b** was obtained (compare Scheme 26c). Based on 2,5-dibromoterephthalic acid, the respective diamide **P8a** was formed according to a procedure by Chou and Wong *et al*.[223] The subsequent dehydration of **P8a** was realized with phosphorus oxychloride to yield 2,5-dibromoterephthalonitrile **P8b** described in the same publication.[223] Here, a further Sonogashira monocoupling should result in the respective building block **B8**.



Scheme 26: Overview of the syntheses of building blocks with electron accepting properties. a) synthesis of building block **B6** based on a benzothiadiazole, b) synthesis of building block **B7** to a benzothiadiazole with methyl side chains for better solubility, c) synthesis of building block **B8** with cyano moieties.

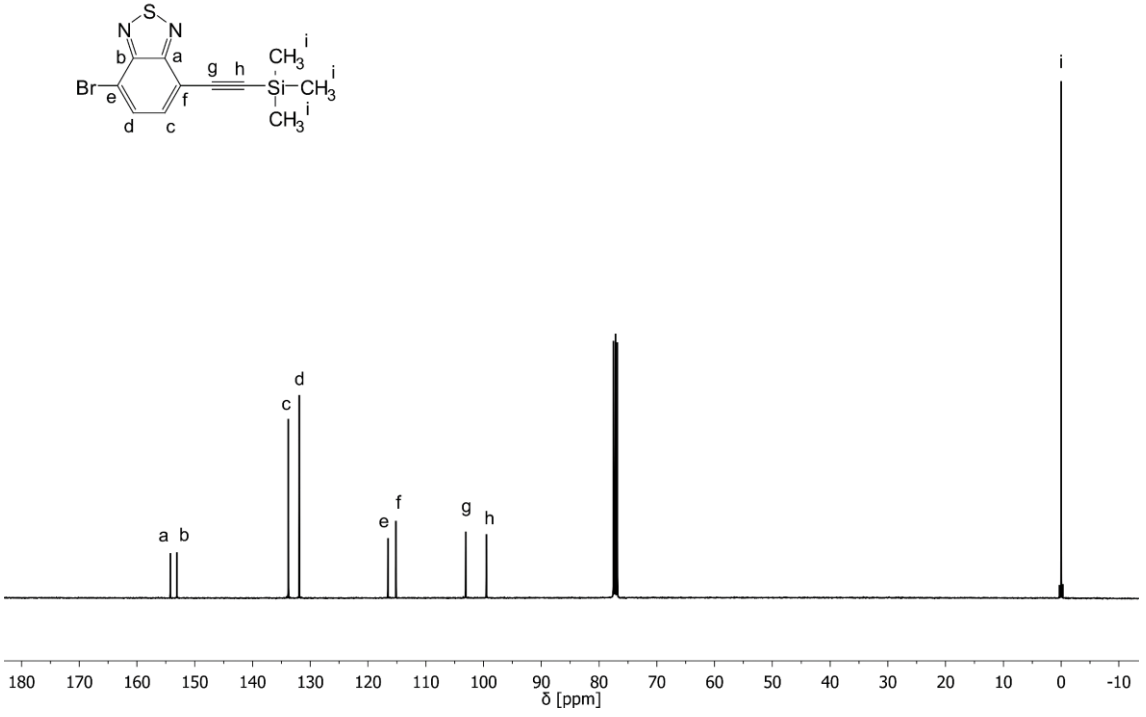


Figure 16: ^{13}C NMR spectrum of building block **B6** with assigned signals.

The benzothiadiazole building block **B6** was obtained in 28%. The Sonogashira cross-coupling of benzothiadiazole **B7** with side groups is pending, as for cyanobenzene building block **B8**. The Sonogashira reaction itself should not pose

a barrier. Electron accepting oligomers (with a low DP) should be possible to obtain with building blocks **B6**-**B8**. However, tetramers or pentamers might be difficult to synthesize due to the lack of solubilizing side groups. The building blocks **B6**-**B8** are suited for targeted incorporation into an electron donor chain, mainly composed of building blocks **B1**-**B5**, which is also an aim of project A4 within the SFB 1176.

4.2 Monodisperse and Sequence-Defined Rod-Like Oligomers

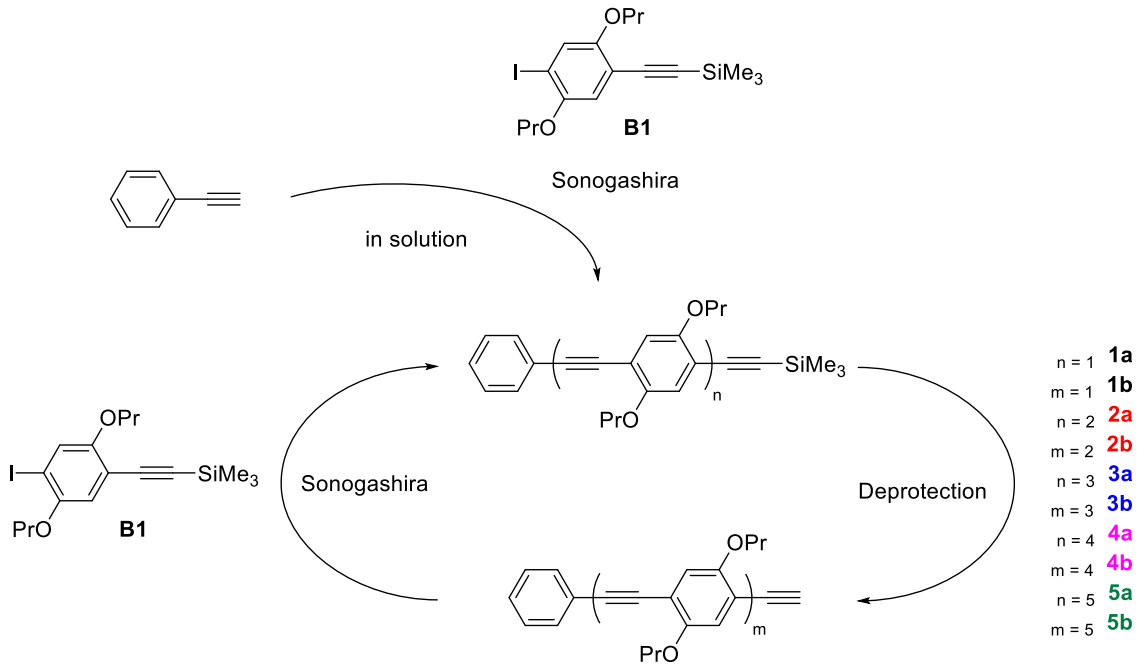
With the building blocks described in chapter 4.1 in hands, the respective rod-like oligomers could be synthesized according to Scheme 24 (chapter 3). Initially, building block **B1** was used to establish the synthesis procedure and therefore a monodisperse pentamer (**5b**) was obtained (chapter 4.2.1). The respective oligomers were termed according to their DP, *e.g.* **1a** for the protected monomer, **1b** for the deprotected monomer. With building block **B6**, an electron accepting monomer **1c** was synthesized and briefly compared to electron donating **1a**. Furthermore, a direct condensation approach was performed as an alternative procedure and compared to the iterative approach (chapter 4.2.2). With the other building blocks **B2**-**B5**, sequence-defined rod-like oligomers were synthesized (chapter 4.2.3) and termed also according to their degree of polymerization.

4.2.1 Monodisperse Rod-Like Oligomers

The synthesis to rod-like oligomers is based on Sonogashira cross-coupling and subsequent deprotection of the trimethylsilyl protecting group. This procedure was similarly applied by the group of Tour as well.[55] First, the building block **B1** is converted with phenylacetylene to the protected monomer **1a** as depicted in the upper part of Scheme 27.

The conversion to monomer **1a** was performed similar to the Sonogashira monocoupling in chapter 4.1 but with 3 equivalents of phenylacetylene. In this way, a high yield should be forced, since the phenylacetylene might also undergo Glaser coupling to 1,4-diphenylbutadiyne. Silica column chromatography was performed twice, once with cyclohexane/dichloromethane and another time with cyclohexane/ethyl acetate to yield the product in a scale of 4.63 grams and 99% yield. Since the reaction proceeded with this high yield, no attempts for an optimization were made. The deprotection was performed with 2 equivalents of

potassium carbonate in a methanol dichloromethane mixture.[55] Deprotected monomer **1b** was obtained with 3.15 grams and a yield of 97%. In Table 10, the scale and yield for each reaction are summarized. The purity of the respective oligomers is depicted at Figure 22, where the SEC traces of all monodisperse oligomers are illustrated.



Scheme 27: Synthesis procedure to monodisperse rod-like oligomers by iterative Sonogashira cross-coupling and subsequent deprotection.

The next Sonogashira cross-coupling to dimer **2a** is more complicated, since the alkyne is not the building block but the monomer **1b**. An excess of the alkyne is no longer desirable, as it is the more valuable compound. Therefore, an excess for the building block **B1** of 3 equivalents was applied to prevent Glaser coupling. The amount of catalyst was also increased to 5 mol% to force the Sonogashira cross-coupling. Three test reactions were performed for 72 hours in order to screen for the ideal temperature. The product **2a** cannot be detected by GC-MS any longer, therefore, the conversion was monitored by SEC (compare Figure 17). Unfortunately, building block **B1** and reagent **1b** exhibit the same retention time and cannot be distinguished by SEC. Although oxygen-free conditions were provided by applying Schlenk techniques, Glaser coupling could not be prevented as shown in Figure 17. Lower temperatures, as depicted for the black trace (room temperature), did not necessarily lead to less Glaser product in comparison to product **2a**. Furthermore, an additional peak between product **2a**

and building block **B1** is detected for the room temperature approach. In the approach at 40 °C the least and in the 60 °C approach the most Glaser product was formed. Therefore, a temperature of 40-45 °C was applied for the following reactions.

Purification of the product **2a** was demanding, since the Glaser side product and **2a** elute similar by silica column chromatography. Often, mixed fractions were collected, which required further purification. Nevertheless, **2a** could be isolated without impurities (3.20 grams, 84%) as depicted in Figure 22 and as a positive side effect, building block **B1** was recollected.

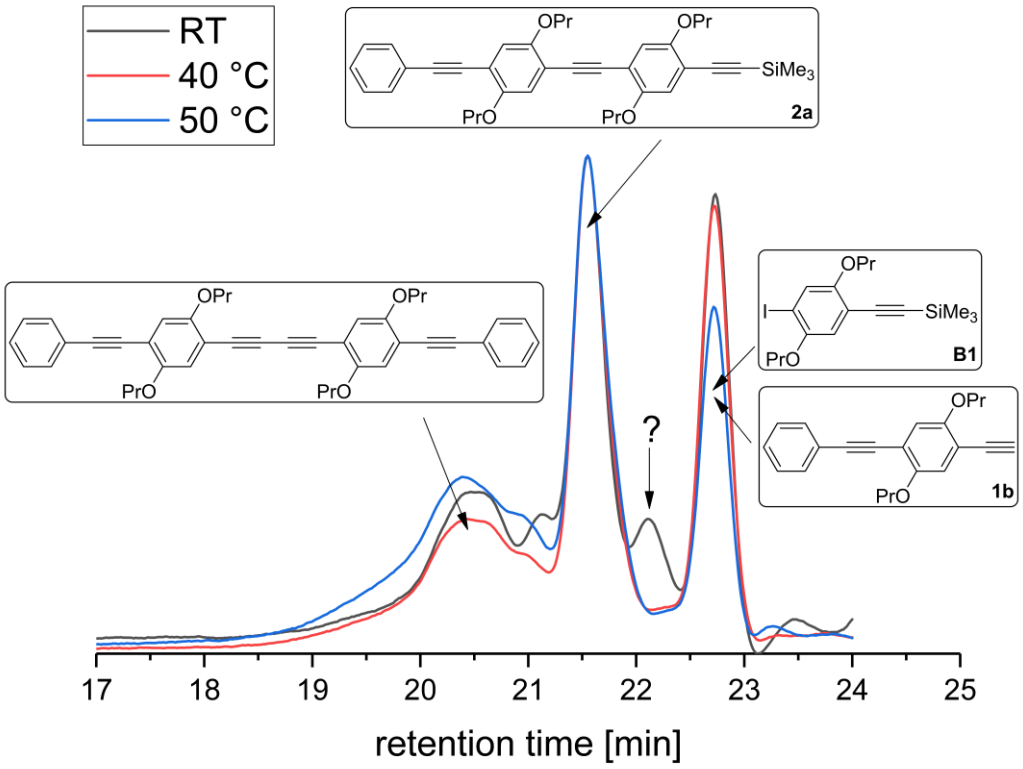


Figure 17: SEC traces of three crude mixtures for dimer **2a** formation, performed at different temperature (black: room temperature, red: 40 °C, blue: 50 °C). The respective compounds are assigned to the maximum intensities within the traces (from lower to higher retention times): Glaser side product, dimer **2a**, unknown (for room temperature trace only), building block **B1** and monomer **1b**, which exhibit the same retention time.

In related master thesis by Kevin Waibel, a test reaction to the monomer **1a** was performed without copper iodide.[224] In this way, Glaser coupling is completely suppressed. Elevated temperatures of 50 °C along with a higher catalyst loading

of 5 mol% and triethylamine as sole solvent were promising conditions in a cooper-free alternative according to GC-MS. However, product **1a** precipitated in triethylamine, preventing the transfer of the conditions to any other oligomer formation. Still, a transfer of the former conditions to the synthesis of **2a** was tested. As mentioned before, column chromatography of the Glaser side product and **2a** turned out to be difficult, and a reaction procedure without any Glaser coupling formation would be preferable. For this test reaction, copper iodide was not applied, and the amount of catalyst was increased to 10 mol%, the amount of triethylamine to 100 equivalents. However, no full conversion to **2a** could be achieved, resulting in a mixture of product **2a** and reagents **1b** and **B1**. Surprisingly, the separation of **2a** and **1b** by silica column chromatography was not easier compared to **2a** and the Glaser product. Therefore, further test reactions without copper iodide were not pursued. Probably, a complete change of the synthesis strategy would enable a copper-free Sonogashira reaction. Other amines, such as pyridine, might solubilize the product better compared to triethylamine. In chapter 2.2.1, an unconventional copper-free Sonogashira without solvents but with TBAF was described.[142] Unfortunately, TBAF also deprotects the TMS group and would result in further side product formation here. As mentioned before, traces of copper are often present within the palladium catalysts and complete copper-free variations are often not guaranteed.[140]

The deprotection to dimer **2b** did not proceed as straightforward as for **1b**. Figure 18 depicts the crude ^{1}H NMR of **2b**, where the signal of the emerging hydrogen atom is marked in red. In comparison to the other signals, the hydrogen signal is too low with an integral of 0.6 instead of 1.0. Since the trimethylsilyl signal at 0.26 ppm completely vanished, the Glaser coupled side product of **2b** might have formed, which was later confirmed by TLC. Obviously, traces of copper are still present in compound **2a**, which complicate the deprotection. Although the reaction was performed under oxygen-free conditions, Glaser coupling occurred.

When performing a further column chromatography with protected dimer **2a** with cyclohexane and ethyl acetate, Glaser coupling did not occur during deprotection to **2b**. Therefore, column chromatography was performed twice after the Sonogashira reaction, once with cyclohexane and dichloromethane and a second time with ethyl acetate.

Furthermore, crude product **2b** (compare Figure 18) exhibits significant amounts of hydrocarbon grease (0.88 and 1.26 ppm) and silicon grease (0.07 ppm). With recrystallization in a cyclohexane/ethyl acetate mixture, the hydrocarbon grease can be removed. Since **2b** does not crystallize in the mentioned mixture, column chromatography was performed as well. Deprotected dimer **2b** was obtained in a scale of 2.63 grams and 100% yield.

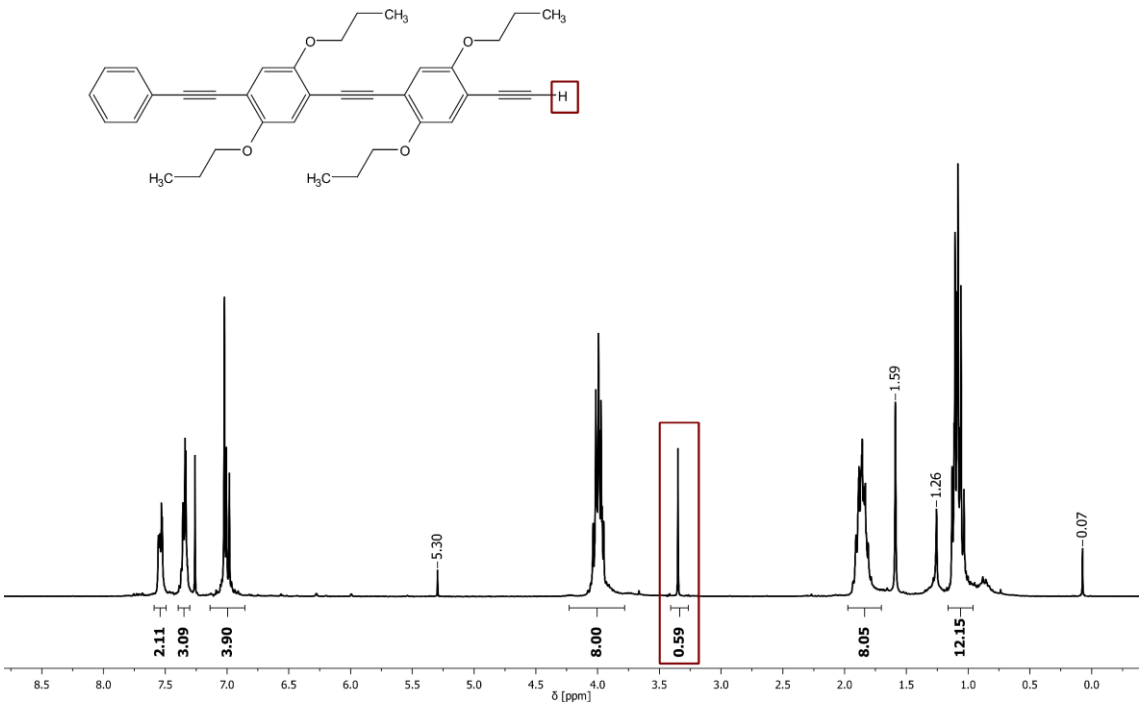


Figure 18: ^{1}H NMR spectrum of crude, deprotected dimer **2b**. The product is not pure, as the signal for the free hydrogen is too low (compare rectangles). However, the signals for the trimethylsilyl group around 0.26 ppm vanished, indicating that Glaser side product of **2b** is present.

The Sonogashira reaction to trimer **3a** was performed as for **2a**. Here, purification was also challenging, since the Glaser side product and the product **3a** do not differ significantly at this point. The crude SEC trace of **3a** is illustrated as dotted trace in Figure 19. In grey, the building block **B1** is superimposed. Nonetheless, trimer **3a** could be isolated by dual column chromatography in a 2.10 gram scale (68%). The purified product **3a** is depicted as blue SEC trace in bold (Figure 19).

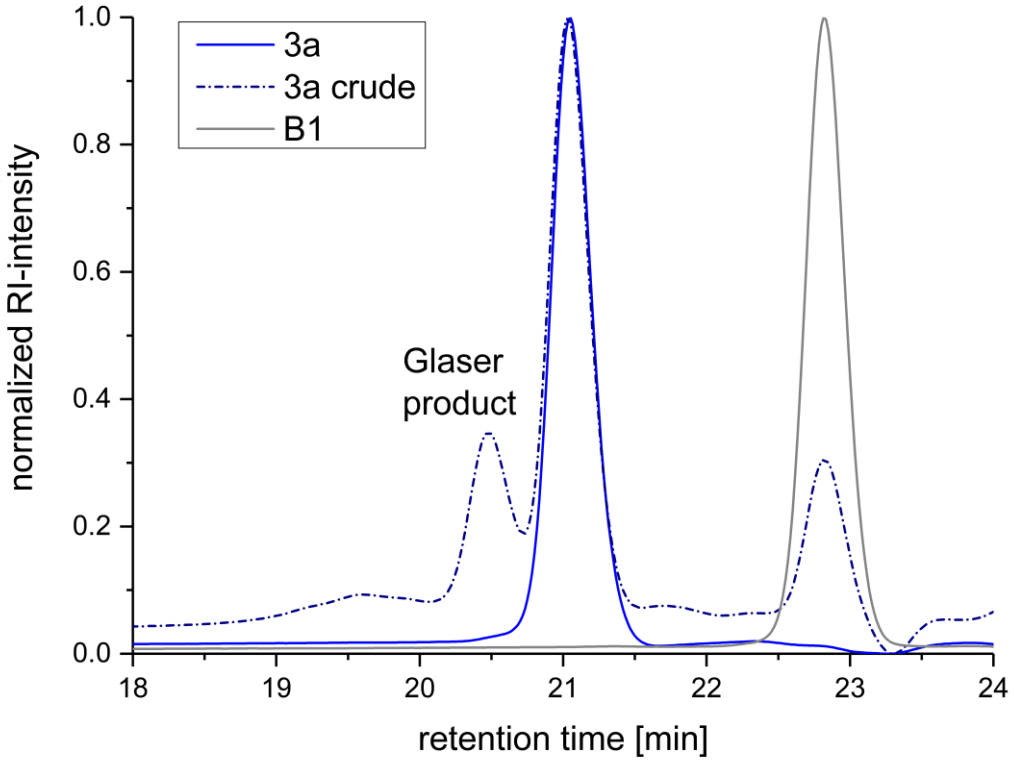


Figure 19: SEC trace of crude reaction mixture of trimer **3a** (dotted) in comparison to purified trimer **3a** (blue, bold) and the building block **B1** (grey, bold).

The deprotection to trimer **3b** proceeded smoothly and it was obtained with 1.74 grams and 98%. Column chromatography was performed in order to remove the hydrocarbon grease.

The Sonogashira cross-coupling to tetramer **4a** yielded the product in 65% and in a scale of 1.22 gram. From the tetramer step on, column chromatography with cyclohexane and ethyl acetate could not be performed any longer, since the product precipitated on the silica column. Tetramer **4a** is soluble in hot ethyl acetate, but small amounts of cyclohexane lead to precipitation. In order to remove grease, the product should elute after the grease, which is not guaranteed if the cyclohexane/ethyl acetate mixture is too polar.
Therefore, recrystallization from *n*-hexane was performed after column chromatography with dichloromethane and cyclohexane. After the deprotection to **4b**, recrystallization from *n*-hexane was performed as well. The deprotected tetramer was obtained with 682 milligrams (99%). The SEC traces are depicted in Figure 22.

The pentamer **5a** was obtained in a yield of 53% and a scale of 307 milligrams. The crude SEC trace is depicted in Figure 20, the reagent **4b** (pink, dotted) was completely converted. Also, the purification by column chromatography is facilitated in comparison to the dimer and the trimer. Apart from building block **B1**, the product **5a** and the Glaser coupling side product, a further peak emerges.

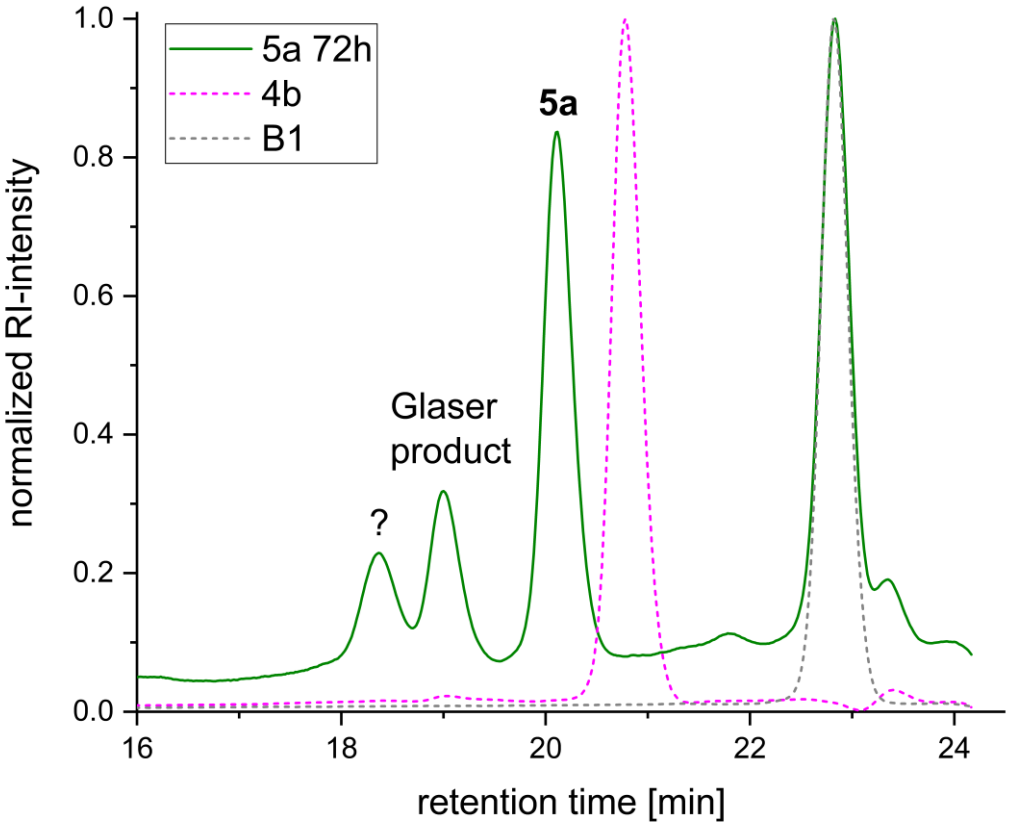


Figure 20: SEC trace of crude reaction mixture **5a** (green) in order to check conversion from **4b** (pink). The building block **B1** is depicted in grey. Apart from the Glaser side product, a signal with lower retention time emerges.

Since silica column chromatography with a high content of dichloromethane requires more time, the Glaser side product and the further side product were not purified. As the unknown side product has a higher hydrodynamic volume, it exhibits probably a higher molecular weight as well. Since the rod-like oligomers are not detected reliable within SEC-ESI-MS measurements, a conclusion based on mass spectrometry could not be made. Possibly, this signal of higher hydrodynamic volume can be ascribed to Hiyama cross-coupling as side reaction.[225] According to this reaction, organohalides react with organosilanes

under palladium catalysis and the influence of a fluoride or a base. The building block **B1** exhibits both functionalities and might polymerase as AB-type monomer. However, this assumed side reaction was not clearly observed before. For instance, the crude SEC trace of trimer **3a** (Figure 19) exhibits only a small shoulder before the respective Glaser side product. The amount of **B1** was increased from 3 equivalents for the synthesis of **3a** to 5 equivalents in the Sonogashira cross-coupling of **4a** and **5a**, though. Potentially, Hiyama cross-coupling occurred increasingly, since the amount of **B1** was almost doubled. Alternatively, triethylamine as base might deprotect small amounts of the triple bond in the building block **B1**. In this way, the deprotected building block could also react with the alkyne **4b** or with **B1** resulting in oligomers of higher molecular weight.

The deprotected pentamer **5b** was obtained in a yield of 98% and a scale of 116 milligrams. The ^{1}H NMR of **5b** is shown in Figure 21 with assigned signals. The intensity of signal *e* of the alkyne proton is a bit too low with 0.9, but the SEC trace confirms that Glaser side product is not present (compare Figure 22).

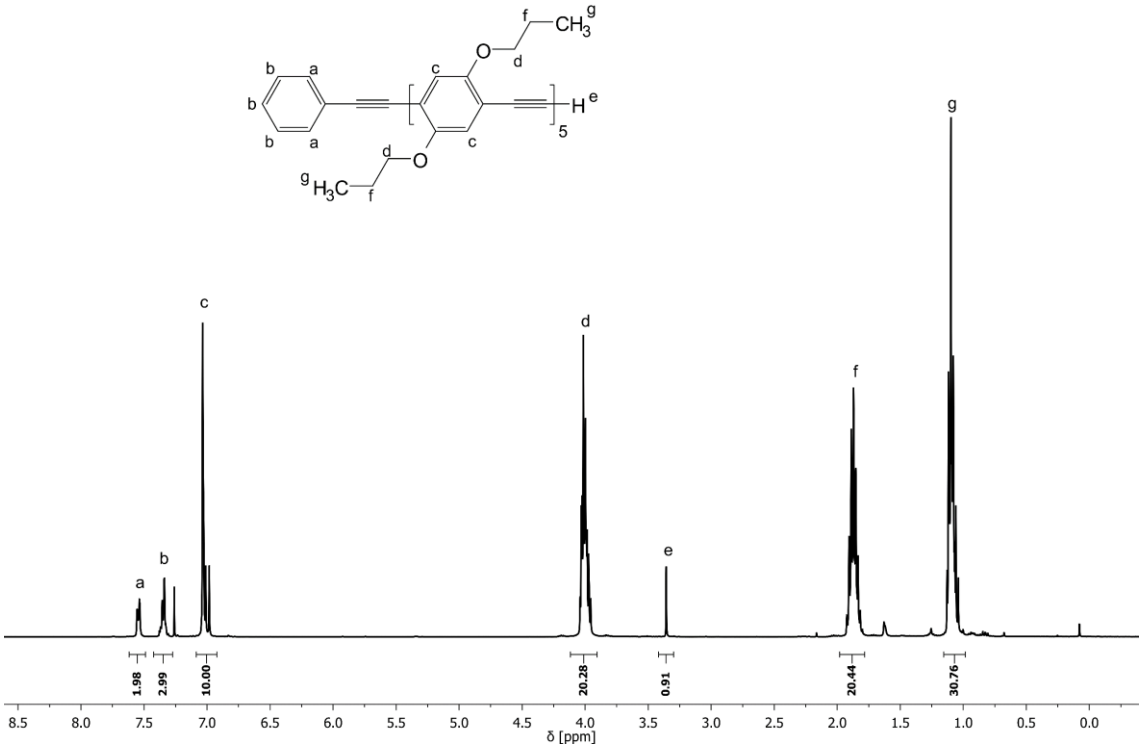


Figure 21: ^{1}H NMR of pentamer **5b** with assigned signals.

As mentioned before, Figure 22 depicts the overview of the monodisperse oligomers **1a**-**5b**. As expected, the oligomers with higher DP elute first and therefore exhibit a lower retention time. Since the deprotected (dotted) representatives have a lower molecular weight, they elute later than their protected (bold) versions. As the molecular weight difference of **1a** and **1b** is higher than that of **5a** and **5b**, for instance, the SEC traces of the protected and deprotected version can be distinguished more easily for the lower molecular weights. In general, SEC is a good method to detect the purity of the compounds and can be also used to check the conversion of a crude mixture (compare Figure 17, Figure 19, Figure 20).

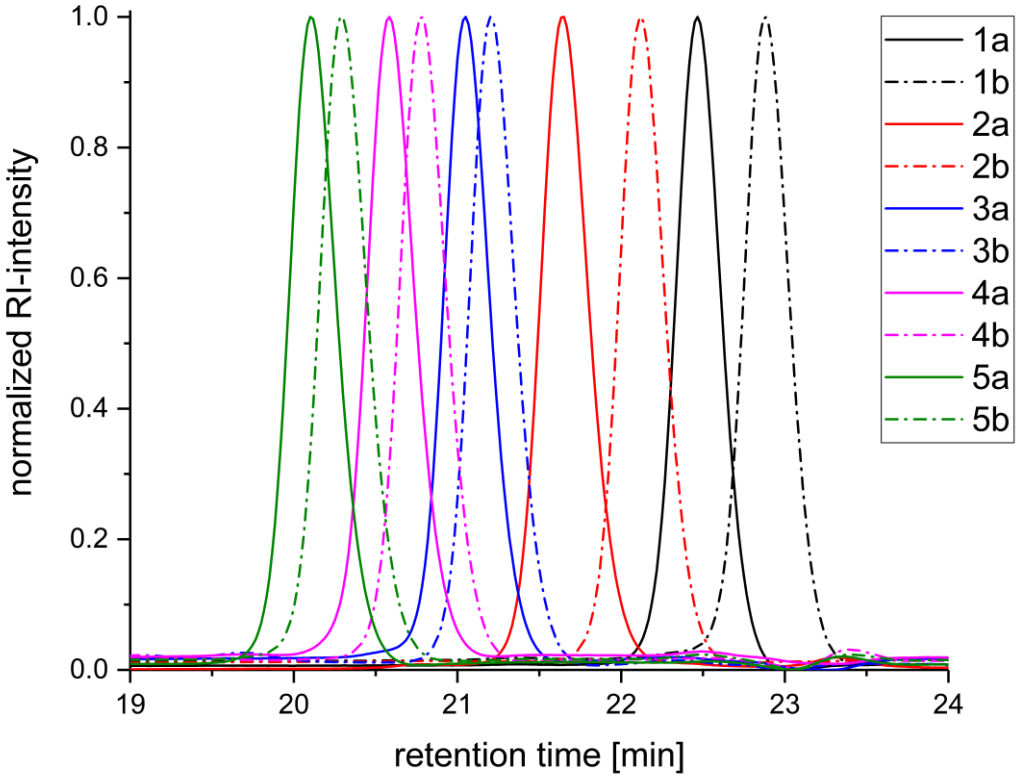


Figure 22: SEC traces of the monodisperse oligomers. The bold line represents the protected, the dotted line the deprotected representatives.

The yields and scales are depicted in Table 10 and an overall yield for the deprotected pentamer **5b** of 18% was achieved over ten steps. This is indeed similar to a solution approach towards a sequence-defined pentamer by subsequent Passerini and thiol-ene reaction.[26] However, different reaction procedures are not comparable and another Passerini-based approach towards

sequence-defined oligomers yielded a pentamer with 67%.[26] Since side reactions for the Sonogashira cross-coupling emerge, higher yields are difficult to obtain. In the previously mentioned approach of Tour towards sequence-defined OPEs, 24 trimers were prepared in overall yields ranging from 12-39% and in scales of 14 to 125 milligrams.[55] The synthesis of trimer **3a** (Hwang and Tour performed a Sonogashira reaction as last step) over five steps yielded 2.10 grams in an overall yield of 55%. In comparison, the approach represented herein resulted in higher yields; however, Hwang and Tour might not have focused on scales and yields but on creating a library for OPEs.[55]

Table 10: Overview of scales and yields for the individual reaction steps and the overall yield of the deprotected monodisperse pentamer **5b** over all steps. Additionally, the molecular weight (MW), the melting points (T_m) and the glass transition temperature (T_g) are depicted.

compound	MW	T_m	T_g	scale	yield
1a	390.60	84.8 °C	-	4.63 g	99%
1b	318.42	100.5 °C	-	3.15 g	97%
2a	606.88	129.2 °C	19.3 °C	3.20 g	84%
2b	534.70	92.6 °C	18.3 °C	2.63 g	100%
3a	823.16	121.0 °C	34.4 °C	2.10 g	68%
3b	750.98	-[a]	39.2 °C	1.74 g	98%
4a	1,039.44	160.5 °C	45.6 °C	1.22 g	65%
4b	967.26	125.3 °C	44.9 °C	682 mg	99%
5a	1,255.72	186.8 °C	-[b]	307 mg	53%
5b	1,183.54	153.3 °C	49.4 °C	116 mg	98%
overall					**18%**

[a]a clear melting point was not observed; the measurement was repeated several times (also in a new crucible to exclude weighing errors *etc*.). [b]a glass transition temperature was not detected (measurements were repeated as well).

Table 10 depicts also the respective T_m and T_g values detected by differential scanning calorimetry (DSC). The melting points increase with progressing chain length: monomer **1a** exhibits a T_m of 84.8 °C, pentamer **5a** of 186.8 °C. Apart from the monomers, the protected version **a** always exhibits a higher T_m of 30-40 K as the deprotected version **b**. For instance, protected dimer **2a** exhibits a T_m of 129.2 °C and deprotected dimer **2b** of 92.6 °C, resulting in a difference

ΔT_m of 36.6 K. In a publication by Meier *et al.*, similar OPEs were synthesized and the melting points were detected by a melting point apparatus.[34,65] The molecules differ in the protecting group, which is the bulkier triisopropylsilyl group and the missing phenylacetylene starting unit in the Meier publication. A comparison is therefore challenging, *e.g.* the higher T_m of the protected in relation to the deprotected version cannot be observed here; the deprotected versions usually exhibit a higher T_m. The deprotected molecule with five repeating units of Meier *et al.* exhibits a T_m of 152 °C. The deprotected pentamer **5b** exhibits a similar T_m of 153 °C; however, it comprises one phenylacetylene starting unit more.[34] The same applies to the deprotected molecule with four repeating units (126 °C) and the deprotected tetramer **4b** (125 °C).[65] In general, the T_m increases as expected with advancing chain length.[34,65]
Glass transitions are also detected. Interestingly, already the dimers exhibit a T_g close to 20 °C. As for the melting point, the glass transition temperatures increase with the chain length. For instance, the tetramers exhibit a T_g of approximately 45 °C. For the protected pentamer **5a**, no T_g was observed; however, deprotected pentamer **5b** exhibited a T_g of 48.4 °C. Since Meier *et al.* used an optical detection of the melting point, glass transitions were not reported.[34,65]

Apart from thermal properties, photophysical properties were analyzed (Figure 23). The optical attenuation serves as measure for the absorption. It is detected by the transmission of a reference, *i.e*. dichloromethane, compared to a solution. The photoluminescence (PL) is a measure for the emission. As expected, the absorption maxima λ_{max} shift from shorter to longer wavelengths with increasing chain length. This phenomenon is known as bathochromic or red-shift. The monomer **1a** exhibits a λ_{max} of 307 nm, whilst the pentamer **5a** has the maximum wavelength at 424 nm. The PL intensity shows the same behavior: monomer **1a** exhibits the emission maximum at 434 nm and the pentamer **5a** at 465 nm. From the trimer **3a** until the pentamer **5a**, the Stokes shift is around 40 nm. Interestingly, the emission maxima of the dimer **2a** (bold red, Figure 23) with 444 nm and the trimer **3a** (blue bold) with 446 nm are quite similar. The PL trace of the dimer **2a** is comparably poor resolved and broadened, which is why the PL spectrum of **3a** is more reliable.

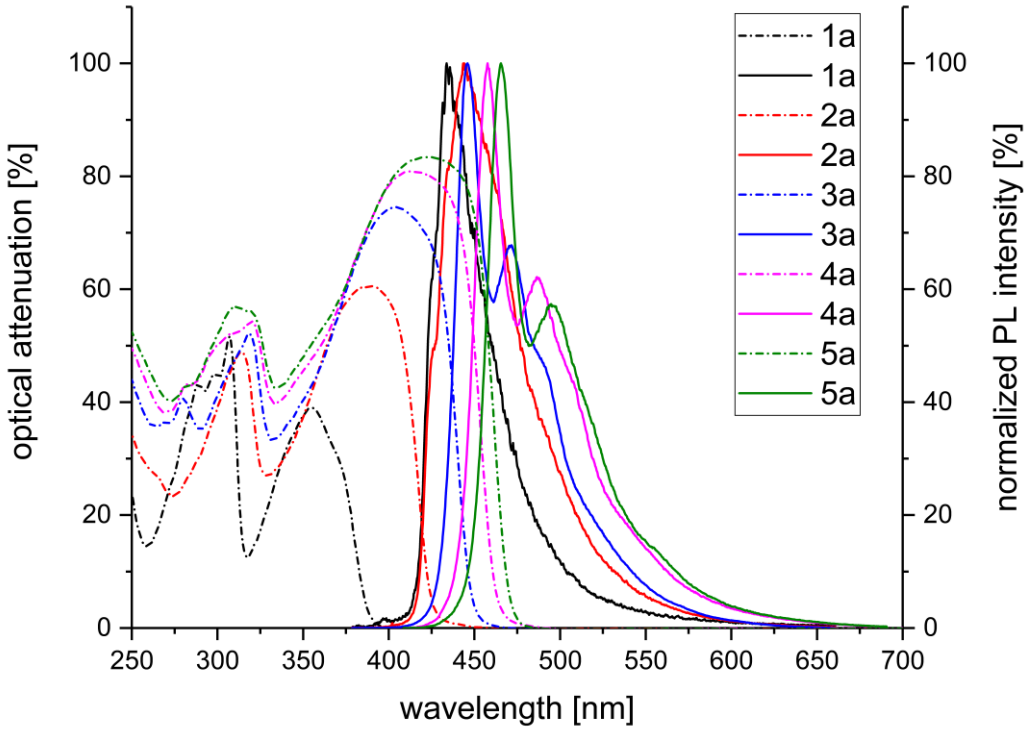


Figure 23: Absorption spectra (dotted) and PL spectra (bold) of protected monodisperse rod-like oligomers **1a**-**5a** in dichloromethane.

So far, the monodisperse pentamer and its intermediates exhibit only electron donating properties. With benzothiadiazole building block **B6**, another monomer could be synthesized, generating **1c** with electron accepting properties.
The Sonogashira reaction was performed with 500 milligrams of **B6** and with the same conditions as for **1a**. The respective product was obtained after column chromatography in a scale of 492 milligrams and a yield of 92%. The ^{1}H NMR of **1c** is depicted in Figure 24 with assigned signals. In comparison to building block **B6**, signals *b* and *c* emerged (compare Figure 56, chapter 6.3.2). The yield is improvable, since this was a first test reaction. Theoretically, similar yield and scale to **1a** should be possible.

Benzothiadiazole monomer **1c** was also analyzed by DSC and compared to monomer **1a** (Figure 25). As for **1a**, no T_g was detected, but the melting point accounted to 95.4 °C and is 10.6 K higher as for **1a**.

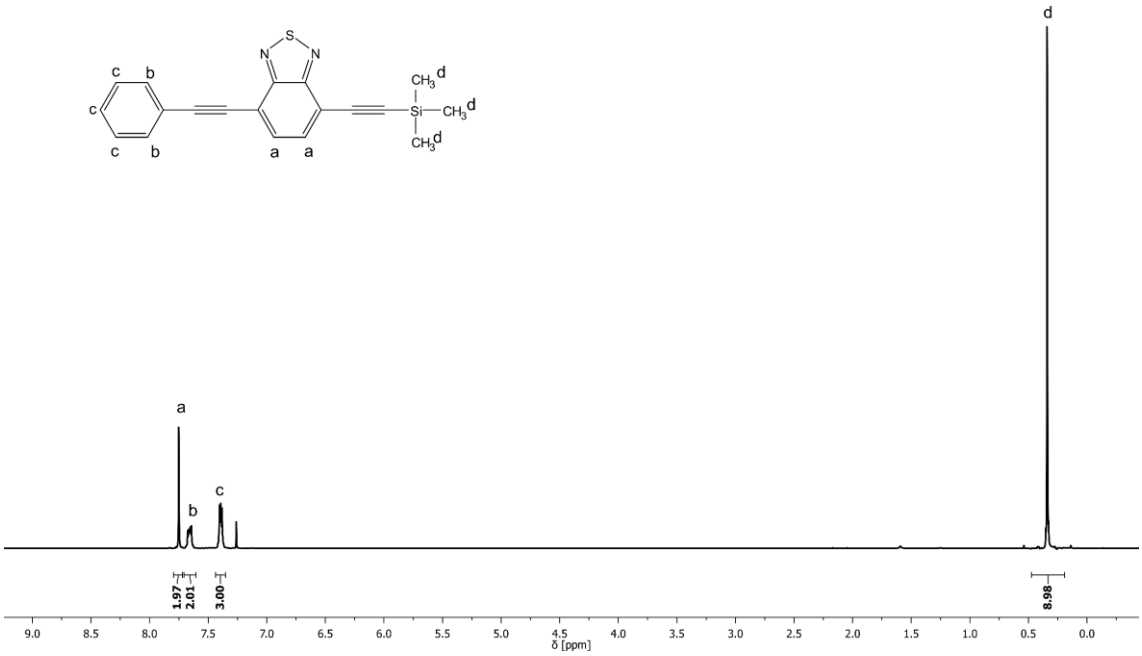


Figure 24: ^{1}H NMR of benzothiadiazole monomer **1c** with assigned signals.

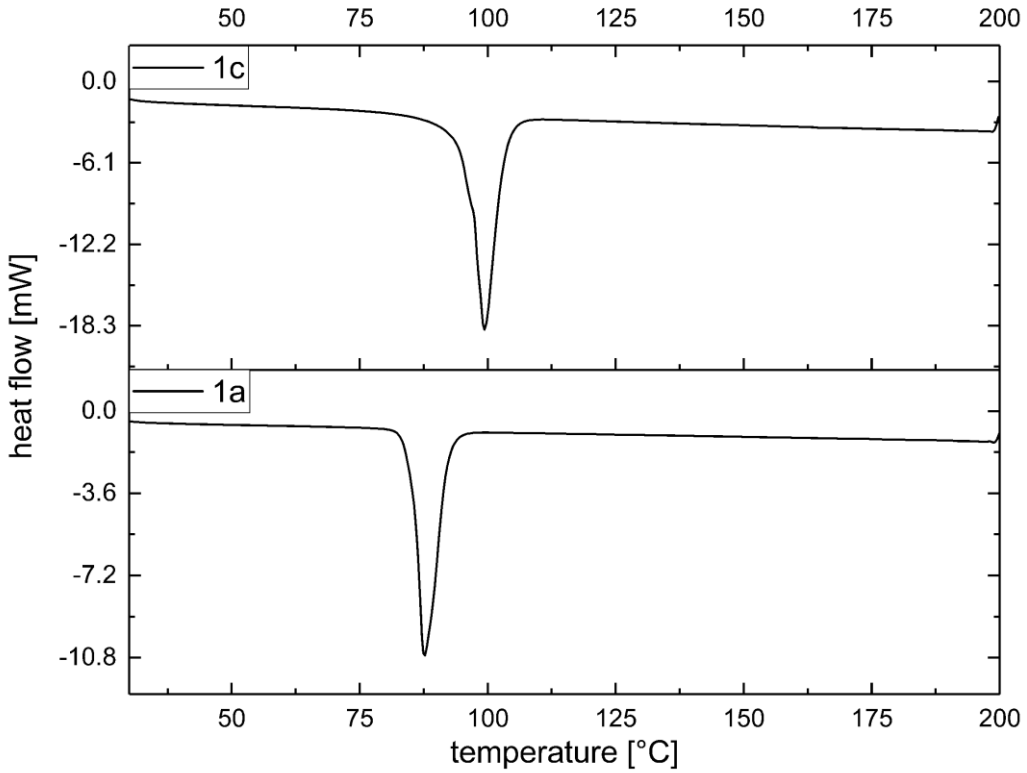


Figure 25: DSC trace of benzothiadiazole monomer **1c** in comparison to **1a**. The T_m of **1a** is with 84.8 °C significantly lower than for **1c** with 95.4 °C. Further thermal events were not detected.

Furthermore, the absorption and PL spectra of **1c** (black dotted) were recorded and compared to monomer **1a** (grey dotted, Figure 26). Benzothiadiazole monomer **1c** exhibits a λ_{max} for the absorption at 289 nm and a further local absorption maximum at 399 nm (**1a**: 307 nm – global maximum, 355 nm – local maximum). Especially the local maximum for **1c** is clearly red-shifted with 44 nm compared to **1a**. Also, the emission maximum of **1c** exhibits a λ_{max} of 494 nm compared to 434 nm of **1a** ($\Delta\lambda_{max}$ = 60 nm). This is in accordance with the results of Kitamura *et al.,*[226] who connected a benzothiadiazole with two thiophenes and detected a λ_{max} of 435 nm for absorption, which is red-shifted compared to conventional oligo(thiophene)s (λ_{max} of dimer: 344 nm, tetramer: 402 nm).[227]

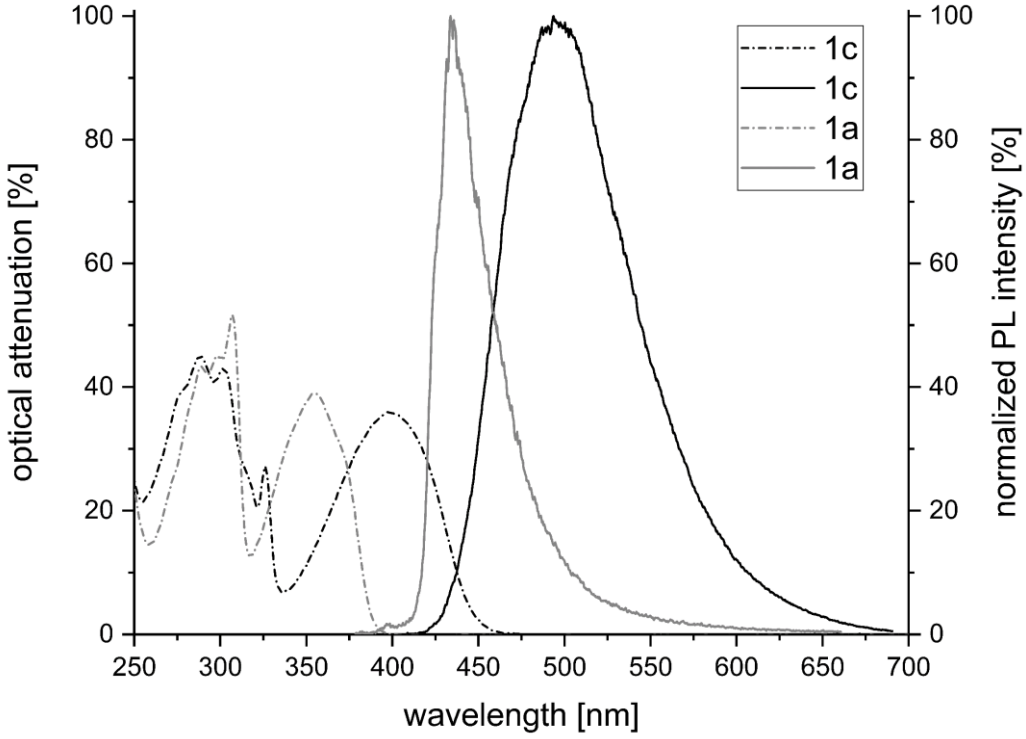


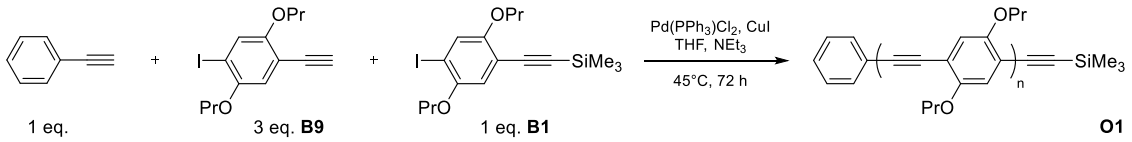
Figure 26: Absorption spectrum (dotted) and PL spectrum (bold) of **1c** in comparison to **1a** (grey).

The reaction procedure to monodisperse oligomers (compare Scheme 27) was performed until the deprotected pentamer **5b**. Reaction steps were slightly altered according to the DP of the respective products. Therefore, the synthesis procedure should be applicable for further OPE syntheses in the same range of DP. Especially the synthesis of electron accepting monomer **1c** enables the comparison with electron donating monomer **1a** indicating that iterative reaction

procedures are a valuable tool to detect structure-property relationship investigations.

4.2.2 Direct Oligomerization Approach

A direct oligomerization approach was performed in order to investigate a more direct way to the previously synthesized monodisperse oligomers. In Scheme 28, the oligomerization approach towards **O1** is illustrated. It is a polycondensation with a chain stopper. First, building block **B1** was deprotected with potassium carbonate to yield the building block **B9**. As usual, a high yield of 99% was obtained for the deprotection. Building block **B1** served as chain stopper; phenylacetylene was introduced as starting unit. By applying the ratio 1:3:1 (starting unit, building block **B9**, chain stopper **B1**) for the Sonogashira cross-coupling, short chain oligomers like the tetramer **4a** were expected to form preferentially within **O1**. After the work-up, TLC analysis was performed in order to determine the number of different products. However, more than 20 spots were detected, and SEC was performed to gain more insight (Figure 27).



Scheme 28: Oligomerization approach towards oligomer **O1** with phenylacetylene as starting unit, **B9** as building block and **B1** as chain stopper. In this way, short chain oligomers should form preferentially.

According to SEC analysis, a widespread mixture of different oligomers is obtained and not a targeted formation of short chain oligomers. In Figure 27, the SEC trace of **O1** is illustrated in brown with the respective traces of the protected version of the monomer **1a** until the pentamer **5a** and the chain stopper **B1**. The respective oligomers were clearly formed within **O1**: the intensity of trimer **3a** is the highest indicating that **3a** originates most. Furthermore, respective higher oligomers were formed and the chain stopper **B1** and presumably also the building block **B9** (with similar molecular weight and thus a similar retention time) are still present in the mixture. Additionally, a multitude of Glaser side products is very likely in the product mixture and comparably complicated to detect. The mixture of **O1** might be purified by recycling SEC systems, but conventional

column chromatography would result in mixed fractions. Further characterization, such as ^{1}H NMR, was therefore not performed. A DSC analysis was implemented in order to confirm the melting points of the respective oligomers, but thermal transitions were not detected.

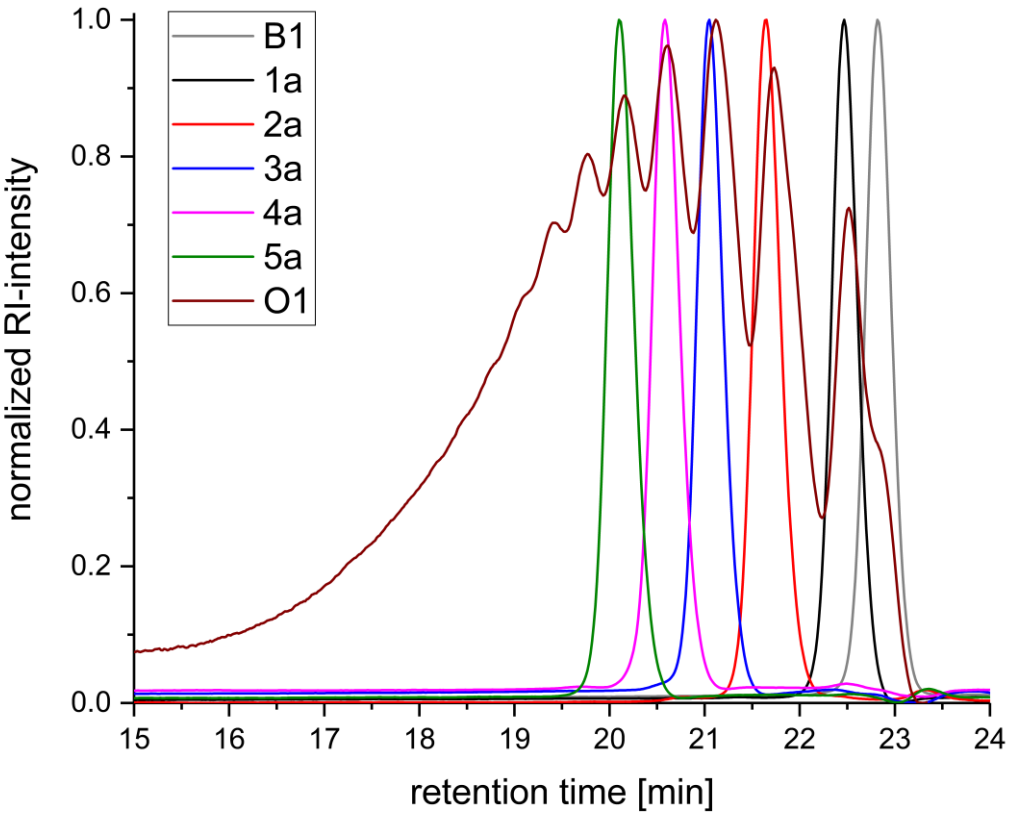


Figure 27: SEC traces of the oligomer mixture **O1** (brown) and the respective chain stopper **B1** (grey), and the protected versions of the monomer (black), dimer (red), trimer (blue), tetramer (pink) and pentamer (green).

The photophysical properties of the oligomer mixture **O1** were analyzed and compared to the respective monodisperse oligomers (Figure 28). The absorption and PL spectrum is depicted on top in brown following with pentamer **5a** (green) until the monomer **1a** (black).

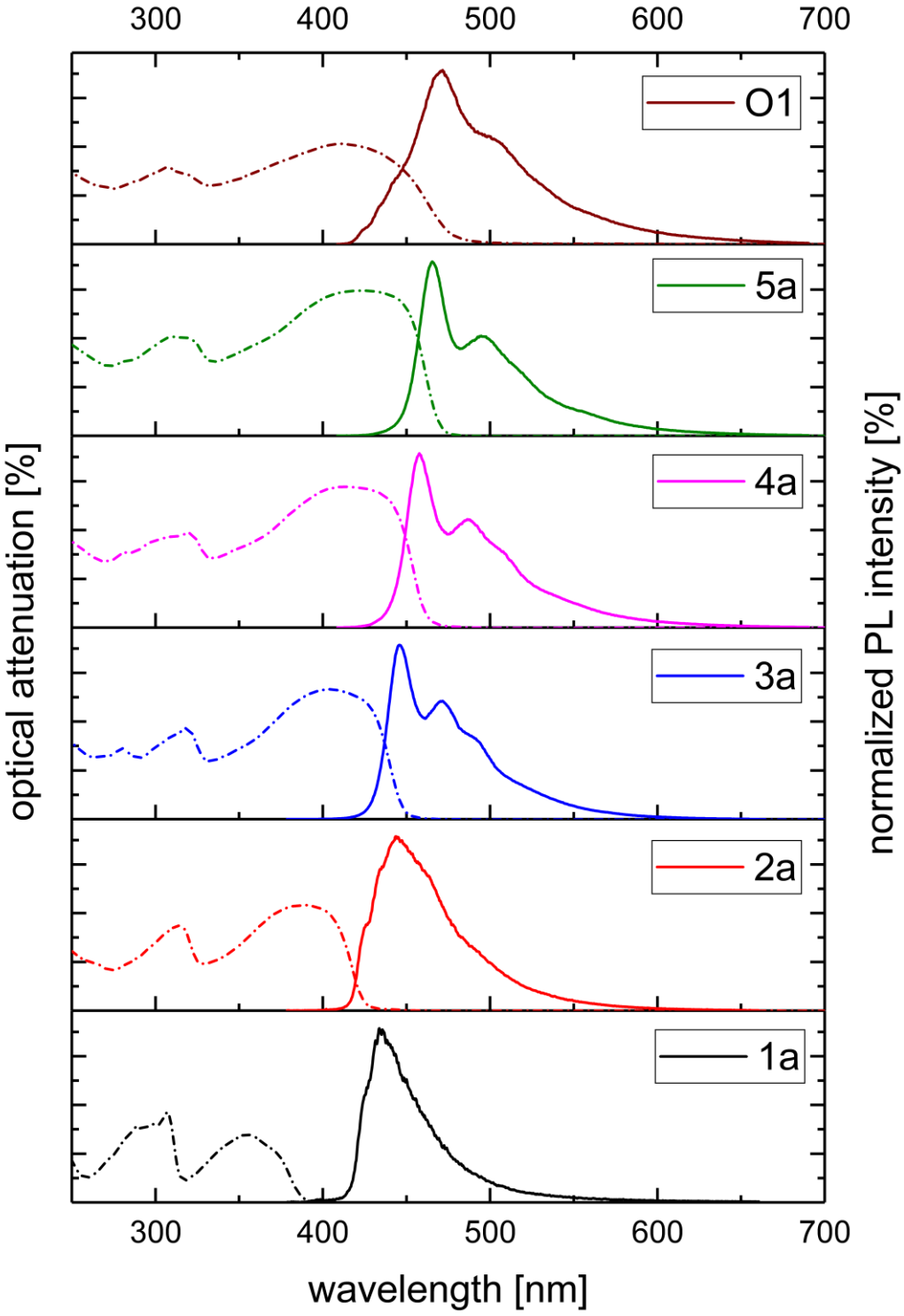


Figure 28: Absorption spectrum (dotted) and PL spectrum (bold) of **O1** (brown) in comparison to the other protected monodisperse rod-like oligomers **5a**-**1a**.

The λ_{max} of **O1** for the absorption totals to 410 nm and is located between the λ_{max} of trimer **3a** (404 nm) and tetramer **4a** (413 nm). This is in accordance with

the results obtained by SEC (Figure 27). The maximum PL intensity amounts to 472 nm and is higher than that of pentamer **5a** (465 nm). In the oligomer mixture, oligomers with a higher DP of five are present, which results in the higher λ_{max} of **O1** in the emission spectrum. The PL spectrum of **O1** is clearly broadened compared to the monodisperse representatives. It covers also the PL spectrum of the other oligomers, for instance, monomer **1a,** which is still present in the mixture **O1**.
Absorption and photoluminescence spectra can thus be used to analyses an oligomer mixture if spectra of monodisperse oligomers are available. The absorption spectrum gives a hint of the oligomer with most occurring DP and the PL spectrum of the oligomers with higher DP.

Indeed, the direct oligomerization with a chain stopper is a polycondensation reaction and not an alternative to iterative approaches to monodisperse oligomers. In this way, the complex purification by column chromatography can be justified.

4.2.3 Sequence-Defined Rod-Like Oligomers

With the optimized reaction conditions from chapter 4.2.1, an approach towards a sequence-defined pentamer was performed. The building blocks **B1**-**B5** were incorporated according to their number, *e.g.* **B1** was incorporated first, **B2** second, and so on.
The previously described monomer **1b** and building block **B2** were applied in the synthesis towards sequence-defined dimer **2c**. At position two, **2c** exhibits isopropoxy instead of propoxy side chains and compound **2c** still exhibits the same molecular weight as **2a**. The yield, however, is significantly lower for **2c** (64% in comparison to 84%). The sterically more demanding isopropoxy side chain is probably responsible for the lower conversion. Yields and scales for each reaction are depicted in Table 11. An overview of the respective SEC traces of sequence-defined rod-like oligomers is depicted in Figure 34. A COSY spectrum of **2c** is depicted in Figure 29: propoxy side chain signals are depicted with black and grey rectangles and isopropoxy signals with reddish ellipsoids. Aromatic signals do not differ from the monodisperse pentamer **5b** (Figure 21) and are not assigned. In comparison to the ^{1}H NMR of **5b**, the isopropoxy signals emerged, which are clearly distinguishable from the propoxy signals and are shifted to the

low field. Obviously, the trimethylsilyl signal around 0 ppm, can be detected, which was not apparent in the deprotected version of the pentamer **5b** (but the alkyne-hydrogen).

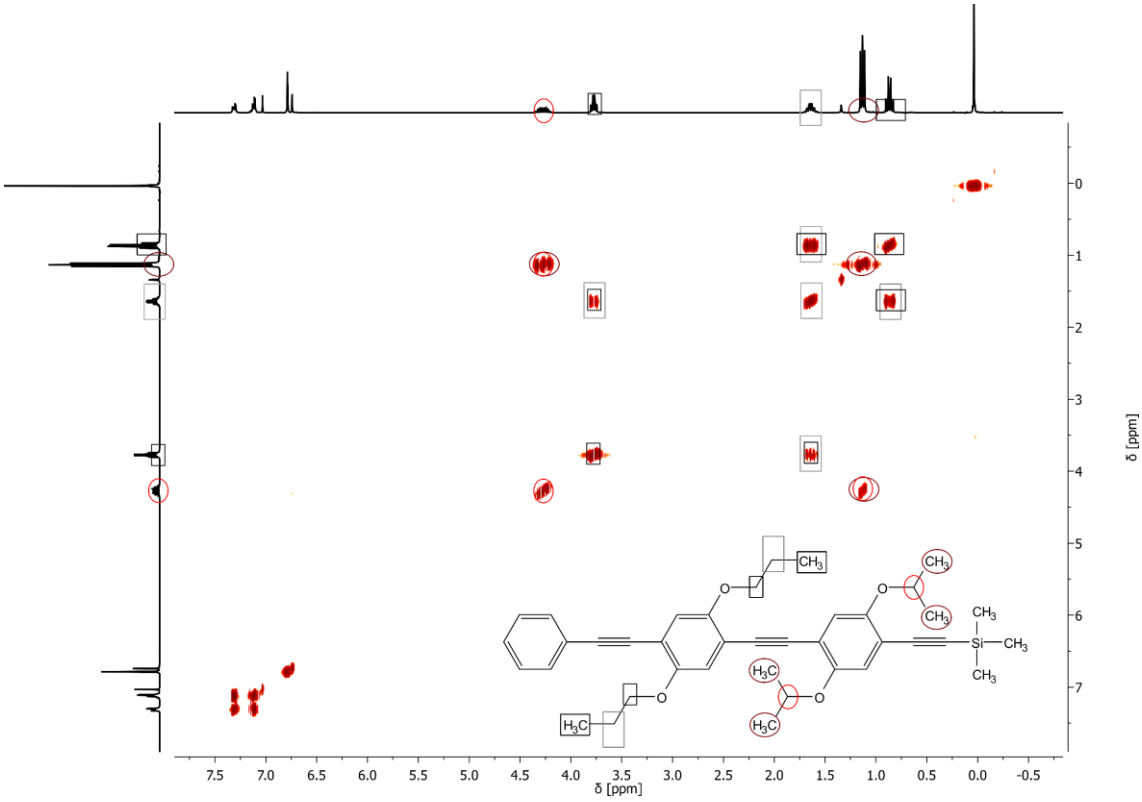


Figure 29: COSY spectrum of protected sequence-defined dimer **2c** with assigned signals for the side chains (black and grey rectangles for the propoxy and reddish ellipsoids for the isopropoxy signals).

The deprotection towards **2d** proceeded as usual in a high yield of 98% and in a scale of 688 milligrams.

The Sonogashira reaction to protected trimer **3c** with building block **B3** is even more challenging, since the cyclohexyloxy side chain is more sterically demanding. Indeed, problems occurred during the reaction. Dimer **2d** did not fully convert; neither to the respective trimer **3c** nor to the Glaser side product. The addition of further catalyst, copper iodide or triethylamine did not result in further conversion. An elevated temperature of 50 °C did not help either. Therefore, trimer **3c** was obtained after purification in a low yield of 54%; the scale amounted to 1.40 grams. The heteronuclear single quantum coherence (HSQC) spectrum (between hydrogen and carbon) of protected sequence-defined trimer **3c** is depicted in Figure 30. The protons next to the oxygen are assigned: The black labelled signal (rectangle) of the propoxy-hydrogen can be assigned as it is the

only CH_2 signal. The chemical shift δ of these protons with 4.01 ppm is still very similar to the equivalent signal of the sequence-defined dimer **2c** with δ = 4.00 ppm (Figure 29). The red labelled signal corresponds to the isopropoxy-hydrogen, as the chemical shift of the protons corresponds to 4.54 ppm compared to δ = 4.50 ppm for the same protons in the sequence-defined dimer **2c**. The signals of the isopropoxy carbons (δ = 73.14, 73.19 ppm) are similar to the propoxy carbon signals (δ = 71.23, 71.27 ppm). The cyclohexyloxy-hydrogen (δ = 4.26 ppm) is denoted with a blue triangle; the respective carbon signals exhibit a chemical shift of 77.37 and 77.89 ppm.

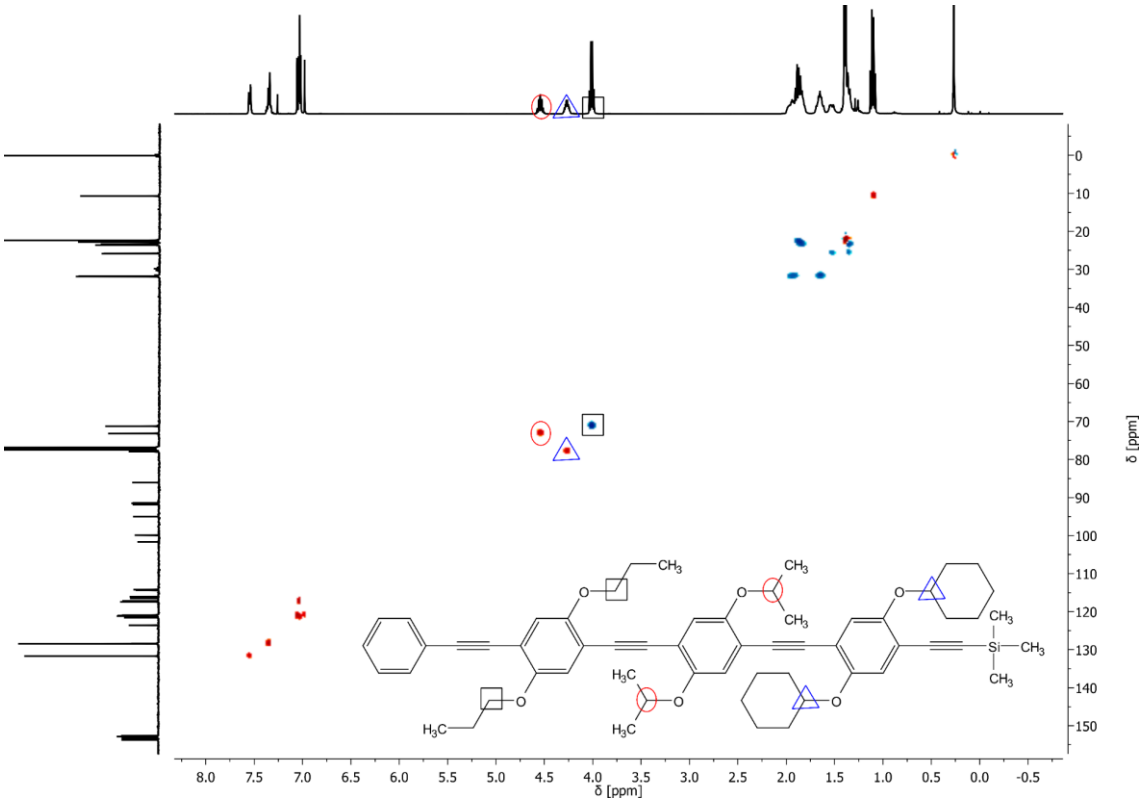


Figure 30: HSQC spectrum of protected sequence-defined trimer **3c** with assigned signals vicinal to the oxygen atom.

As usual, the deprotection resulted in a high yield of 98%, and 1.22 grams deprotected sequence-defined trimer **3d** were obtained.

For the next Sonogashira reaction to tetramer **4c**, building block **B4** with simple methoxy groups was incorporated. The incorporation of a sterically less demanding unit could increase the yield; however, the yield of **4c** was even lower than for **3c** (37% in comparison to 54%). This time, the trimer **3d** was fully converted, but a significant amount of Glaser coupled side product had formed.

The deprotected tetramer **4d** was obtained in a lower yield of 85% and in a scale of 397 milligrams. It remains unclear, why less product as usual was obtained. Probably, it results from a weighing error. Besides, copper residues might be present and lead to Glaser side product, since more copper iodide was utilized in the reaction to sequence-defined trimer **3c**.

In Figure 31, the IR spectra of **4c** and **4d** are depicted. Both spectra exhibit symmetric stretching vibrations of the CH_3 groups around 2965 cm^{-1}, asymmetric stretching vibrations of the CH_2 groups around 2930 cm^{-1} and the symmetric stretching vibrations of the CH_2 groups around 2855 cm^{-1}. The most intense signal corresponds to the aryl-alkyl ether vibration (~1200 cm^{-1}). The main difference is the C≡C-H vibration at 3280 cm^{-1} for **4d**. The protected and deprotected representatives are therefore easily distinguished by IR. Additionally, the protected version **4c** exhibits a signal at 2150 cm^{-1}, which can be assigned to C≡C vibrations and is not detectable for **4d**.

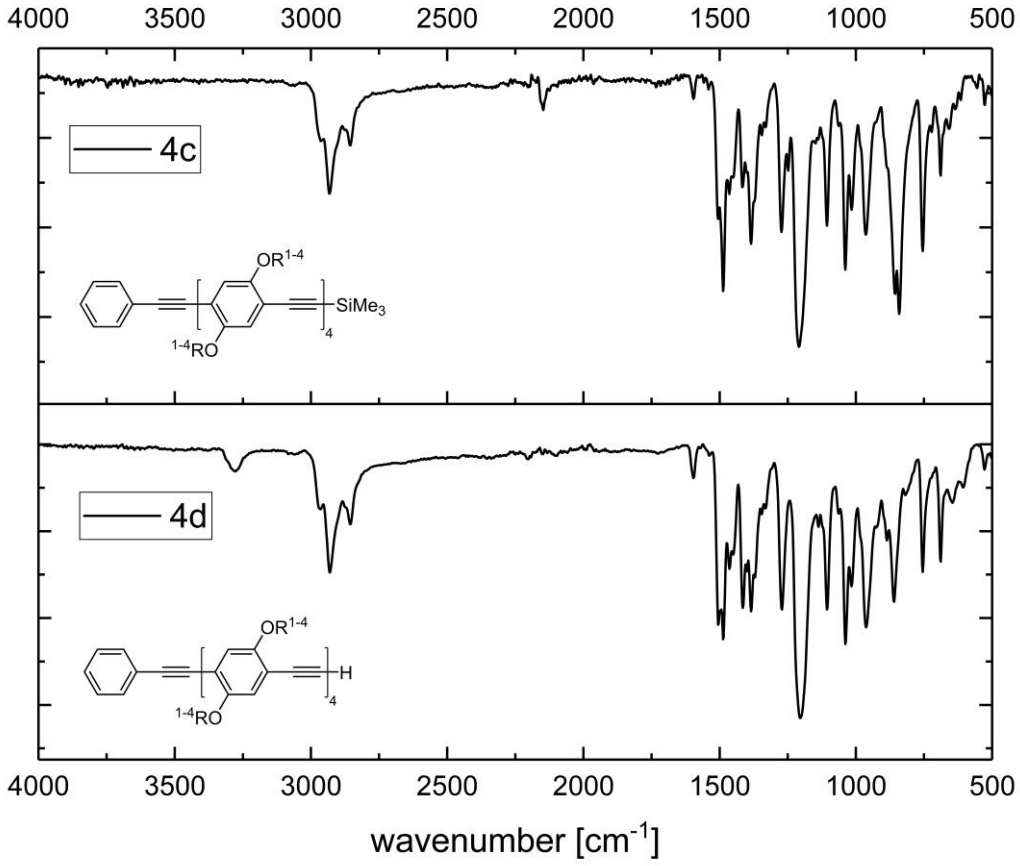


Figure 31: IR spectra of sequence-defined tetramers **4c** and **4d**.

The final Sonogashira reaction was performed with building block **B5** exhibiting octyloxy side chains and the deprotected tetramer **4c**. Although the octyloxy side chains are more flexible, the bulkiness might also have influenced the yield here. Sequence-defined pentamer **5c** was obtained with 33% (20% less than for **5a**) and in a scale of 140 milligrams. The product was also analyzed by ESI-MS; the observed isotope pattern is depicted in Figure 32. It coincides well with the calculated pattern on the right.

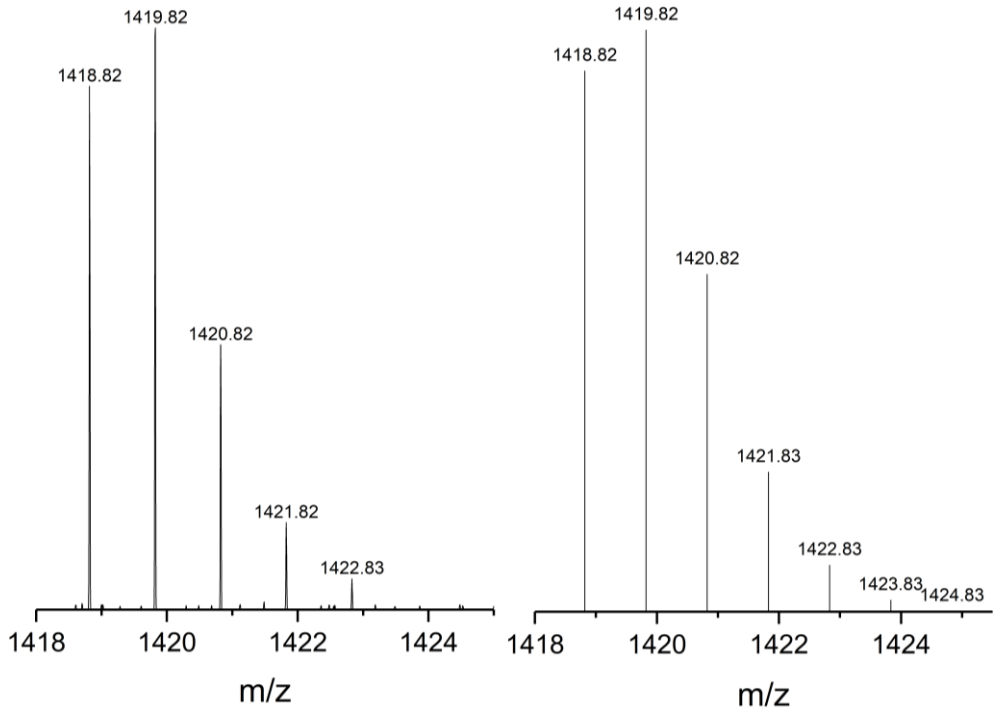


Figure 32: Isotope pattern of **5c** detected by ESI-MS (left) and calculated.

The deprotection proceeded smoothly: 73.6 milligrams sequence-defined pentamer **5d** (97%) were obtained. Figure 33 depicts the ^{1}H NMR of **5d**; the signals were assigned with the aid of the COSY spectrum, since several signals overlay. For instance, signal *m* consists of the isopropoxy CH_3 groups, some axial protons of the cyclohexyl moiety and CH_2 groups of the octyloxy side chain. As for **5b** in Figure 21, the alkyne proton signal is too small (intensity of 0.81) compared to the other signals. Nevertheless, the respective SEC trace illustrated in Figure 34 confirms the purity.

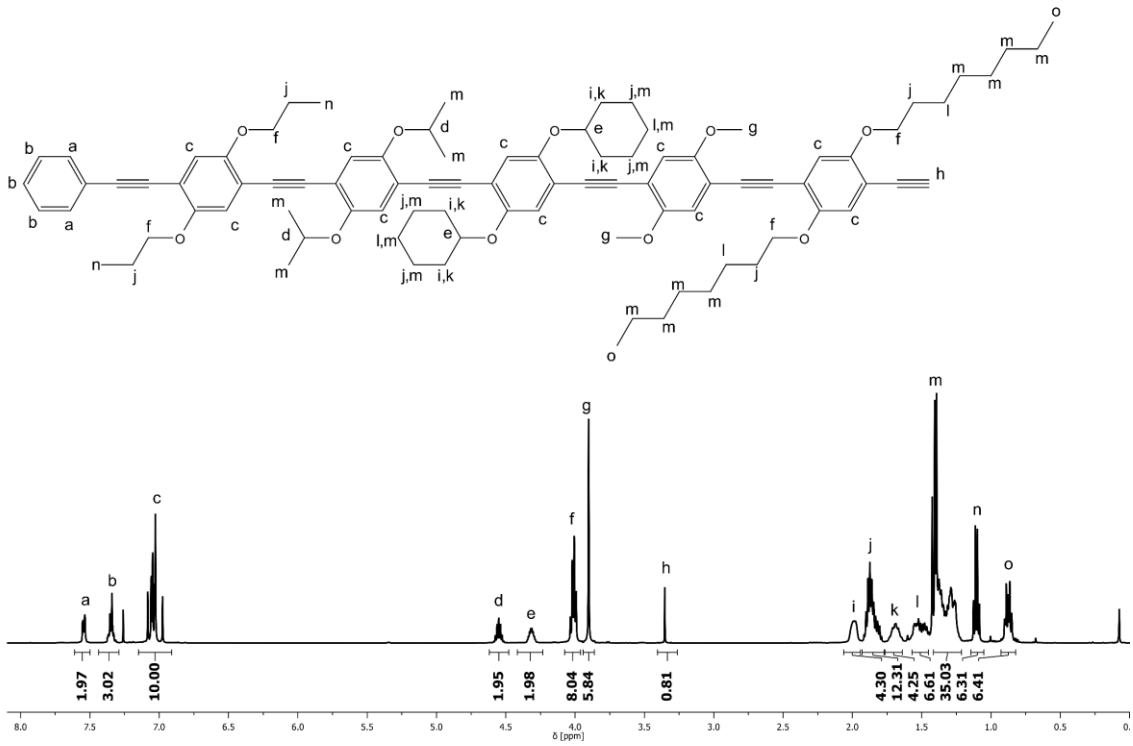


Figure 33: ^{1}H NMR of deprotected, sequence-defined pentamer **5d** with assigned signals.

The SEC traces for the monodisperse oligomers were more consistent, as the same molecular weight of 216.28 Da was added within the protected or deprotected versions of the oligomers (Figure 22). For the sequence-defined oligomers, the added molecular weight differs and so does the retention time (Figure 34). The trimer **3c** and the tetramer **4c** exhibit an inferior difference within their molecular weight as tetramer **4c** and pentamer **5c**. The same trend emerges for the retention times: pentamer **5c** elutes at a retention time of less than 18 minutes, whilst tetramer **4c** elutes around 19 minutes and trimer **3c** shortly after.

The yields are significantly lower than for the monodisperse rod-like oligomers (chapter 4.2.1). The overall yield of pentamer **5b** amounted to 18% (Table 10); for the sequence-defined pentamer **5d** an overall yield of 3.2% over ten steps is achieved. However, when comparing sequence-defined trimer **3c** with Hwang and Tour's overall yields, the overall yield of 32% is within the scope of 12-39%.[55] Especially the scale of **3c** with 1.40 grams is satisfying.

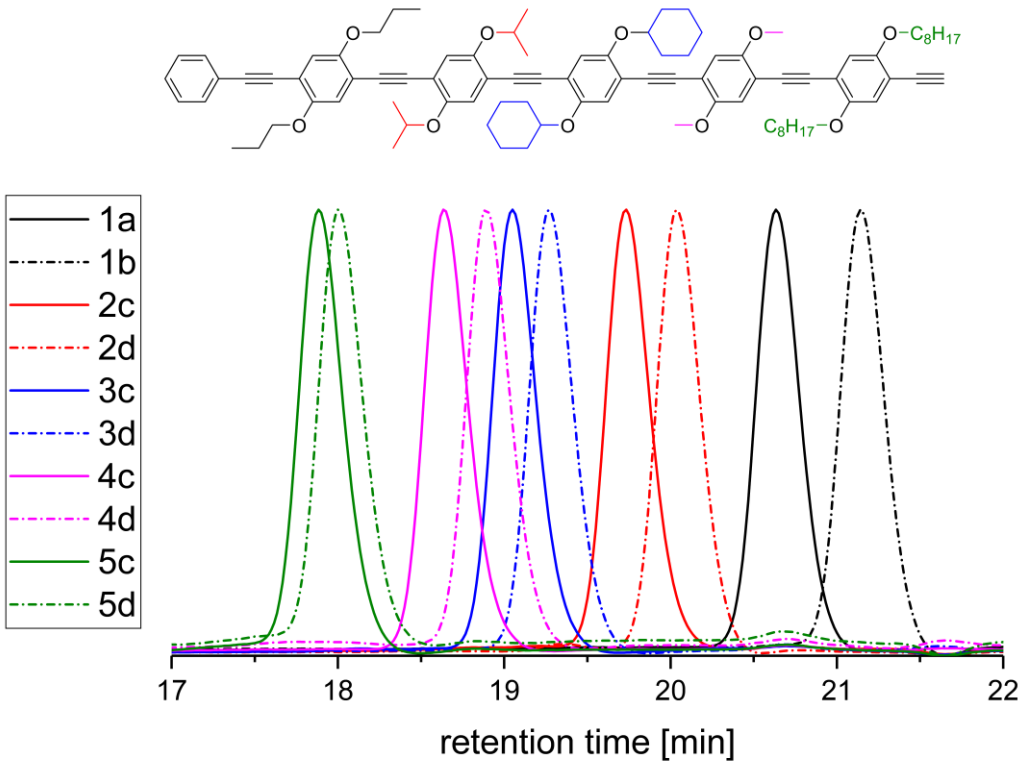


Figure 34: SEC traces of the sequence-defined oligomers. The bold line represents the protected, the dotted line the deprotected representatives.

Table 11: Overview of scales and yields for the individual reaction steps and the overall yield of the deprotected sequence-defined pentamer **5d** over all steps. Additionally, the molecular weight (MW), the melting points (T_m) and the glass transitions (T_g) are depicted.

compound	MW	T_m	T_g	scale	yield
1a	390.60	84.8 °C	-	4.63 g	99%
1b	318.42	100.5 °C	-	3.15 g	97%
2c	606.88	123.2 °C	22.9 °C	1.84 g	64%
2d	534.70	104.8 °C	23.4 °C	688 mg	98%
3c	903.29	189.2 °C	52.7 °C	1.40 g	54%
3d	831.11	-	51.3 °C	1.22 g	98%
4c	1,063.46	176.6 °C	67.7 °C	568 mg	37%
4d	991.28	160.3 °C	70.7 °C	397 mg	85%
5c	1,420.01	-	-	140 mg	33%
5d	1,347.83	-	-	73.6 mg	97%
overall					**3.2%**

Again, melting point and glass transition temperatures are depicted in Table 11. The thermal properties of the sequence-defined oligomers in comparison to the monodisperse representatives is depicted in Table 12. The protected dimer **2c** does not distinguish significantly from the monodisperse protected dimer **2a** (ΔT_m = 6.0 K, ΔT_g = 3.6 K). The T_m of **2c** is lower than **2a**, whilst the T_g is higher. The T_m of deprotected dimer **2d** is 12.2 K higher than of **2b** and also the glass transition occurs at slightly higher temperatures (ΔT_g = 5.1 K). The difference of the monodisperse to the sequence-defined dimers is not relevant so far. The sterically more demanding isopropoxy groups result in a slightly increased glass transition. Sequence-defined trimer **3c** exhibits a significant higher melting point than monodisperse trimer **3a**. Due to the bulky cyclohexyl side groups, the ΔT_m corresponds to 68.2 K and also the T_g augments to 52.7 °C compared to 34.4 °C for **3a** (ΔT_g = 16.8 K). As for **3b**, no clear melting point is observed for **3d**, the T_g is higher with 51.3 °C (ΔT_g = 12.1 K). The tetramer **4c** has a methoxy side group on position four resulting in a more similar melting point of 176.6 °C compared to 160.5 °C for **4a** (ΔT_m = 16.1 K). The glass transition is ΔT_g = 22.1 K higher for **4c**. Also, the deprotected tetramers **4b** and **4d** differ significantly (ΔT_m = 35.0 K, ΔT_g = 25.8 K). The sequence-defined pentamers do not longer exhibit a melting point and also glass transitions cannot be detected, probably a result of their regular structure, due to the different chains, preventing crystallization. When heating until 300 °C, decomposition is indicated at higher temperatures. In comparison to the monodisperse oligomers, the melting points vary less between the protected and the deprotected version (approximately 15-20 K). The melting points are usually higher for the sequence-defined representatives as the molecular weight increases. The glass transitions are also higher as the bulkiness of the side groups is higher. High rotational barriers have a significant impact on the glass transition temperature. The rotation around backbone carbon-carbon bonds is dependent on the size of the side groups. A methyl group results in a low barrier to rotation, a phenyl group increases the rotation barrier and the T_g.[228]

Glass transition temperatures of PPE are rarely reported in literature. For PPE with dimethoxy side groups and a number average molecular weight of 13,940 Da (dispersity: 3.2), a T_g of 184 °C was described.[229] Didodecyloxy side groups resulted in a T_g of -42 °C, although the number average molecular weight was not described.[230] In a more recent publication by Lendlein *et al.*, a polymer with

dual octyloxy, 2-ethylheptyloxy and methoxy side chains was described.[231] Depending on the methoxy building block content, different number average molecular weights of 4,800-9,800 Da (dispersities: 1.4-3.4) were obtained and T_g varied from 60-87 °C. This glass transition is similar to the T_g of sequence-defined tetramers **4c** and **4d** around 70 °C. The moieties of the sequence-defined oligomers (*e.g.* tetramers **4c** and **4d**) with higher DP are similar diverse as the side groups of the respective polymers described by Lendlein *et al*. Similar glass transition temperatures are therefore reasonable.

Table 12: Overview of the melting points (T_m) and glass transition temperatures (T_g) of the monodisperse and sequence-defined oligomers and their comparison (ΔT_m and ΔT_g).

	T_m	T_g		T_m	T_g	**ΔT_m**	**ΔT_g**
2a	129.2 °C	19.3 °C	**2c**	123.2 °C	22.9 °C	**6.0 K**	**3.6 K**
2b	92.6 °C	18.3 °C	**2d**	104.8 °C	23.4 °C	**12.2 K**	**5.1 K**
3a	121.0 °C	34.4 °C	**3c**	189.2 °C	52.7 °C	**68.2 K**	**16.8 K**
3b	-	39.2 °C	**3d**	-	51.3 °C	**-**	**12.1 K**
4a	160.5 °C	45.6 °C	**4c**	176.6 °C	67.7 °C	**16.1 K**	**22.1 K**
4b	125.3 °C	44.9 °C	**4d**	160.3 °C	70.7 °C	**35.0 K**	**25.8 K**
5a	186.8 °C	-	**5c**	-	-	**-**	**-**
5b	153.3 °C	49.4 °C	**5d**	-	-	**-**	**-**

For the sequence-defined oligomers, absorption and photoluminescence spectra were recorded as well (Figure 35). The wavelengths of maximum intensity for the sequence-defined and monodisperse oligomers are depicted in Table 13. The sequence-defined oligomers do not vary significantly from the monodisperse oligomers in terms of electronic properties. The different alkyl chains have a significant influence on the thermal properties, but the electronegativity does only change slightly. The λ_{max} values are therefore quite similar and do not differ more than 5 nm for the absorption and 2 nm for the emission. Dimer **2c** is similarly poor resolved as dimer **2a** (Figure 23) and might give a hint for a low dilution. For the sequence-defined dimer **2c** and the trimer **3c**, the λ_{max} value for the photoluminescence is equal to 444 nm. Presumably, the value for **3c** is more reasonable due to the possible dilution problem of **2c**.

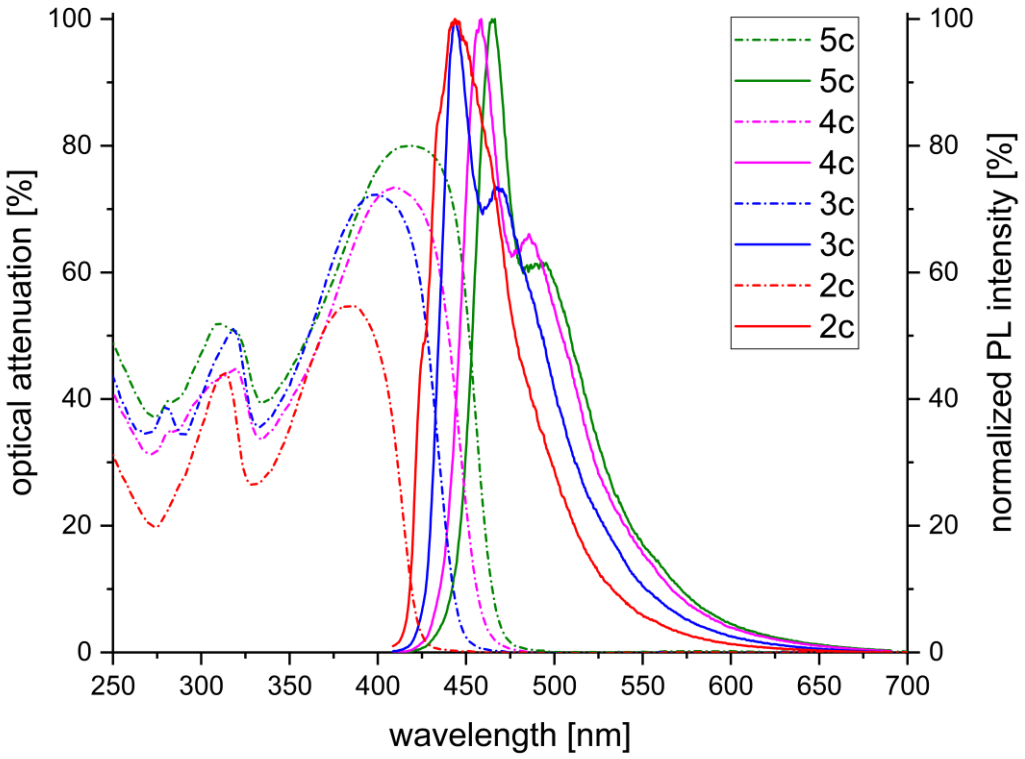


Figure 35: Absorption (dotted) and PL (bold) spectra of sequence-defined, protected oligomers **2c**-**5c**.

Table 13: Overview of maximum intensity wavelengths for absorption (A) and PL of sequence-defined in comparison to monodisperse oligomers.

compound	λ_{max} (A)	λ_{max} (PL)	compound	λ_{max} (A)	λ_{max} (PL)
2c	385 nm	444 nm	**2a**	390 nm	444 nm
3c	399 nm	444 nm	**3a**	404 nm	446 nm
4c	409 nm	459 nm	**4a**	413 nm	458 nm
5c	421 nm	466 nm	**5a**	424 nm	465 nm

The previously established synthesis procedure can be applied for other building blocks as well. However, the yields also depend on the bulkiness of the building block and its moieties. Probably, the overall yield can be improved by smart choice of the order of the building blocks. For instance, building block **B3** could be incorporated into the monomer.

Since the Glaser coupling always proceeds to some extent, the Sonogashira reaction might not be the best procedure to generate rod-like oligomers, but the alteration of reaction and deprotection is simple and target-aimed.

4.3 Conjugated Stiff Oligomers-TADF Conjugates

As described in chapter 3, the sequence-defined oligomers should be connected with a dye, which is suitable for TADF. Fabian Hundemer of the Bräse group (KIT) synthesized a molecule with TADF function based on Adachi *et al.* with an iodine moiety (compare compound **T**, Figure 36).[199] The denotation of the oligomer-TADF adducts is dependent on the DP of the connected oligomer, *e.g.* **T1** for the monomer-TADF adduct. Overall, a library of three oligomer-TADF adducts was synthesized: **T1**, **T3** and **T5** (Figure 36).

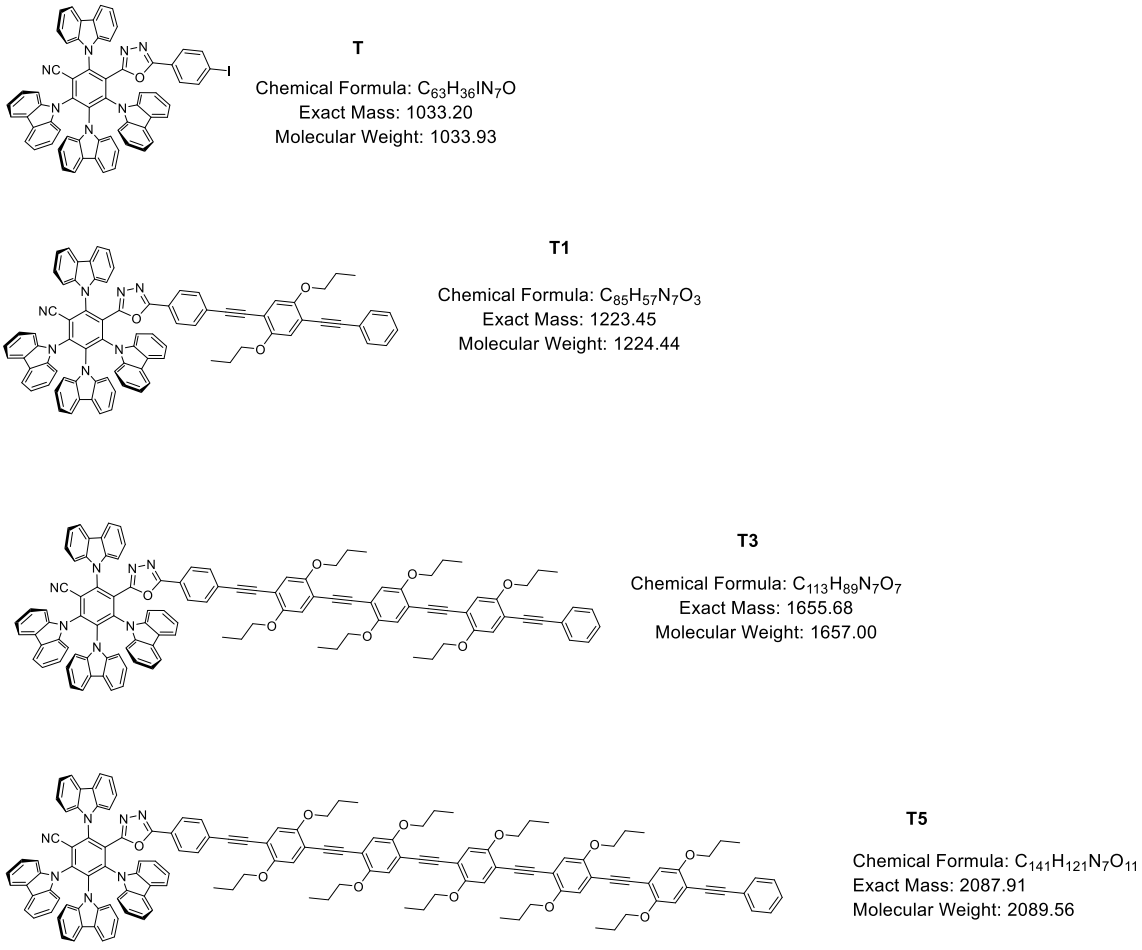


Figure 36: Overview of the synthesized TADF-conjugates **T1**, **T3** and **T5**. The initial compound **T** with TADF function was provided by Fabian Hundemer (AK Bräse).

The Sonogashira reaction of TADF molecule **T** and the deprotected monomer **1b** proceeded smoothly. The monomer **1b** was utilized in excess and the respective monomer-TADF adduct **T1** was obtained with 53.6 milligrams and a yield of 90%.

The respective SEC traces of the oligomer-TADF adducts are depicted in Figure 41. The carbon NMR is depicted in Figure 37 and the peaks were

assigned with the respective COSY, HSQC and HMBC (heteronuclear multiple bond correlation) spectra. The signals of the carbazole units are depicted with arrows in various colors. However, the exact assignment of the different carbazole units was not possible with the formerly mentioned NMR experiments.

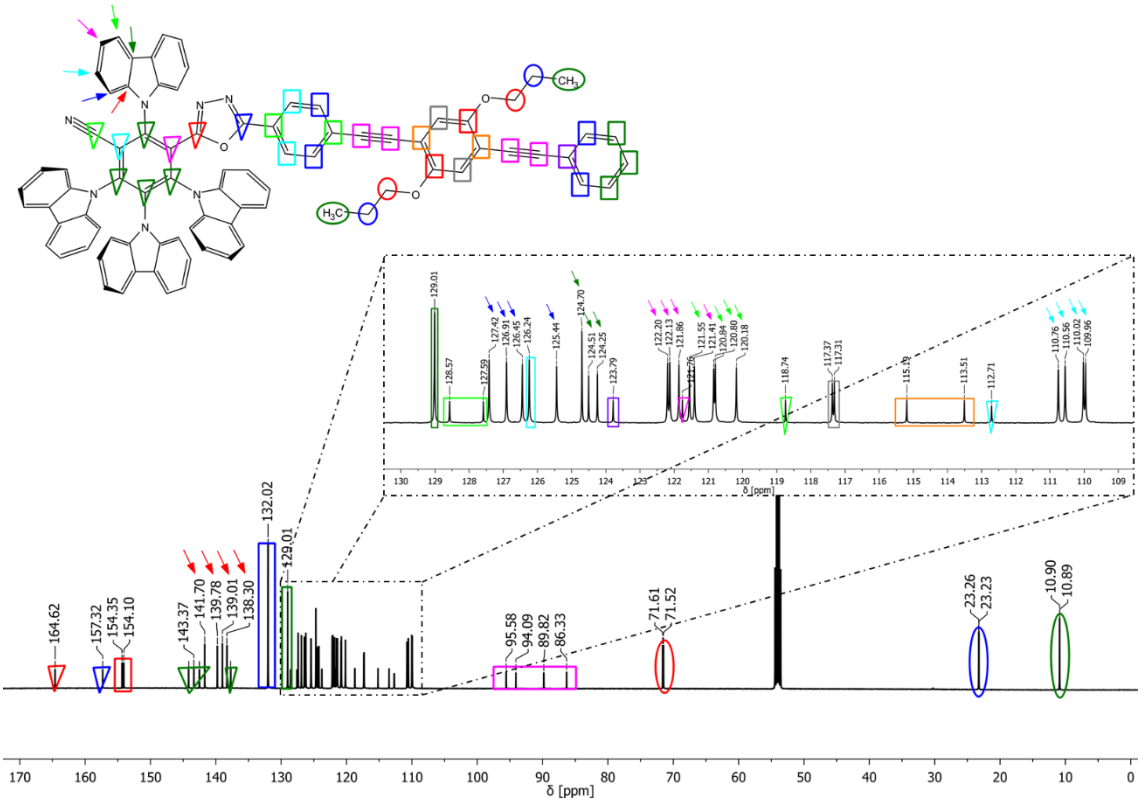


Figure 37: ^{13}C NMR spectrum of monomer-TADF adduct **T1** with assigned signals. The spectrum was recorded in dichloromethane-d_2 in order to suppress interference of the reference signals with other signals. The carbazole unit signals are assigned by arrows in various colors, further aromatic signals are either allocated with rectangles or triangles and the propoxy signals with ellipsoids.

The Sonogashira reaction of the trimer **3b** with the TADF molecule **T** was monitored after 67 h *via* SEC (compare Figure 38). The trimer **3b** was incorporated with an excess of 2 equivalents and is therefore still present in the crude mixture (blue SEC trace). The respective TADF molecule **T**, however, was completely converted (orange SEC trace). Furthermore, an extract depicting the Glaser side product of **3b** was overlaid in grey (dotted). The extract was taken from the crude SEC trace of the Sonogashira reaction to monodisperse tetramer **4a**. According to SEC, the product **T3** representing the highest peak of the black SEC trace elutes similar to the Glaser side product of **3b**. The purification by silica column chromatography yielded re-isolated **3b**

(4.5 milligrams), Glaser coupled side product (4.1 milligrams) and trimer-TADF adduct with 70.3 milligrams and 88% yield. The SEC trace of purified trimer-TADF adduct **T3** is depicted in Figure 41 without any traces of the Glaser side product.

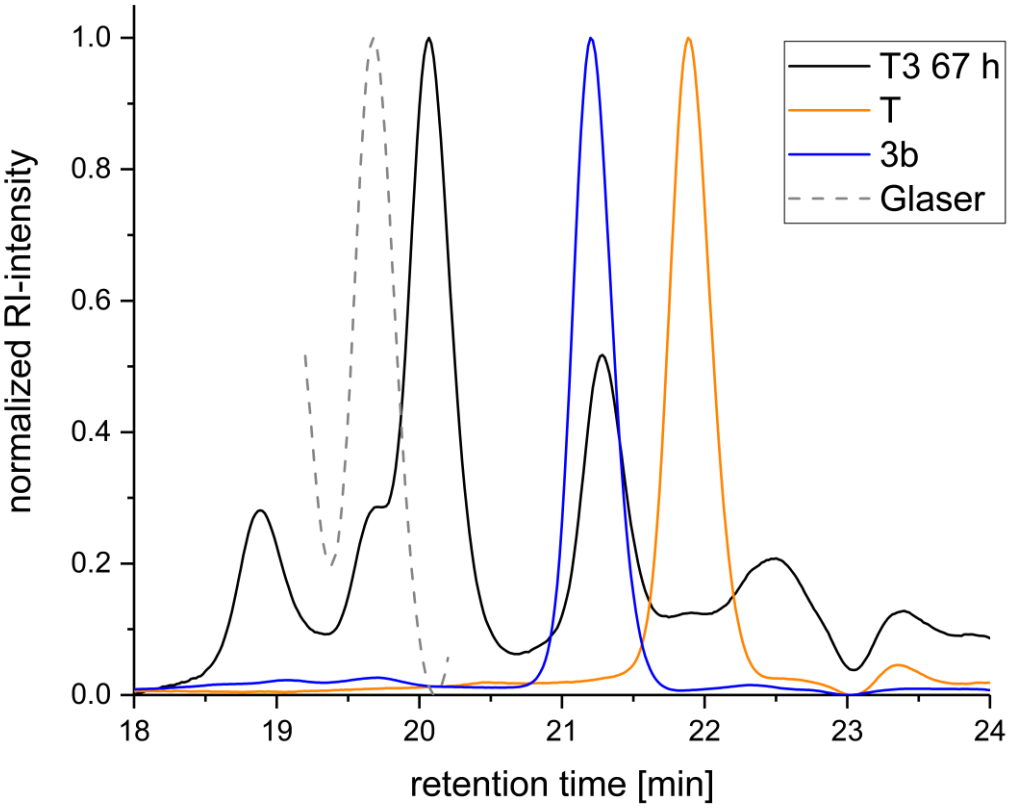


Figure 38: SEC trace of crude Trimer-TADF adduct **T3** (black) overlaid with reagent compound **T** (orange) and trimer **3b** (blue) and an extract of the Glaser side product of **3b** (grey, dotted).

The pentamer **5b** was incorporated within **T5** with an excess of 2 equivalents respectively to the TADF molecule **T**. Since SEC could not be used to check the conversion of **T5** (the device was out of order), TLC was applied. After 74 hours, TADF molecule **T** was incorporated completely and silica column chromatography was performed in order to purify the crude product. The TLC of the crude reaction mixture of **T5** is depicted in Figure 39a). Despite TLC confirmed the full conversion of **T**, a significant amount of 16.1 milligrams of **T** were obtained (first spot on TLC b): R_f = 0.69, Figure 39). Also, 31.1 milligrams of pentamer **5b** could be re-isolated (second spot on TLC b): R_f = 0.50, Figure 39). Pure dichloromethane was applied to collect pentamer-TADF adduct **T5**, but the Glaser side product of **5b** eluted simultaneously, which was later confirmed by ^{1}H NMR (third spot on TLC b): R_f = 0.34, Figure 39). TLC with

aluminium oxide as stationary phase (Figure 39c) revealed an excellent separation of **T5** and the Glaser side product with dichloromethane as mobile phase. Aluminium oxide column chromatography with pure dichloromethane yielded pure pentamer-TADF adduct **T5** with 35.5 milligrams and 35% yield.

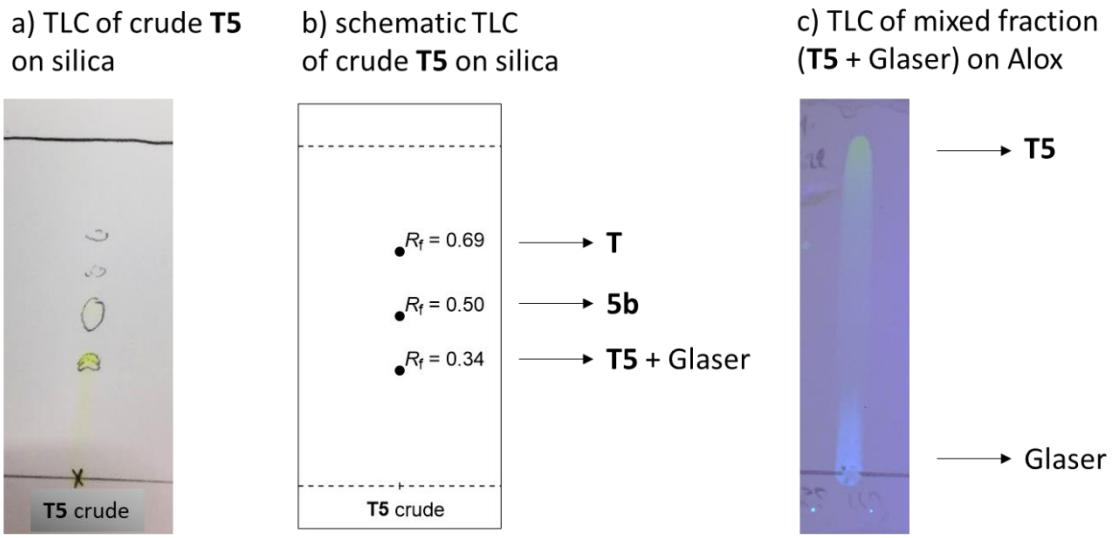


Figure 39: TLC of crude **T5**: a) original TLC with silica gel as stationary phase and dichloromethane/cyclohexane 5:1 as mobile phase. The product **T5** can be detected without UV irradiation as a yellow spot; b) schematic TLC of crude **T5** with respective retardation factor (R_f) values and their assignment to the respective molecules. The fraction with R_f = 0.34 corresponds to the mixed fraction of **T5** and the Glaser side product of **5b**; c) original TLC under UV irradiation of the formerly mentioned mixed fraction with aluminium oxide (neutral) as stationary phase and dichloromethane as mobile phase. Product **T5** exhibits a R_f close to 1.0 and emits yellow, the Glaser side product does almost not move and emits in blue.

In Figure 40, the proton NMR of pentamer-TADF adduct **T5** is depicted. The propoxy signals are assigned with ellipsoids. Since it was recorded in dichloromethane-d_2, the ratio of 51 aromatic protons compared to 30 CH_3 signals can be confirmed. Furthermore, the SEC trace on Figure 41 confirms the purity of **T5** (and the other adducts **T3** and **T1**).

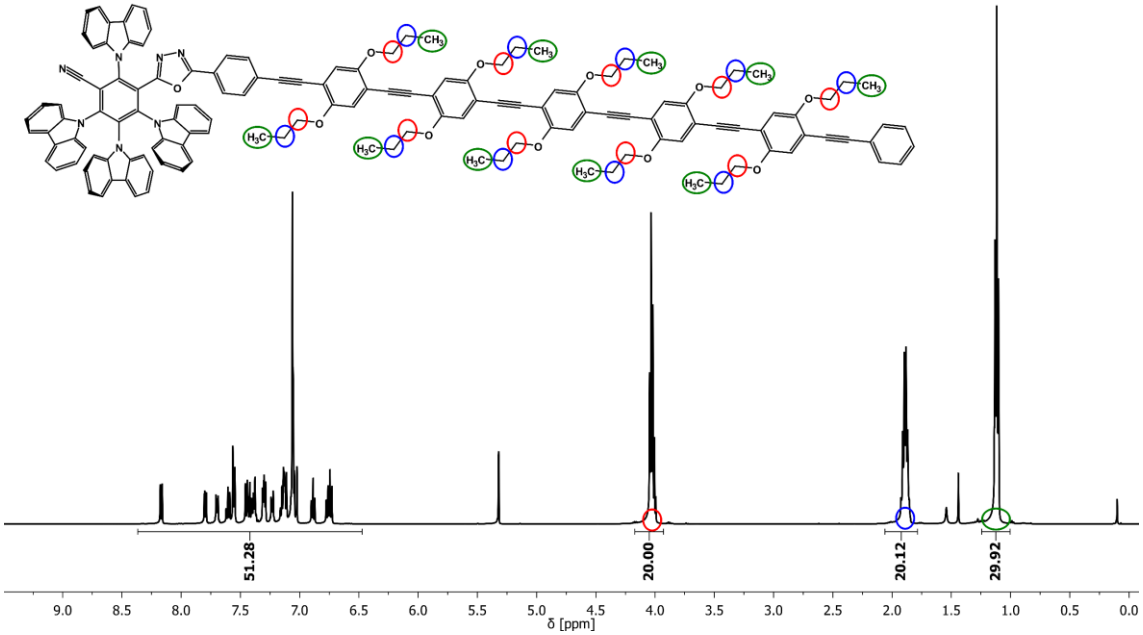


Figure 40: ^{1}H NMR of pentamer-TADF adduct **T5** with assigned propoxy signals. The spectrum was recorded in dichloromethane-d_2 in order to suppress interference of the reference signals with other signals. The intensity of the aromatic signals amounts to 51, which corresponds to 51 aromatic protons.

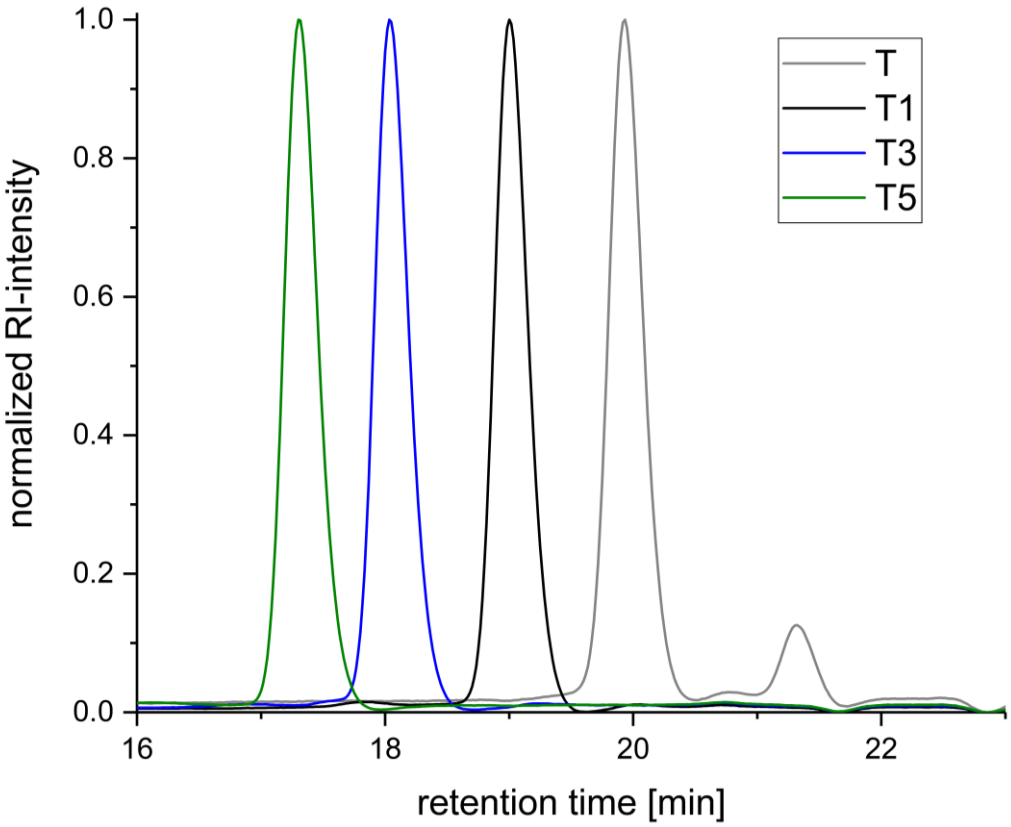


Figure 41: SEC traces of molecule **T** with TADF function (grey) and oligomer-TADF conjugates **T1** (black), **T3** (blue) and **T5** (green). The TADF molecule **T** exhibits a small impurity of 8% at a retention time of 21 min.

Currently, the HOMO-LUMO-distances of the molecules depicted in Figure 36 are calculated by Dr. Angela Bihlmeier (KIT). Furthermore, approaches to check the exciton dynamics with these first oligomer-TADF adducts are performed by the Lemmer group (KIT). So far, only donor-TADF adducts were synthesized, but with a heterofunctional TADF molecule also donor-TADF-acceptor adducts become possible. The donor-TADF adducts, however, are a first step to oligomer-dye conjugates, which can be used for investigating exciton dynamics and an important step towards the planned donor-TADF-acceptor adducts.

5. Conclusions and Outlook

Several monodisperse oligo(phenylene ethynylene)s were synthesized by various groups, especially by the group of Tour.[55,58,62,102] Apart from one example of Hwang and Tour, no iterative approaches towards sequence-defined OPEs are known to date.[55] The sequence-defined trimers **3a** and **3c** described within this work exhibit better scales and in the case of **3a** also a better overall yield. Furthermore, a linear procedure towards OPEs was never performed until the pentamer stage. Within the PhD thesis of Mathias Lang, an alternative route to sequence-defined OPEs *via* SPOS was investigated.[232] However, the synthesis procedure established within this thesis could not be transferred for SPOS and further optimizations were necessary. With the optimized synthesis strategy, a monomer with triazene moiety was obtained after cleavage in an overall yield of 60% and a scale of 6.8 milligrams. Initial approaches to synthesize a dimer were not successful yet. In comparison, the solution approach towards OPEs is matured: it was applied in a related master thesis, where a fluorene building block was specifically positioned within a trimer(phenylene ethynylene) yielding three different trimers.[224] Interestingly, the position of the fluorene unit influences the thermal and optical properties significantly.

Often, procedures to monodisperse but not sequence-defined OPEs are based on rather complicated syntheses, where Glaser coupling can be avoided. This is the case in a more recent approach by Bunz *et al.*, where a monodisperse monomer, dimer, trimer and tetramer were synthesized. However, the procedure was not iterative.[233] Therefore, it is not a suitable route towards sequence-defined OPEs and cannot be compared to Tour's procedure.

In general, defects cannot occur during the synthesis procedures, since all intermediates are subsequently purified and characterized. In polymerizations based on Sonogashira reactions, defects occur frequently.[154] Still, this synthesis procedure described herein is not ideal for obtaining OPEs. The formation of side product clearly diminishes overall yields and complicates the purification by silica column chromatography. An alternative procedure to OPEs based on other reactions is therefore favored. Possibly, a procedure based on OPVs could remedy: an elimination reaction could transfer OPVs to OPEs. In this way, other palladium catalyzed reactions such as the Heck reaction could be applied.[112] An

iodobenzene with a protected double bond can be converted with a styrene derivative, subsequent elimination and deprotection could afford a second reaction cycle. This iterative procedure would require a further step due to the elimination. If Sonogashira cross-coupling and its complicated purification and low conversion are avoided, a further step is justifiable.

For donor-TADF-acceptor adducts, an acceptor chain has to be synthesized. An acceptor chain based on benzothiadiazole building block **B6** would definitely lead to solubility problems in an elongating acceptor chain. So far, only one benzothiadiazole building block **B7** with two methyl chains is planned. However, two methyl moieties might not be enough for changing the solubility significantly. Precursor molecule **P7b** might be incorporated in a Wohl-Ziegler bromination yielding 5,6-*bis*(bromomethyl)-4,7-diiodobenzo[*c*][1,2,5]thiadiazole. In a further substitution reaction with a Grignard reagent, diether compounds can be generated.[234] The Grignard reagents can be varied and different building blocks with diverse solubilizing side chains can be synthesized. With these building blocks in hand, the synthesis of the acceptor chain should be possible. Furthermore, the acceptor chain should be connected to the TADF-donor adduct. This is not possible so far, since the molecule with TADF function only exhibits one iodine moiety. With a further azide moiety, an azide-alkyne cycloaddition with the acceptor chain should be possible. So far, the targeted incorporation of a molecule with TADF function within a polymer or oligomer was not reported. Instead, polymers with TADF function were synthesized, which were based on monomers with TADF function.[235] Also, one example of an oligomer with TADF function based on monomers without TADF function was reported.[236] However, the oligomer is not monodisperse and no targeted design with a molecule with TADF function within an oligomer is reported. These novel donor-TADF adducts are therefore interesting compounds for investigating photophysical properties.

6. Experimental Section

6.1 Materials

The following chemicals were used as received: hydroquinone (≥99%, Bayer), 1-bromopropane (99%, Fluka), 2-bromopropane (99%, TCI), bromocyclohexane (98%, Merck), 1-bromooctane (98%, TCI), potassium hydroxide (≥99.97%, Sigma Aldrich), 1,4-dimethoxybenzene (98%, Alfa Aesar), iodine (≥99.8%, VWR Chemicals), periodic acid (99%, Fisher Bioreagents), potassium metabisulfite (≥96%, Roth), *bis*(triphenylphosphine)palladium(II) dichloride (≥99%, Sigma-Aldrich), copper(I) iodide (≥99.5%, Sigma-Aldrich), trimethylsilylacetylene (98%, abcr), ammonium chloride (≥99%, BASF), 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (98%, OXCHEM), 4,5-dimethyl-1,2-phenylenediamine monohydrate (98%, abcr), thionyl chloride (99.5%, Acros), sodium iodate (99%, Alfa Aesar), sulfuric acid (95%, Sigma Aldrich), acetic acid (96%, Roth), 2,5-dibromoterephthalic acid (98%, OXCHEM), ammonium hydroxide solution (28-30% in water, Acros), phosphorus oxychloride (99%, Acros), phenylacetylene (98%, Sigma-Aldrich), potassium carbonate (≥99.5%, Evonik), anhydrous dichloromethane (≥99.8%, Sigma-Aldrich), anhydrous methanol (≥99.8%, Sigma-Aldrich), anhydrous tetrahydrofuran (≥99.9%, Sigma-Aldrich), sodium sulphate (>99%, Sigma Aldrich), toluene (99.7%, Bernd Kraft), ethanol (HPLC-grade, VWR Chemicals), methanol (HPLC-grade, VWR Chemicals), isopropanol (HPLC-grade, VWR Chemicals), dichloromethane (HPLC-grade, VWR Chemicals), dimethylformamide (HPLC-grade, VWR chemicals), 1,4-dioxane (HPLC-grade, VWR chemicals), chloroform-d (99.8 atom% D, Euriso-top), dimethylsulfoxide-d_6 (99.8 atom% D, Euriso-top), dichloromethane-d_2 (99.9 atom% D, Euriso-top).

Cyclohexane and ethyl acetate in technical grade were distilled before use. Triethylamine (≥99.5%, Roth) was dried over calcium hydride and subsequently distilled under argon.

Tetrahydrofuran in HPLC grade (≥99.7%, VWR Chemicals) was dried over sodium and subsequently distilled under argon. Benzophenone was used to indicate the abstinence of water and oxygen.

6.2 Equipment

NMR: NMR spectra were either recorded on a Bruker AVANCE DPX spectrometer operating at 300 MHz for ^{1}H- and 75 MHz for ^{13}C-measurements, on a Bruker AVANCE DRX spectrometer operating at 400 MHz for ^{1}H- and 100 MHz for ^{13}C-measurements or on a WB Bruker AVANCE I spectrometer operating at 500 MHz for ^{1}H- and 125 MHz for ^{13}C-measurement. $CDCl_3$, DMSO-d_6 and CD_2Cl_2 were used as solvents and the resonance signal serves as reference for the chemical shift δ: ^{1}H: $CDCl_3$ = 7.26 ppm, DMSO-d_6 = 2.50 ppm, CD_2Cl_2 = 5.32 ppm; ^{13}C: $CDCl_3$ = 77.16 ppm, DMSO-d_6 = 39.52 ppm, CD_2Cl_2 = 54.00 ppm.

GC-MS: GC-MS (electron impact (EI)) measurements were performed on the following system: Varian 431 GC instrument with a capillary column FactorFour VF – 5 ms (30 m × 0.25 mm × 0.25 mm) and a Varian 210 ion trap mass detector. Scans were performed from 40 to 650 m/z at a rate of 1.0 scans/s. The oven temperature was adjusted as follows: initial temperature 95 °C, hold for 1 min, ramp at 15 °C/min to 220 °C, hold for 4 min, ramp at 15 °C/min to 300 °C, hold for 2 min. The injector transfer line temperature was set to 250 °C. Measurements were performed in the split-split mode (split ratio 50:1) using helium as carrier gas (flow rate 1.0 mL/min).

DSC: Thermal properties of the prepared polymers were studied with a Mettler Toledo DSC star^{e} system operating under nitrogen atmosphere. Therefore, about 5 mg of the polymer was used for all analyses. The melting transitions were recorded on the first heating scan, the glass transitions were recorded on the second heating scan by using the following methods: Starting from = 0 °C – 200 °C (heating rate of 20 °C/min), cooling from 200 °C – 0 °C (cooling rate of 20 °C/min), isothermal segment at 0 °C for 10 min and heating from 0 °C – 200 °C (heating rate of 20 °C/min). For higher melting compounds: Starting from = 0 °C – 300 °C (heating rate of 20 °C/min), cooling from 300 °C – 0 °C (cooling rate of 20 °C/min), isothermal segment at 0 °C for 10 min and heating from 0 °C – 300 °C (heating rate of 20 °C/min).

TLC: All thin layer chromatography experiments were performed on silica gel coated aluminium foil (silica gel 60 F_{254}, Aldrich) or aluminium oxide coated

aluminium foil (aluminium oxide 60 F_{254} neutral, Aldrich). The spots of reactants and product were visualized by irradiation with UV-lamp (256 nm and 365 nm) or by staining with Seebach-solution (mixture of phosphomolybdic acid hydrate, cerium(IV)-sulphate, sulfuric acid and water).

SEC: Size exclusion chromatography was performed on a Varian 390-LC gel permeation chromatography (GPC) system equipped with a LC-290 pump (Varian), refractive index detector (24 °C), PL AS RT GPC-autosampler (Polymer laboratories) and a Varian Pro Star column oven Model 510, operating at 40 °C. For separation, two systems were used. System A consisted of two SDV 5 µm linear S columns (8 x 300 mm) and a guard column (8 x 50 mm). System B consisted of two SDA 3 µm linear S columns (8 x 300 mm) and a guard column (8 x 50 mm).

IR: Infrared spectra were recorded on a Bruker Alpha-p instrument in a frequency range from 3,997.21 to 373.94 cm^{-1} applying ATR-technology (attenuated total reflection).

Orbitrap Electrospray-Ionization Mass Spectrometry (ESI-MS): mass spectra were recorded on a Q Excative (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with an atmospheric pressure ionization source operating in the nebulizer assisted electrospray mode. The instrument was calibrated in the m/z-range 150-2,000 using premixed calibration solutions. A constant spray voltage of 3.5 kV and a dimensionless sheath gas of 6. The capillary voltage and the S-lens RF level were set to 68.0 V and 320 °C, respectively.

FAB: Fast atom bombardment mass spectra were recorded on a Finnigan MAT 95 instrument. The protonated molecular ion is expressed by the term: $[(M+H)]^+$.

Optical attenuation (relative measure for absorption): Optical attenuation was recorded on a UV/Vis spectrophotometer (LAMBDA 1050, PerkinElmer), which was additionally equipped with an integrating sphere.

Photoluminescence (PL): PL spectra were taken from a 100 µMol concentrated solution at an excitation wavelength of 355 nm and with an excitation power of 300 µW. The Photoluminescence was spectrally dissolved by a spectrometer

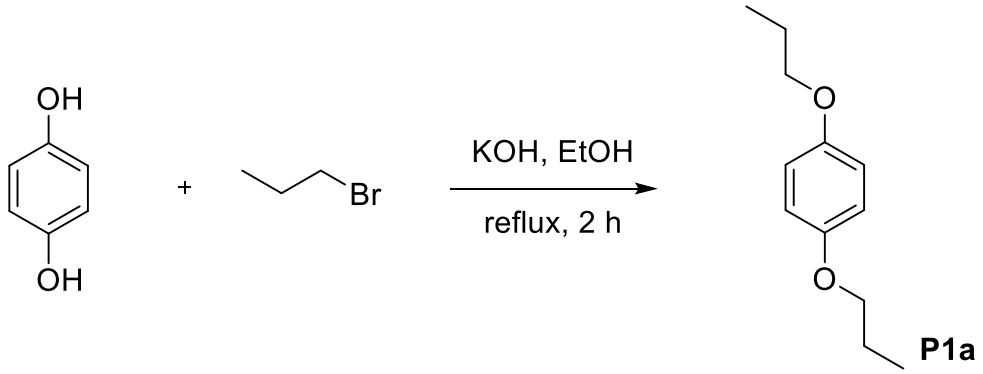
(Acton SpectraPro SP-2300, Princeton Instruments) and detected by a CCD-camera (PI-MAX4, Princeton Instruments).

6.3 Syntheses

6.3.1 Syntheses of Building Blocks with Electron Donating Properties

Synthesis of 1,4-dipropoxybenzene **P1a**

The Williamson Ether syntheses are based on a procedure published by H. Meier *et al.*[34]



Hydroquinone (30.0 g, 272 mmol, 1.00 eq.) was dissolved in 250 mL absolute ethanol. Potassium hydroxide (38.2 g, 681 mmol, 2.50 eq.) was added and the mixture was stirred for 30 minutes under reflux. Subsequently, 1-bromopropane (54.7 mL, 73.8 g, 600 mmol, 2.20 eq.) was slowly added over a 1 hour time period and stirred under reflux for another 2 hours. Ethanol was removed with a rotary evaporator and the residue was taken up in dichloromethane. The organic phase was washed with water three times and once more with saturated $NaHCO_3$ solution. It was then dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure and the crude product was recrystallized from methanol to yield colorless crystals (40.0 g, 76%). TLC (hexane/dichloromethane 9:1) R_f = 0.27; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 6.83 (d, J = 0.9 Hz, 4 H, 4 C**H**$_{aromatic}$), 3.87 (t, J = 6.6 Hz, 4 H, 2 C**H**$_2$O), 1.79 (sex, J = 7.4 Hz, 4 H, 2 C**H**$_2$CH$_3$), 1.03 (t, J = 7.4 Hz, 6 H, 2 C**H**$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 153.28, 115.41, 70.12, 22.77, 10.56; FAB of $C_{12}H_{18}O_2$ ($M+H^+$ = 195.1); HRMS (FAB) of $C_{12}H_{18}O_2$ [$M+H^+$] calc. 194.1301, found 194.1299; IR (ATR) v = 2962.6, 2935.5, 2874.7, 1504.8, 1460.9, 1391.7, 1275.2, 1218.5, 1115.5, 1068.7, 1049.5, 1025.8, 1005.1, 978.7, 824.2, 805.7, 770.2, 723.0, 531.2 cm^{-1}.

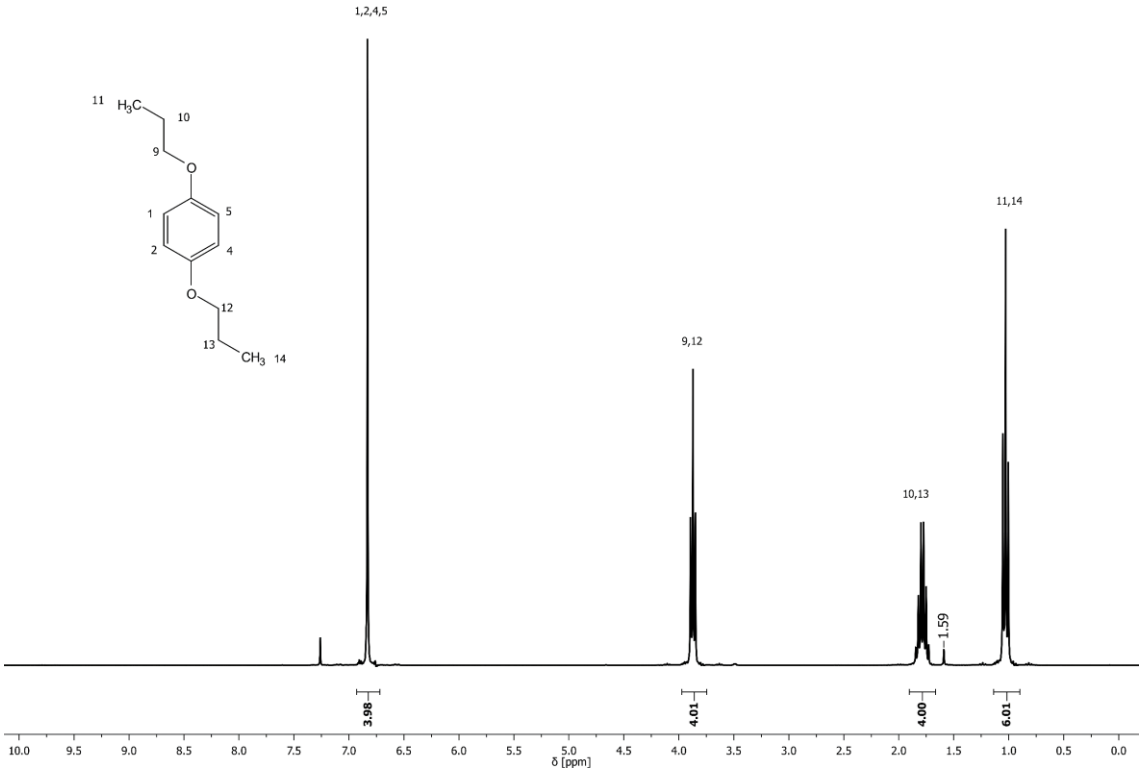
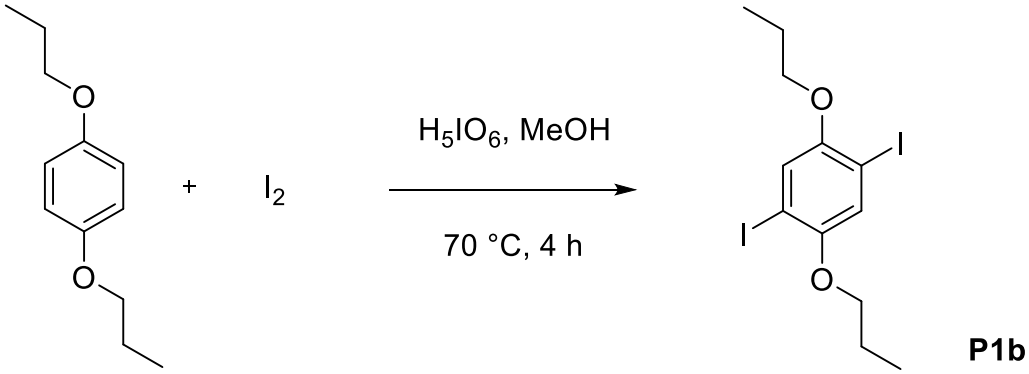


Figure 42: ^{1}H NMR spectrum of precursor **P1a** with assigned signals.

Synthesis of 1,4-diiodo-2,5-dipropoxybenzene **P1b**

The iodinations are based on a procedure published by Park *et al.*[220]



P1b

Periodic acid (3.20 g, 14.0 mmol, 0.636 eq.) was dissolved in 25 mL methanol and stirred for 10 minutes. Subsequently, iodine (6.97 g, 27.0 mmol, 1.23 eq.) was added and after an additional stirring time of 10 minutes, 1,4-dipropoxybenzene (4.27 g, 22.0 mmol, 1.00 eq.) was added. The reaction mixture was stirred at 70 °C for 4 hours. The residue was carefully poured into 50 mL water containing potassium disulphite. The precipitate was washed with methanol and dissolved in dichloromethane. The solution was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by recrystallization from methanol to yield the product as a white solid (8.20 g, 84%). TLC (hexane/dichloromethane 9:1) R_f = 0.38; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.17 (s, 2 H, 2 C**H**$_{aromatic}$), 3.90 (t, J = 6.4 Hz, 4 H, 2 C**H**$_2$O), 1.83 (sex, J = 7.4 Hz, 4 H, 2 C**H**$_2$CH$_3$), 1.07 (t, J = 7.4 Hz, 6 H, 2 C**H**$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 152.87, 122.83, 86.43, 71.88, 22.69, 10.82; FAB of $C_{12}H_{16}I_2O_2$ ($M+H^+$ = 446.9); HRMS (FAB) of $C_{12}H_{16}I_2O_2$ [$M+H^+$] calc. 445.9234, found 445.9234; IR (ATR) v = 2957.9, 2907.4, 2869.2, 1680.4, 1486.6, 1461.7, 1446.9, 1392.1, 1347.0, 1262.8, 1205.8, 1054.0, 1005.3, 909.4, 849.7, 795.2, 768.0, 621.1, 434.0, 394.9 cm^{-1}.

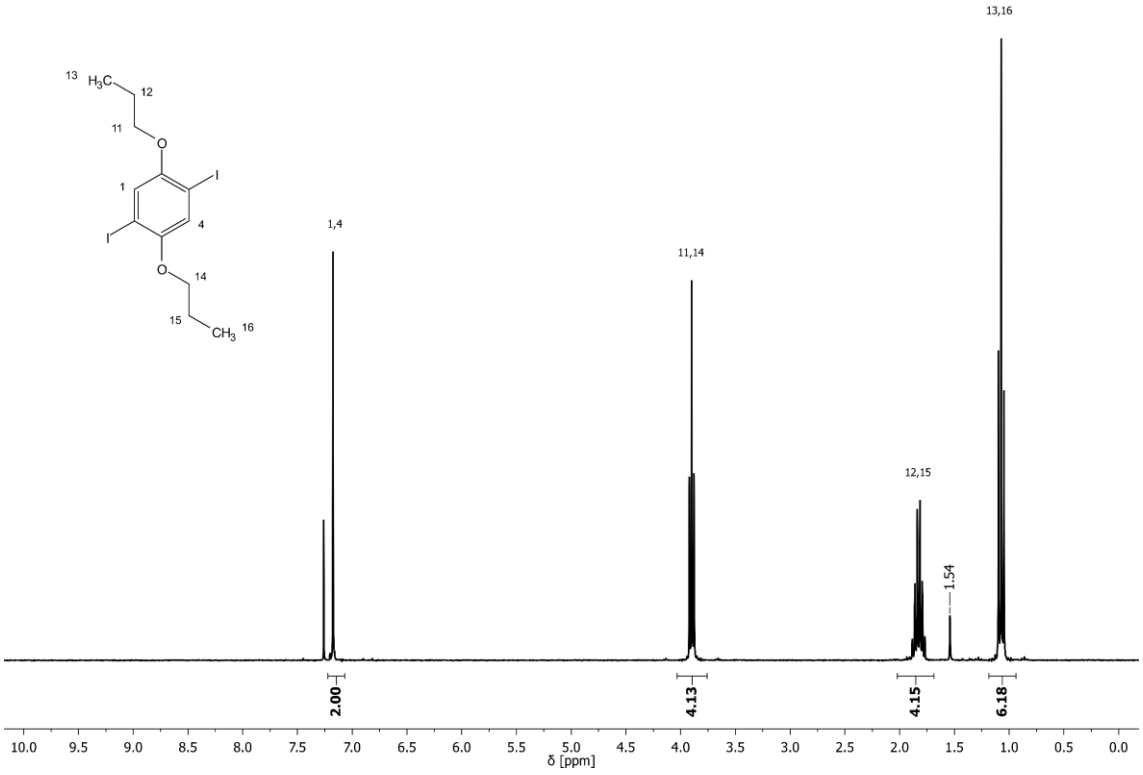
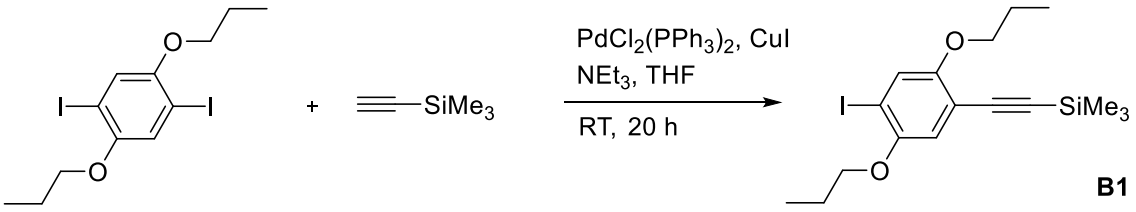


Figure 43: ^{1}H NMR spectrum of precursor **P1b** with assigned signals.

Synthesis of 1,4-*bis*(propyloxy)-2-iodo-5-trimethylsilylacetylenebenzene **B1**

The Sonogashira reactions are based on a procedure published by Tour *et al.*[221] All Sonogashira reactions were performed under continuous argon atmosphere.



1,4-Diiodo-2,5-dipropoxybenzene (10.0 g, 22.4 mmol, 1.00 eq.), 2.5 mol% *bis*(triphenylphosphine)palladium(II) dichloride (393 mg, 0.560 mmol) and 5 mol% copper(I) iodide (214 mg, 1.12 mmol) were placed into a Schlenk flask and degassed. Under continuous argon flow, 400 mL dry THF and 31.1 mL dry triethylamine were added, and the mixture was stirred for 10 minutes. Subsequently, 3.41 mL trimethylsilylacetylene (2.42 g, 24.7 mmol, 1.10 eq.) with 5 mL dry THF was added dropwise with a syringe. The reaction mixture was stirred for 20 hours at room temperature, taken up in dichloromethane and washed with saturated NH_4Cl solution. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (cyclohexane/dichloromethane 9:1) to yield the product as a yellow solid (4.26 g, 46%). TLC (hexane/dichloromethane 9:1) R_f = 0.25; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.26 (s, 1 H, 1 C**H**$_{aromatic}$Cl), 6.84 (s, 1 H, 1 C**H**$_{aromatic}$C-C≡C), 3.91 (t, J = 6.4 Hz, 4 H, 2 C**H**$_2$O), 1.65-2.00 (m, 4 H, 2 C**H**$_2$CH$_3$), 1.07 (t, J = 7.4 Hz, 6 H, 2 C**H**$_3$), 0.25 (s, 9 H, 3 CH_3Si); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 154.99, 151.81, 124.14, 116.38, 113.65, 100.91, 99.54, 88.02, 71.67, 71.45, 22.80, 22.73, 10.83, 10.60, 0.06; FAB of $C_{17}H_{25}IO_2Si$ ($M+H^+$ = 417.1); HRMS (FAB) of $C_{17}H_{25}IO_2Si$ [$M+H^+$] calc. 416.0663, found 416.0662; IR (ATR) v = 2952.6, 2872.0, 2157.4, 1498.6, 1485.5, 1456.6, 1369.2, 1288.9, 1253.9, 1244.0, 1213.8, 1162.9, 1030.7, 1014.4, 972.7, 906.2, 856.1, 833.5, 756.9, 696.3, 664.4, 636.8, 491.3, 395.9 cm^{-1}.

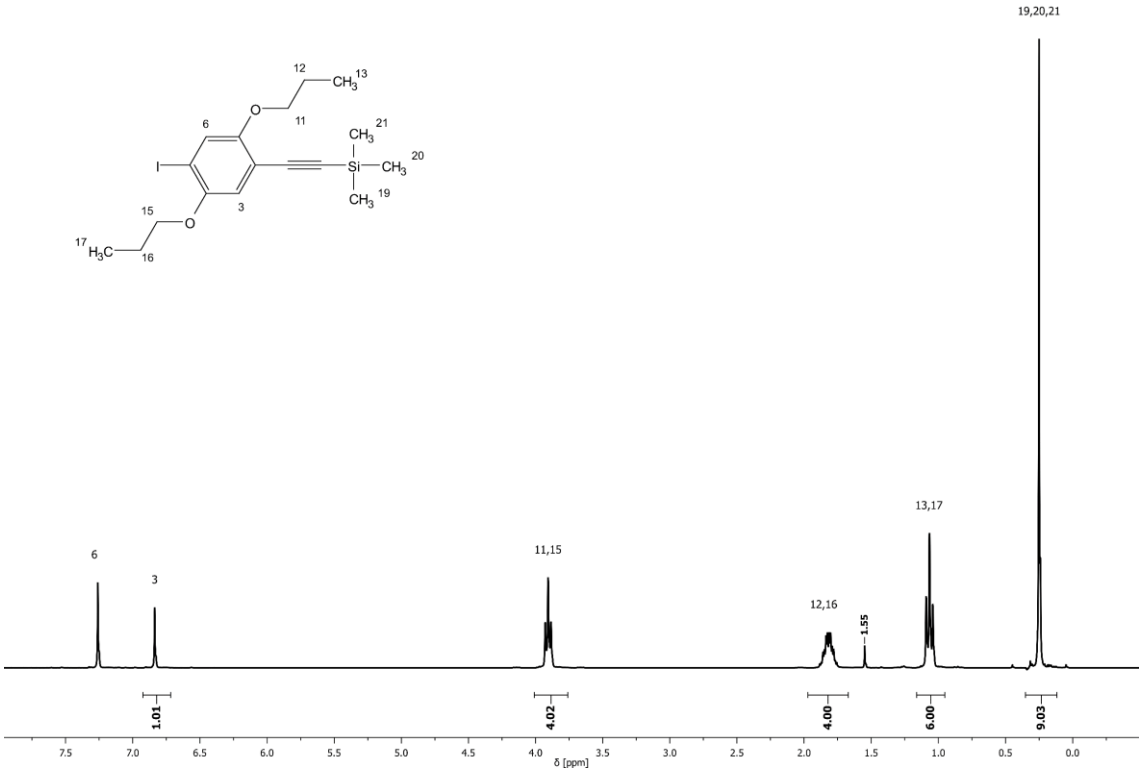
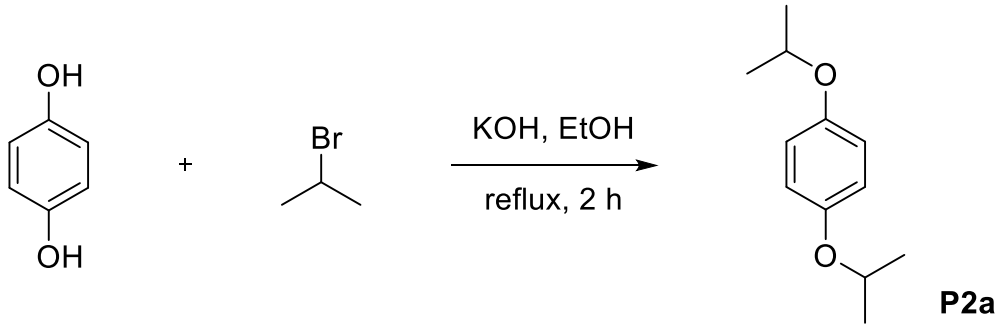


Figure 44: ^{1}H NMR spectrum of building block **B1** with assigned signals.

Synthesis of 1,4-diisopropoxybenzene **P2a**



P2a

Hydroquinone (30.0 g, 272 mmol, 1.00 eq.) was dissolved in 250 mL absolute ethanol. Potassium hydroxide (38.2 g, 681 mmol, 2.50 eq.) was added and the mixture was stirred for 30 minutes under reflux. Subsequently, 2-bromopropane (54.7 mL, 73.8 g, 600 mmol, 2.20 eq.) was slowly added over a 1 hour time period and stirred under reflux for another 2 hours. Ethanol was removed with a rotary evaporator and the residue was taken up in dichloromethane. The organic phase was washed with water three times and once more with saturated $NaHCO_3$ solution. It was then dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by silica column chromatography (cyclohexane/ethyl acetate 20:1) to yield the product as a yellow oil (40.0 g, 76%). TLC (hexane/dichloromethane 4:1) R_f = 0.26; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 6.81 (s, 4 H, 4 C**H**$_{\text{aromatic}}$), 4.42 (hept, J = 6.1 Hz, 2 H, 2 C**H**CH_3), 1.31 (d, J = 6.1 Hz, 12 H, 4 C**H**$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 152.01, 117.36, 70.77, 22.19; FAB of $C_{12}H_{18}O_2$ ($M+H^+$ = 195.1); HRMS (FAB) of $C_{12}H_{18}O_2$ [$M+H^+$] calc. 194.1301, found 194.1301; IR (ATR) v = 2972.7, 1501.5, 1382.0, 1212.3, 1113.1, 957.1, 827.9, 750.4, 527.2 cm^{-1}.

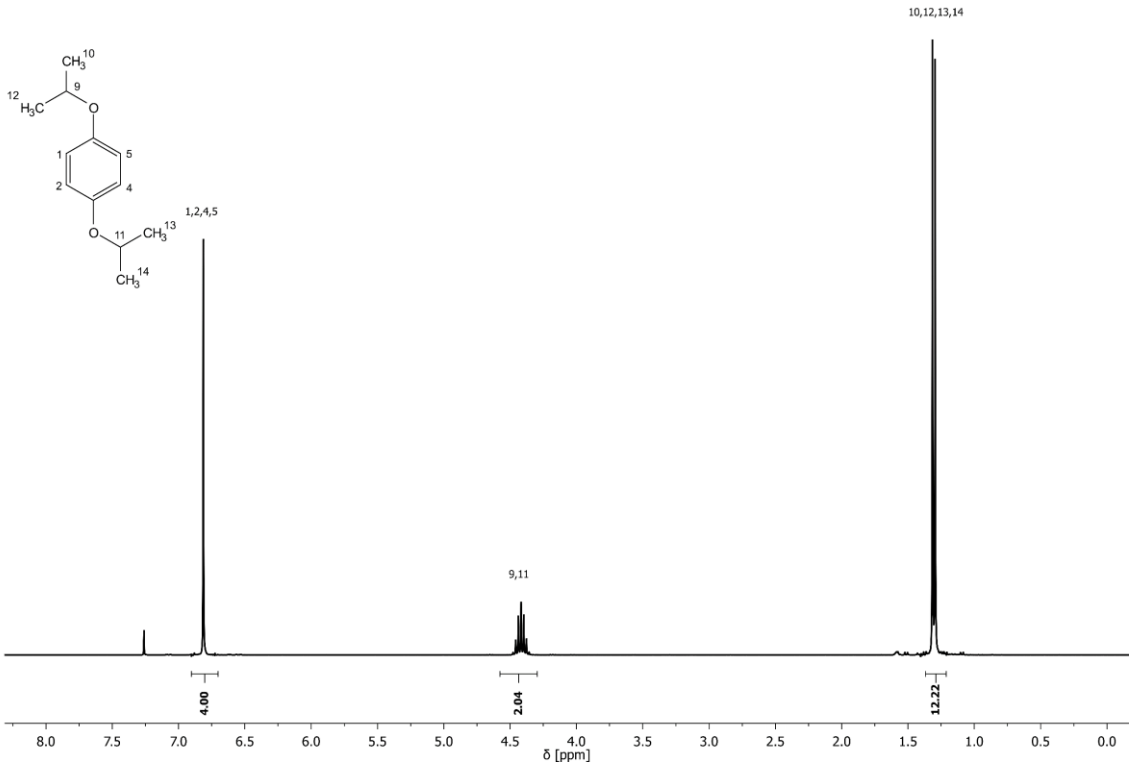
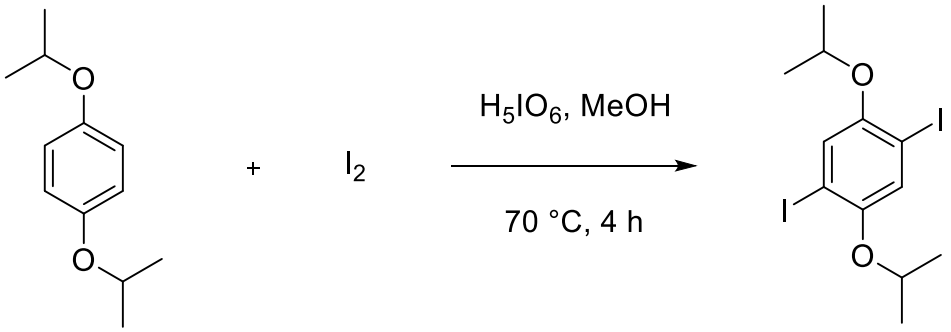


Figure 45: ^{1}H NMR spectrum of precursor **P2a** with assigned signals.

Synthesis of 1,4-diiodo-2,5-diisopropoxybenzene **P2b**



P2b

Periodic acid (6.40 g, 28.0 mmol, 0.636 mmol) was dissolved in 50 mL methanol and stirred for 10 minutes. Subsequently, iodine (13.9 g, 54.0 mmol, 1.23 mmol) was added and after an additional stirring time of 10 minutes, 1,4-diisopropoxybenzene (8.54 g, 44.0 mmol, 1.00 eq.) was added. The reaction mixture was stirred at 70 °C for 4 hours. Subsequently, the residue was carefully poured into 50 mL water containing potassium disulphite. The aqueous phase was extracted three times with dichloromethane, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product crystallized overnight and was purified by recrystallization from methanol to yield the product as a white solid (12.5 g, 64%). TLC (cyclohexane/dichloromethane 4:1) R_f = 0.43; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.21 (s, 2 H, 2 C**H**$_{\text{aromatic}}$), 4.41 (hept, J = 6.1 Hz, 2 H, 2 C**H**CH_3), 1.36 (d, J = 6.1 Hz, 12 H, 4 C**H**$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 152.25, 125.55, 88.69, 73.65, 22.24; FAB of $C_{12}H_{16}I_2O_2$ ($M+H^+$ = 446.7); HRMS (FAB) of $C_{12}H_{16}I_2O_2$ [$M+H^+$] calc. 445.9234, found 445.9233; IR (ATR) v = 2968.9, 2924.6, 1450.8, 1371.5, 1347.6, 1328.9, 1251.4, 1198.2, 1139.9, 1098.2, 1044.3, 944.2, 867.2, 854.1, 762.6, 626.3, 468.3, 423.8 cm^{-1}.

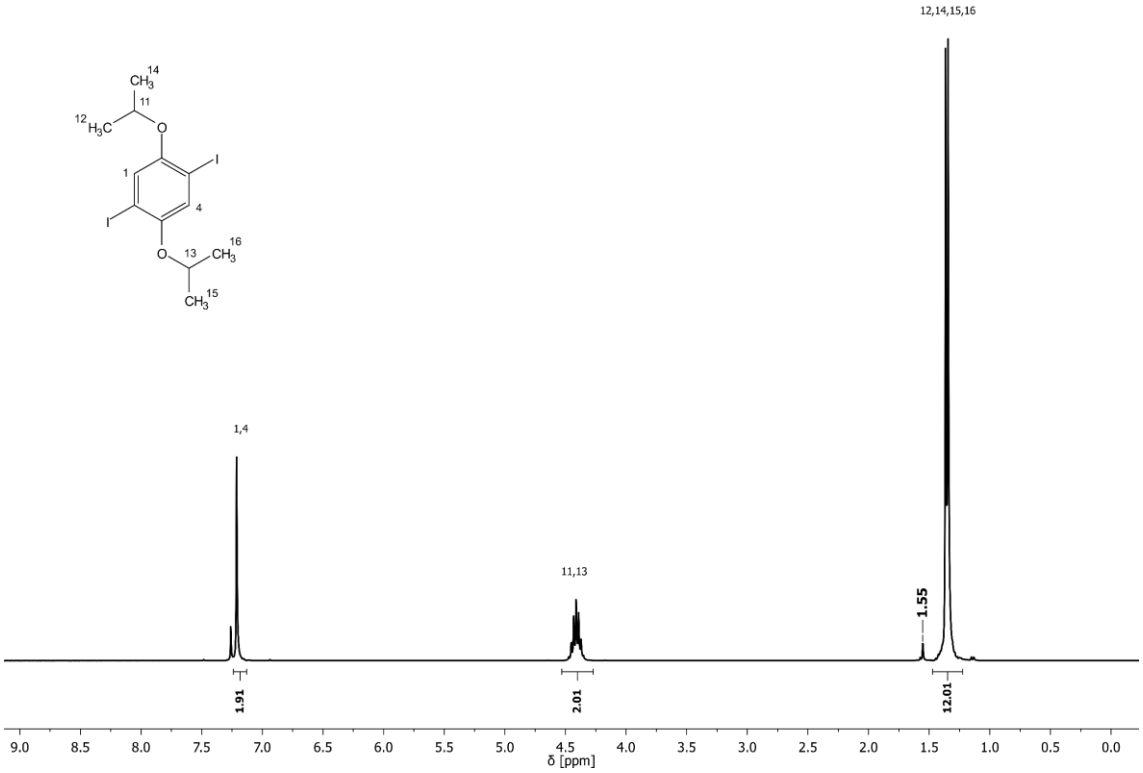
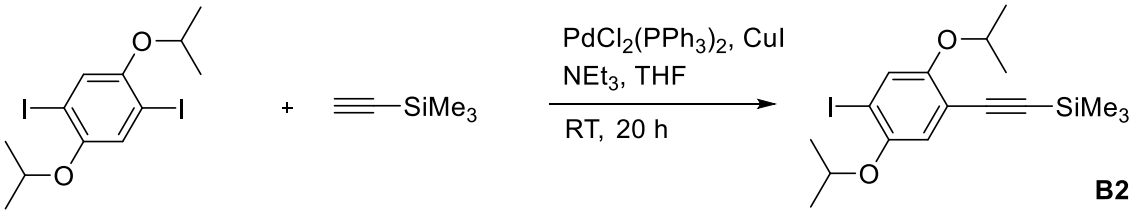


Figure 46: ^{1}H NMR spectrum of precursor **P2b** with assigned signals.

Synthesis of 1,4-*bis*(isopropyloxy)-2-iodo-5-trimethylsilylacetylenebenzene **B2**



B2

1,4-Diiodo-2,5-diisopropoxybenzene (500 mg, 1.12 mmol, 1.00 eq.), 2.5 mol% *bis*(triphenylphosphine)palladium(II) dichloride (19.7 mg, 28.0 µmol) and 5 mol% copper(I) iodide (10.7 mg, 56.0 µmol) were placed into a Schlenk flask. Under continuous argon flow, 20 mL dry THF and 1.55 mL dry triethylamine were added, and the mixture was stirred for 30 minutes. Subsequently, trimethylsilylacetylene (191 µL, 132 mg, 1.34 mmol, 1.20 eq.) in 4 mL THF was added dropwise with a syringe. The reaction mixture was stirred for 24 hours at room temperature, taken up in dichloromethane and washed with saturated NH_4Cl solution. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (cyclohexane/dichloromethane 5:1) to yield the product as a yellow liquid (165 mg, 35%). TLC (cyclohexane/dichloromethane 5:1) R_f = 0.29; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.31 (s, 1 H, 1 C**H**$_{aromatic}$Cl), 6.86 (s, 1 H, 1 C**H**$_{aromatic}$C-C≡C), 4.44 (hept, J = 6.2 Hz, 2 H, 2 C**H**CH_3), 1.34 (dd, J = 9.7, 6.1 Hz, 12 H, 4 C**H$_3$**), 0.25 (s, 9 H, 3 C**H$_3$**Si); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 154.13, 151.51, 128.55, 118.92, 115.91, 101.24, 99.37, 90.11, 73.99, 73.27, 22.31, 22.27, 0.06; FAB of $C_{17}H_{25}IO_2Si$ ($M+H^+$ = 417.0); HRMS (FAB) of $C_{17}H_{25}IO_2Si$ [$M+H^+$] calc. 416.0663, found 416.0661; IR (ATR) v = 2973.6, 2150.5, 1472.5, 1372.8, 1331.0, 1247.7, 1197.3, 1154.3, 1136.5, 1104.5, 1002.2, 944.1, 838.9, 757.9, 698.0, 661.4, 626.4, 417.4 cm^{-1}.

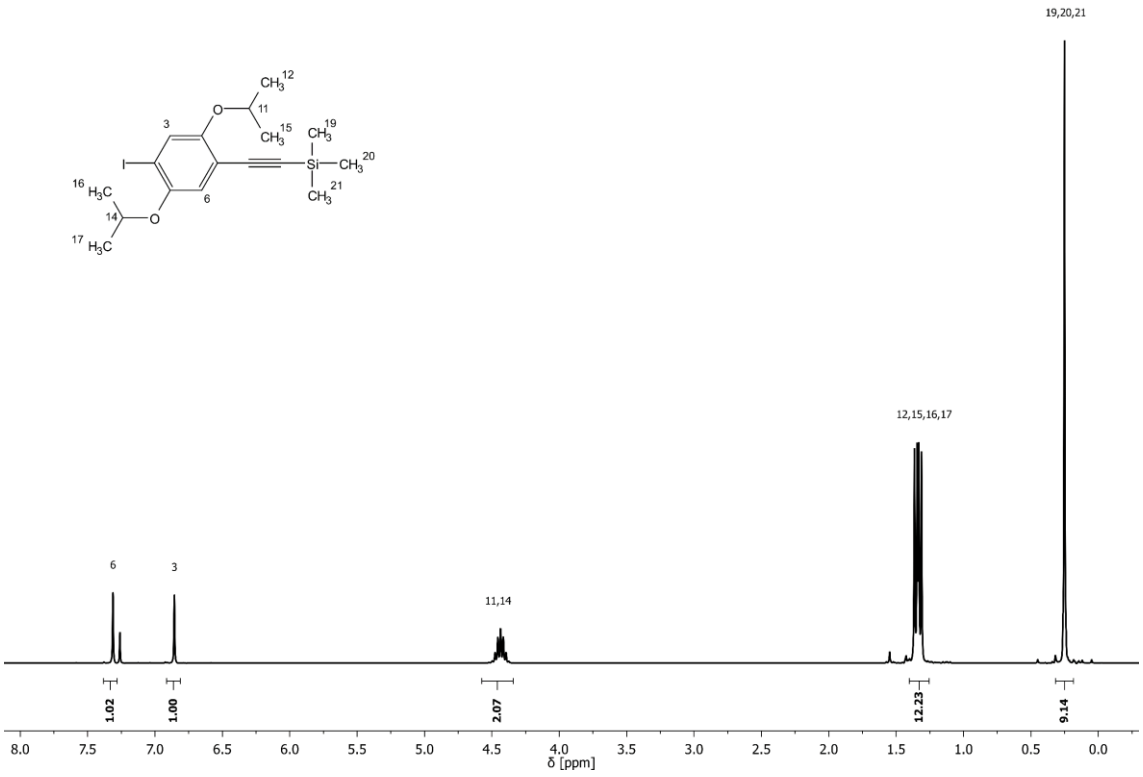
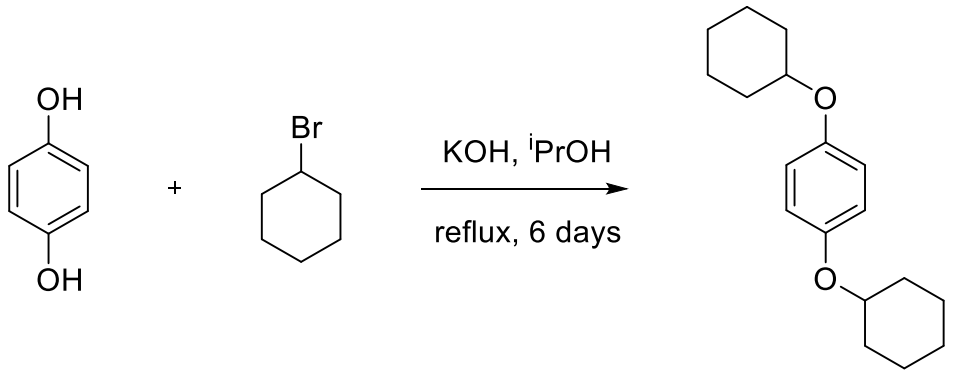


Figure 47: 1H NMR spectrum of building block **B2** with assigned signals.

Synthesis of 1,4-*bis*(cyclohexyloxy)benzene **P3a**



P3a

Hydroquinone (10.0 g, 90 8 mmol, 1.00 eq.) was dissolved in 100 mL isopropanol. Potassium hydroxide (12.7 g, 227 mmol, 1.25 eq. per hydroxy group) was added and the mixture was stirred for 30 minutes under reflux. Subsequently, bromocyclohexane (24.5 mL, 32.6 g, 200 mmol, 1.10 eq. per hydroxy group) was slowly added over a 1 hour time period and stirred under reflux for another 4 hours. The conversion was regularly monitored by GC-MS. If necessary, further potassium hydroxide (6.00 g, 107 mmol) or bromocyclohexane (12.0 mL, 15.9 g, 97.4 mmol) was added. After 6 days, the GC-MS confirmed full conversion and the isopropanol was removed with a rotary evaporator. The residue was taken up in dichloromethane, washed with water three times and once more with saturated $NaHCO_3$ solution. It was then dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure and the crude product was recrystallized from methanol to yield colorless crystals (6.21 g, 28%), TLC (cyclohexane/dichloromethane 9:1) R_f = 0.30; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 6.82 (s, 4 H, 4 C**H**$_{aromatic}$), 4.21-3.97 (m, 2 H, 2 C**H**O), 2.11-1.89 (m, 4 H, 4 C**H**$_{equatorial}$CHO), 1.89-1.68 (m, 4 H, 4 C**H**$_{equatorial}$CH$_2$CHO), 1.66-1.41 (m, 6 H, 4 C**H**$_{axial}$CHO, 2 C**H**$_{equatorial}$CH$_2$CH$_2$CHO), 1.41-1.20 (m, 6 H, 4 C**H**$_{axial}$CH$_2$CHO, 2 C**H**$_{axial}$CH$_2$CH$_2$CHO); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 151.93, 117.57, 76.56, 32.09, 25.79, 23.95; FAB of $C_{18}H_{26}O_2$ ($M+H^+$ = 275.3); HRMS (FAB) of $C_{18}H_{26}O_2$ [$M+H^+$] calc. 274.1927, found 274.1926; IR (ATR) v = 2929.3, 2852.1, 1503.0, 1454.4, 1379.7, 1357.0, 1283.6, 1256.5, 1210.7, 1148.9, 1118.2, 1089.9, 1050.9, 1019.9, 970.3, 889.1, 847.4, 829.8, 815.3, 766.5, 518.2, 470.9 cm^{-1}.

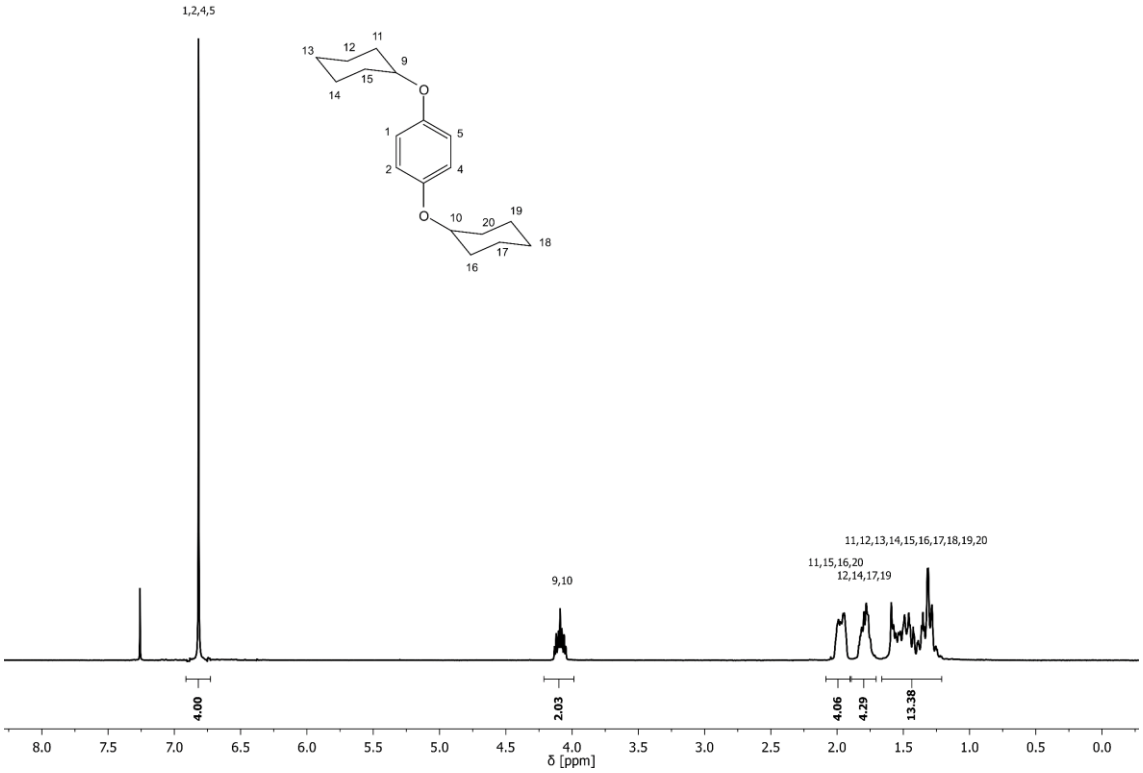
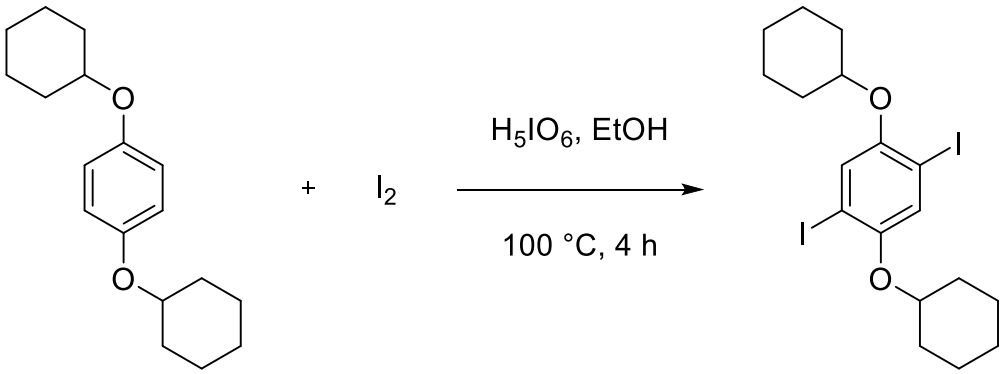


Figure 48: ^{1}H NMR spectrum of precursor **P3a** with assigned signals.

Synthesis of ((2,5-diiodo-1,4-phenylene)*bis*(oxy))dicyclohexane **P3b**



P3b

Periodic acid (1.69 g, 7.42 mmol, 0.636 eq.) was dissolved in 25 mL ethanol and stirred for 10 minutes. Subsequently, iodine (3.64 g, 14.3 mmol, 1.23 mmol) was added and after an additional stirring time of 10 minutes 1,4-*bis*(cyclohexyloxy)benzene (3.20 g, 11.7 mmol, 1.00 eq.) was added. The reaction mixture was stirred at 100 °C for 4 hours. The residue was carefully poured into 50 mL water containing potassium disulphite. The precipitate was washed with ethanol and dissolved in dichloromethane. The solution was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by recrystallization from ethanol to yield the product as a white solid (4.56 g, 74%). TLC (cyclohexane/dichloromethane 9:1) R_f = 0.64; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.20 (s, 2 H, 2 C**H**$_{\text{aromatic}}$), 4.29-4.07 (m, 2 H, 2 C**H**O), 2.03-1.72 (m, 8 H, 4 C**H**$_{\text{equatorial}}$CHO, 4 C**H**$_{\text{equatorial}}$CH$_2$CHO), 1.72-1.57 (m, 4 H, 4 C**H**$_{\text{axial}}$CHO), 1.57-1.47 (m, 2 H, 2 C**H**$_{\text{equatorial}}$CH$_2$CH$_2$CHO), 1.47-1.21 (m, 6 H, 4 C**H**$_{\text{axial}}$CH$_2$CHO, 2 C**H**$_{\text{axial}}$CH$_2$CH$_2$CHO); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 151.85, 125.27, 88.48, 78.09, 31.59, 25.68, 23.39; FAB of $C_{18}H_{24}I_2O_2$ ($M+H^+$ = 526.3); HRMS (FAB) of $C_{18}H_{24}I_2O_2$ [$M+H^+$] calc. 525.9860, found 525.9861; IR (ATR) v = 2925.5, 2845.8, 1472.2, 1452.6, 1364.2, 1342.1, 1315.5, 1259.3, 1234.7, 1200.3, 1153.7, 1120.2, 1047.1, 1024.2, 949.6, 864.0, 852.0, 802.8, 781.4, 650.6, 614.9, 501.5, 480.7, 451.7, 431.9 cm^{-1}.

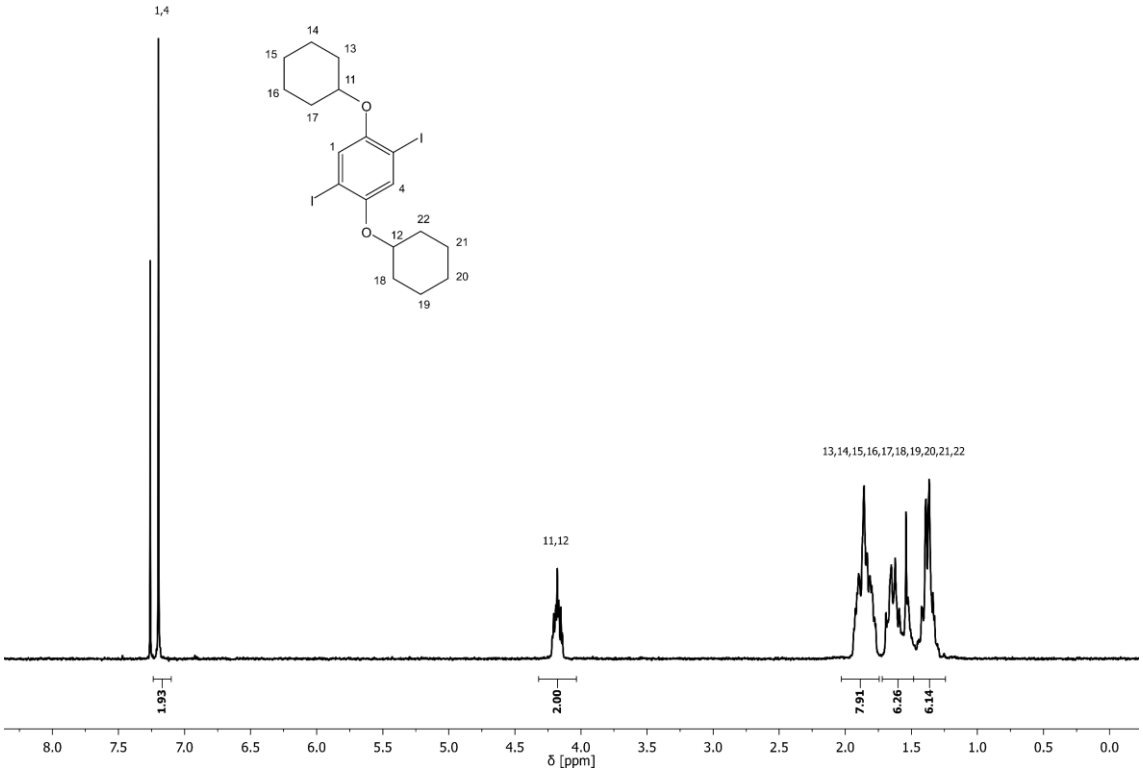
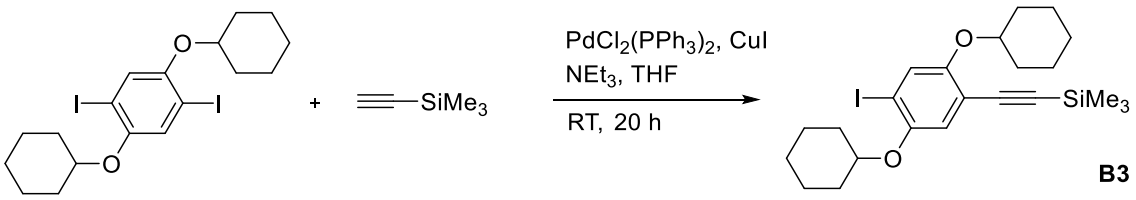


Figure 49: ^{1}H NMR spectrum of precursor **P3b** with assigned signals.

Synthesis of ((2,5-*bis*(cyclohexyloxy)-4-iodophenyl)ethynyl)trimethylsilane **B3**



B3

((2,5-Diiodo-1,4-phenylene)*bis*(oxy))dicyclohexane (3.50 g, 6.65 mmol, 1.00 eq.), 2.5 mol% *bis*(triphenylphosphine)palladium(II) dichloride (117 mg, 0.166 mmol) and 5 mol% copper(I) iodide (63.3 mg, 0.333 mmol) were placed into a Schlenk flask and degassed. Under continuous argon flow, 140 mL dry THF and 9.22 mL dry triethylamine were added, and the mixture was stirred for 10 minutes. Subsequently, 1.04 mL trimethylsilylacetylene (719 mg, 7.32 mmol, 1.10 eq.) with 5 mL dry THF were added dropwise with a syringe. The reaction mixture was stirred for 20 hours at room temperature, taken up in dichloromethane and washed with saturated NH_4Cl solution. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (cyclohexane/ dichloromethane 9:1) to yield the product as a yellow solid (1.40 g, 42%). TLC (cyclohexane/ dichloromethane 9:1) R_f = 0.50; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.31 (s, 1 H, 1 C**H**$_{aromatic}$Cl), 6.85 (s, 1 H, 1 C**H**$_{aromatic}$C-C≡C), 4.30-4.11 (m, 2 H, 2 CHO), 2.05–1.74 (m, 8 H, 4 C**H**$_{equatorial}$CHO, 4 C**H**$_{equatorial}$$CH_2$CHO), 1.74–1.48 (m, 6 H, 4 C**H**$_{axial}$CHO, 2 C**H**$_{equatorial}$$CH_2CH_2$CHO), 1.43–1.18 (m, 6 H, 4 C**H**$_{axial}$$CH_2$CHO, 2 C**H**$_{axial}$$CH_2CH_2$CHO), 0.25 (s, 9 H, 3 C**H**$_3$Si); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 153.71, 150.94, 128.10, 118.39, 115.61, 101.30, 98.97, 89.90, 77.90, 77.48, 31.56, 31.50, 25.70, 25.63, 23.27, 23.05, -0.03; FAB of $C_{23}H_{33}IO_2Si$ ($M+H^+$ = 497.2); HRMS (FAB) of $C_{23}H_{33}IO_2Si$ [$M+H^+$] calc. 496.1295, found 496.1294; IR (ATR) v = 2931.5, 2855.3, 2154.5, 1470.9, 1365.1, 1247.3, 1196.5, 1158.6, 1123.6, 1039.8, 1018.4, 960.9, 837.9, 757.7, 698.2, 671.6, 645.2, 481.4 cm^{-1}.

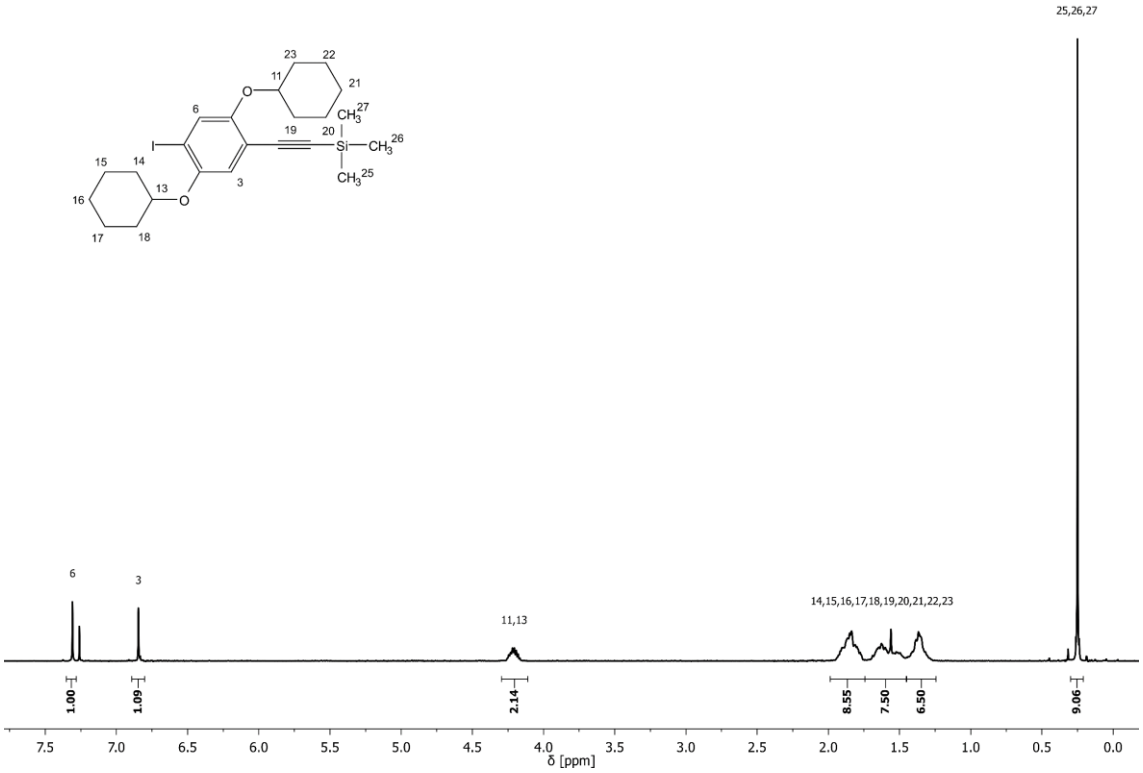
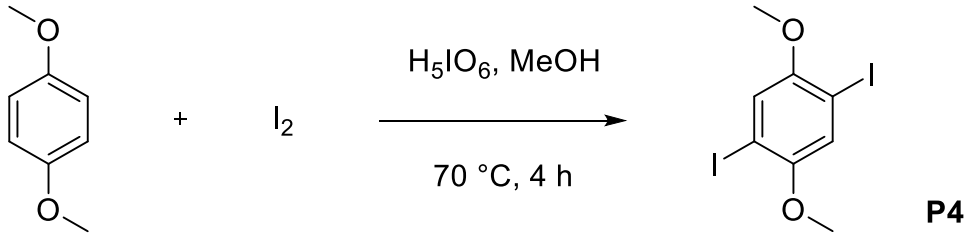


Figure 50: 1H NMR spectrum of building block **B3** with assigned signals.

Synthesis of 1,4-diiodo-2,5-dimethoxybenzene **P4**



P4

Periodic acid (3.20 g, 14.0 mmol, 0.636 eq.) was dissolved in 25 mL methanol and stirred for 10 minutes. Subsequently, iodine (6.97 g, 27.0 mmol, 1.23 eq.) was added and after an additional stirring time of 10 minutes 1,4-dimethoxybenzene (3.04 g, 22.0 mmol, 1.00 eq.) was added. The reaction mixture was stirred at 70 °C for 4 hours. The residue was carefully poured into 50 mL water containing potassium disulfite. The precipitate was washed with methanol and dissolved in dichloromethane. The solution was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by recrystallization from methanol to yield the product as a white solid (7.90 g, 92%). TLC (cyclohexane/dichloromethane 4:1) R_f = 0.48; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.19 (s, 2 H, 2 C**H**$_{\text{aromatic}}$), 3.83 (s, 6 H, 2 C**H**$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 153.47, 121.76, 85.61, 57.33; FAB of $C_8H_8I_2O_2$ ($M+H^+$ = 390.9); HRMS (FAB) of $C_8H_8I_2O_2$ [$M+H^+$] calc. 389.8608, found 389.8609; IR (ATR) v = 2927.6, 2829.6, 1681.0, 1480.0, 1443.7, 1432.1, 1345.3, 1270.9, 1200.3, 1057.4, 1014.2, 850.0, 836.7, 743.7, 615.8, 482.9, 431.8 cm^{-1}.

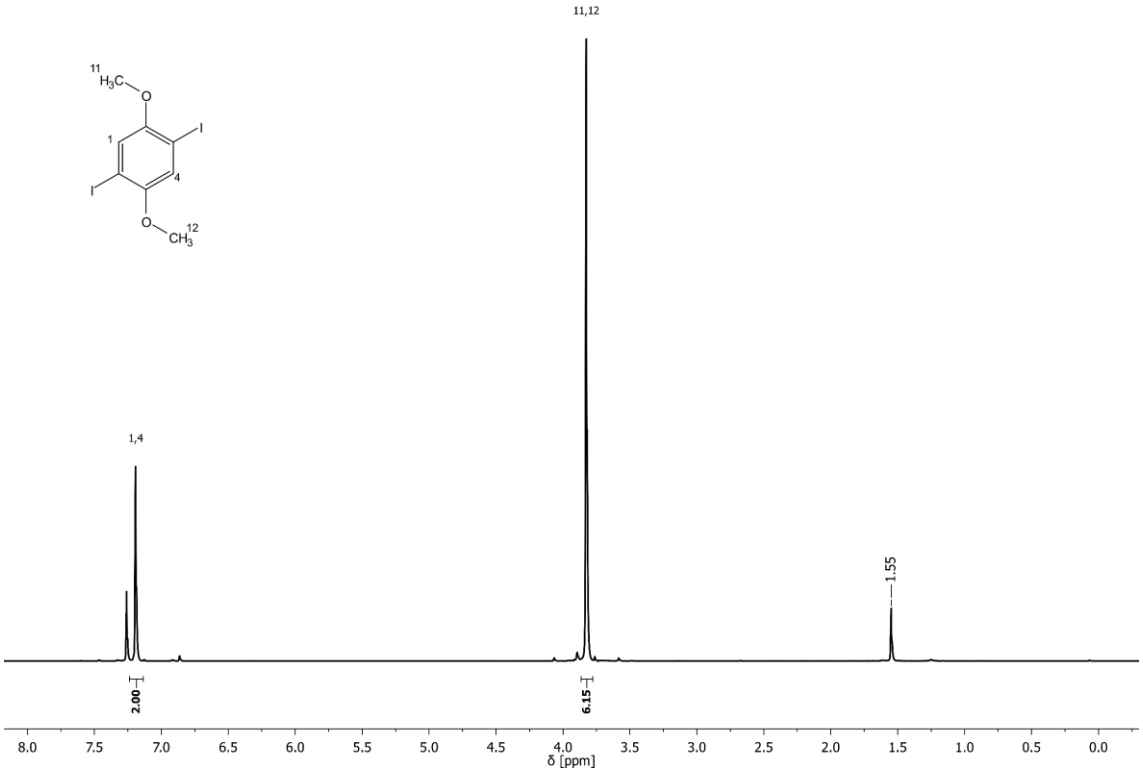
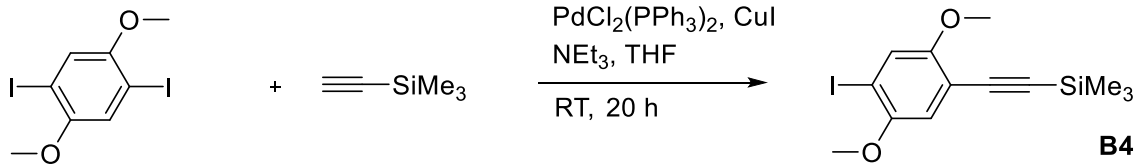


Figure 51: ^{1}H NMR spectrum of precursor **P4** with assigned signals.

Synthesis of ((4-iodo-2,5-dimethoxyphenyl)ethynyl)trimethylsilane **B4**



B4

1,4-Diiodo-2,5-dimethoxybenzene (10.0 g, 25.6 mmol, 1.00 eq.), 2.5 mol% *bis*(triphenylphosphine)palladium(II) dichloride (450 mg, 0.641 mmol) and 5 mol% copper(I) iodide (244 mg, 1.28 mmol) were placed into a Schlenk flask and degassed. Under continuous argon flow, 400 mL dry THF and 35.5 mL dry triethylamine were added, and the mixture was stirred for 10 minutes. Subsequently, 3.91 mL trimethylsilylacetylene (2.77 g, 28.2 mmol, 1.10 eq.) with 5 mL dry THF were added dropwise with a syringe. The reaction mixture was stirred for 20 hours at room temperature, taken up in dichloromethane and washed with saturated NH_4Cl solution. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (cyclohexane/dichloromethane 9:1) to yield the product as a yellow solid (3.10 g, 34%). TLC (cyclohexane/ dichloromethane 4:1) R_f = 0.42; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.26 (s, 1 H, 1 C**H**$_{aromatic}$Cl), 6.87 (s, 1 H, 1 C**H**$_{aromatic}$C-C≡C), 3.83 (s, 6 H, 2 C**H**$_3$), 0.27 (s, 9 H, 3 C**H**$_3$Si); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 155.18, 152.29, 122.53, 115.65, 113.06, 100.65, 99.93, 87.17, 57.09, 56.82, 0.13; FAB of $C_{13}H_{17}IO_2Si$ ($M+H^+$ = 361.3); HRMS (FAB) of $C_{13}H_{17}IO_2Si$ [$M+H^+$] calc. 360.0037, found 360.0038; IR (ATR) v = 2955.2, 2839.8, 2149.5, 1489.8, 1437.0, 1370.9, 1279.2, 1247.0, 1214.5, 1186.9, 1157.2, 1039.1, 954.1, 836.0, 796.4, 756.0, 729.7, 696.4, 663.6, 639.4, 484.6 cm^{-1}.

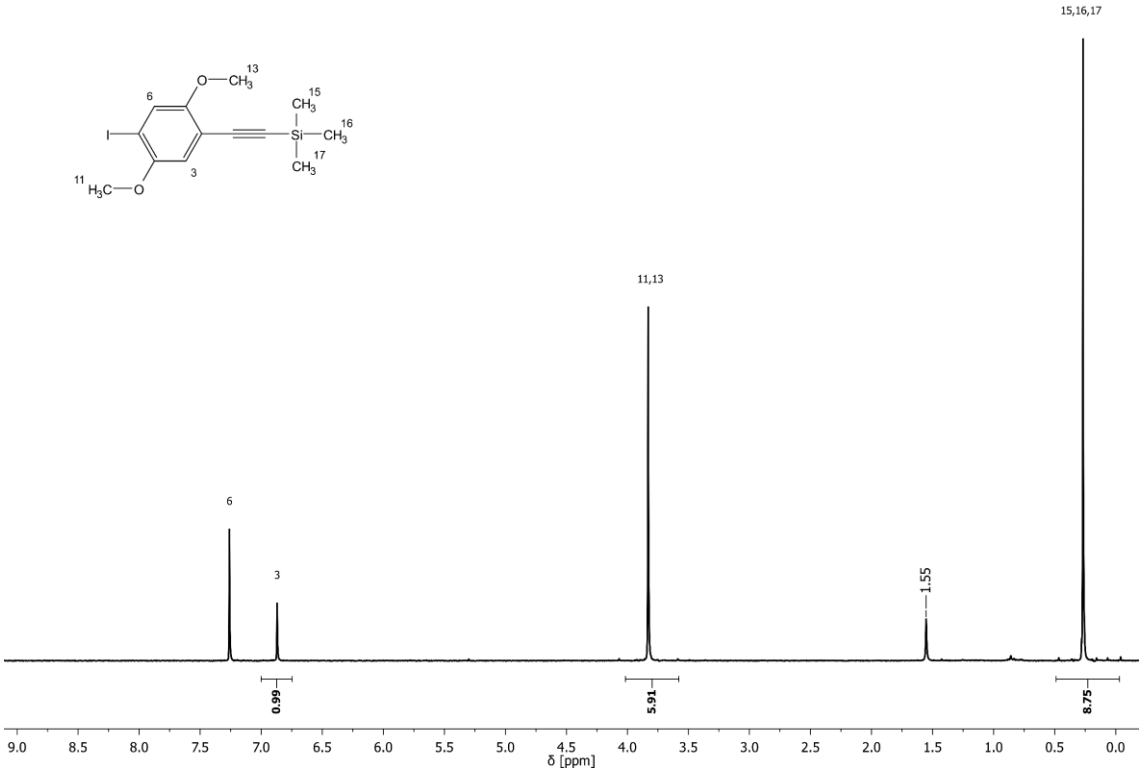
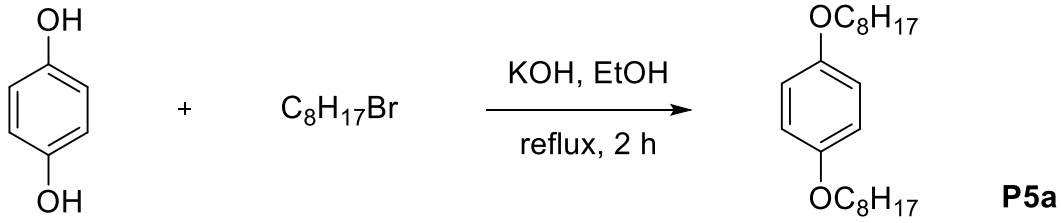


Figure 52: ^{1}H NMR spectrum of building block **B4** with assigned signals.

Synthesis of 1,4-*bis*(octyloxy)benzene **P5a**



P5a

Hydroquinone (30.0 g, 272 mmol, 1.00 eq.) was dissolved in 250 mL absolute ethanol. Potassium hydroxide (38.2 g, 681 mmol, 2.50 eq.) was added and the mixture was stirred for 30 minutes under reflux. Subsequently, 1-bromooctane (104 mL, 116 g, 599 mmol, 2.20 eq.) was slowly added over a 1 hour time period and stirred under reflux for another 2 hours. Ethanol was removed with a rotary evaporator and the residue was taken up in dichloromethane. The organic phase was washed with water three times and once more with saturated $NaHCO_3$ solution. It was then dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure and the crude product was recrystallized from methanol to yield colorless crystals (37.6 g, 41%). TLC (cyclohexane/dichloromethane 9:1) R_f = 0.54; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 6.82 (d, J = 0.9 Hz, 4 H, 4 C**H**$_{aromatic}$), 3.90 (t, J = 6.6 Hz, 4 H, 2 C**H**$_2$O), 1.75 (p, J = 6.7 Hz, 4 H, 2 C**H**$_2$CH$_2$O), 1.51-1.18 (m, 20 H, 10 CH_2), 0.89 (t, J = 6.2 Hz, 6 H, 2 C**H**$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 153.35, 115.53, 68.81, 31.97, 29.54, 29.40, 26.22, 22.81, 14.25; FAB of $C_{22}H_{38}O_2$ ($M+H^+$ = 335.3); HRMS (FAB) of $C_{22}H_{38}O_2$ [$M+H^+$] calc. 334.2866, found 334.2866; IR (ATR) v = 2954.3, 2920.0, 2870.3, 2852.9, 2022.5, 1507.1, 1472.7, 1463.7, 1416.8, 1393.5, 1288.1, 1223.7, 1114.7, 1043.6, 1028.2, 998.6, 942.5, 826.3, 770.1, 720.5, 534.9, 521.8, 507.2, 386.4 cm^{-1}.

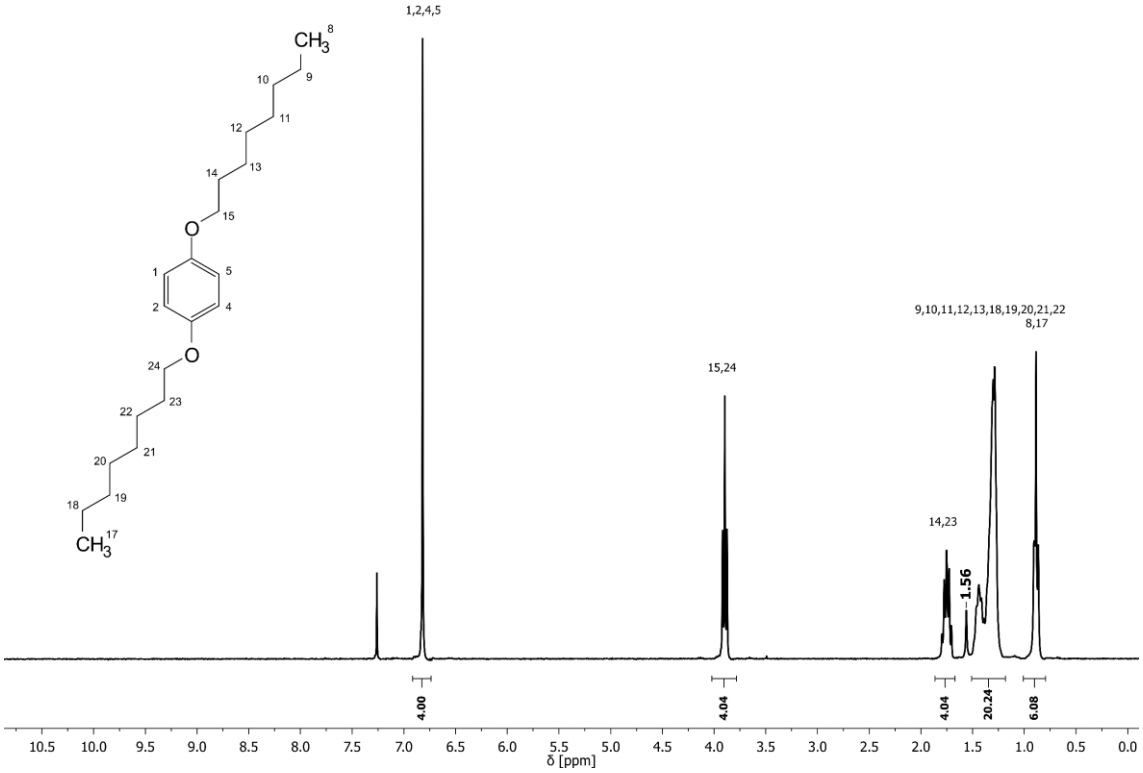
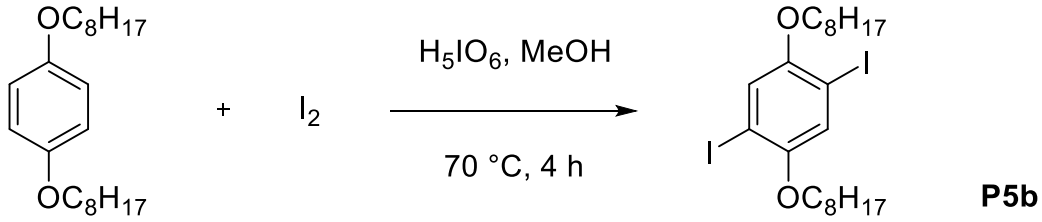


Figure 53: ^{1}H NMR spectrum of precursor **P5a** with assigned signals.

Synthesis of 1,4-diiodo-2,5-*bis*(octyloxy)benzene **P5b**



P5b

Periodic acid (16.0 g, 70.3 mmol, 0.636 eq.) was dissolved in 150 mL methanol and stirred for 10 minutes. Subsequently, iodine (34.5 g, 136 mmol, 1.23 eq.) was added and after an additional stirring time of 10 minutes, 1,4-*bis*(octyloxy)benzene (37.0 g, 111 mmol, 1.00 eq.) was added. The reaction mixture was stirred at 70 °C for 4 hours. The residue was carefully poured into 300 mL water containing potassium disulfite. The precipitate was washed with methanol and dissolved in dichloromethane. The solution was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by recrystallization from methanol to yield the product as a white solid (58.5 g, 90%). TLC (cyclohexane/dichloromethane 9:1) R_f = 0.72; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.17 (s, 2 H, 2 C**H**$_{aromatic}$), 3.92 (t, J = 6.4 Hz, 4 H, 2 C**H**$_2$O), 1.90-1.70 (m, 4 H, 2 C**H**$_2$CH$_2$O), 1.66-1.17 (m, 20 H, 5 C**H**$_2$), 0.89 (t, J = 6.7 Hz, 6 H, 2 C**H**$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 152.99, 122.91, 86.45, 70.48, 31.94, 29.38, 29.36, 29.28, 26.17, 22.80, 14.26; FAB of $C_{22}H_{36}I_2O_2$ ($M+H^+$ = 587.3); HRMS (FAB) of $C_{22}H_{36}I_2O_2$ [$M+H^+$] calc. 586.0799, found 586.0801; IR (ATR) v = 2915.4, 2847.8, 1484.8, 1458.4, 1388.1, 1350.8, 1263.0, 1212.9, 1143.5, 1066.9, 1049.7, 1012.8, 961.6, 900.4, 845.7, 834.3, 785.7, 747.0, 720.1, 533.3, 435.1 cm^{-1}.

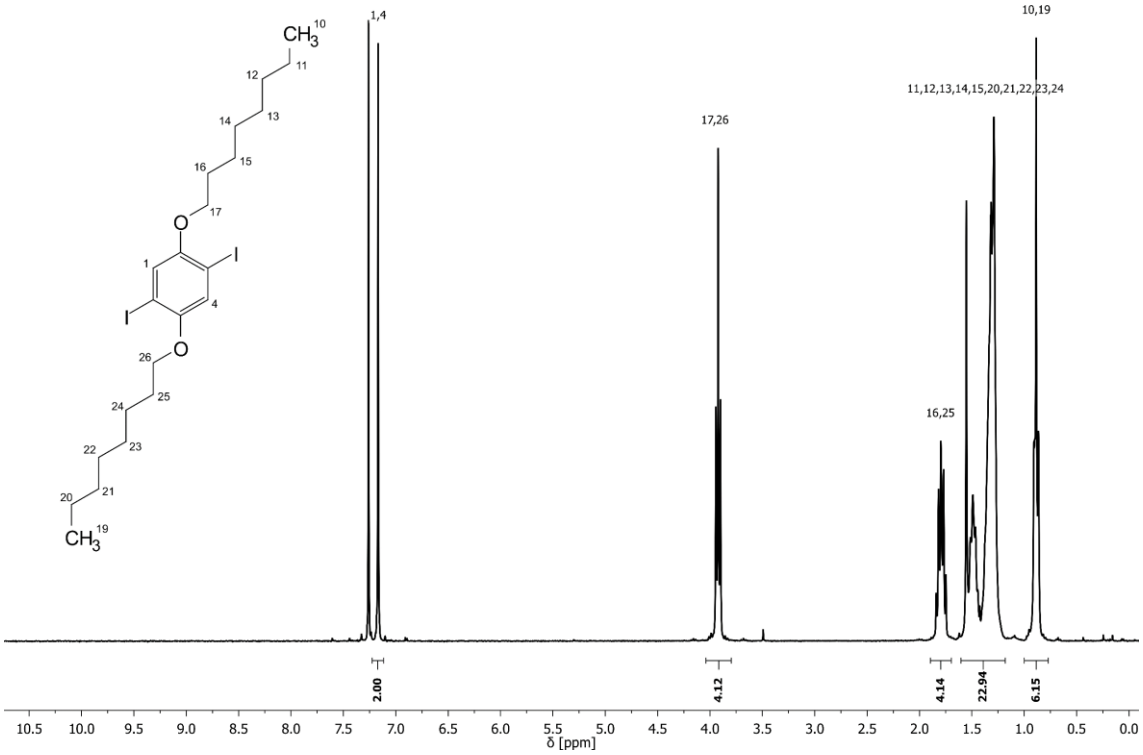
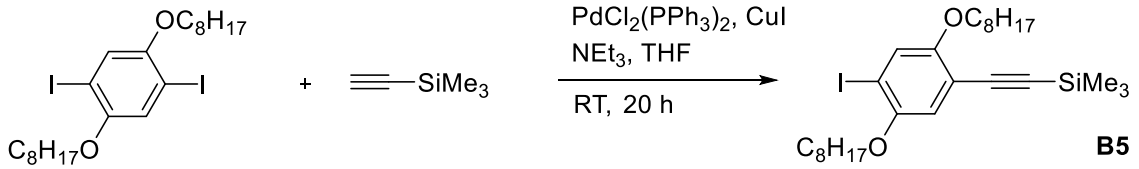


Figure 54: ^{1}H NMR spectrum of precursor **P5b** with assigned signals.

Synthesis of ((4-iodo-2,5-*bis*(octyloxy)phenyl)ethynyl)trimethylsilane **B5**



1,4-Diiodo-2,5-*bis*(octyloxy)benzene (10.0 g, 17.1 mmol, 1.00 eq.), 2.5 mol% *bis*(triphenylphosphine)palladium(II) dichloride (299 mg, 0.426 mmol) and 5 mol% copper(I) iodide (162 mg, 0.853 mmol) were placed into a Schlenk flask and degassed. Under continuous argon flow, 400 mL dry THF and 23.6 mL dry triethylamine were added, and the mixture was stirred for 10 minutes. Subsequently, 2.67 mL trimethylsilylacetylene (1.84 g, 18.8 mmol, 1.10 eq.) with 5 mL dry THF was added dropwise with a syringe. The reaction mixture was stirred for 20 hours at room temperature, taken up in dichloromethane and washed with saturated NH_4Cl solution. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (cyclohexane/dichloromethane 9:1 and cyclohexane/ ethyl acetate 20:1) to yield the product as a yellow liquid (3.17 g, 33%). TLC (cyclohexane / dichloromethane 9:1) R_f = 0.62; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.25 (s, 1 H, 1 C**H**$_{aromatic}$Cl), 6.83 (s, 1 H, 1 C**H**$_{aromatic}$C-C≡C), 3.93 (t, J = 6.3 Hz, 4 H, 2 C**H**$_2$O), 1.89-1.70 (m, 4 H, 2 C**H**$_2$CH$_3$), 1.54-1.41 (m, 4 H, 2 C**H**$_2$CH$_2$CH$_3$), 1.41-1.19 (m, 16 H, 8 C**H**$_2$), 0.88 (t, J = 6.5 Hz, 6 H, 2 C**H**$_3$), 0.25 (s, 9 H, 3 C**H**$_3$Si); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 155.01, 151.82, 123.94, 116.42, 113.53, 100.92, 99.55, 88.04, 70.21, 69.90, 31.98, 31.95, 29.52, 29.47, 29.43, 29.40, 29.37, 29.31, 27.05, 26.20, 26.14, 22.81, 14.26, 14.24, 0.08; FAB of $C_{27}H_{45}IO_2Si$ ($M+H^+$ = 557.3); HRMS (FAB) of $C_{27}H_{45}IO_2Si$ [$M+H^+$] calc. 556.2234, found 556.2233; IR (ATR) v = 2922.5, 2853.9, 2155.3, 1578.1, 1484.0, 1463.2, 1369.7, 1247.9, 1214.0, 1159.2, 1030.7, 841.1, 758.6, 721.9, 698.7, 664.2, 636.2 cm^{-1}.

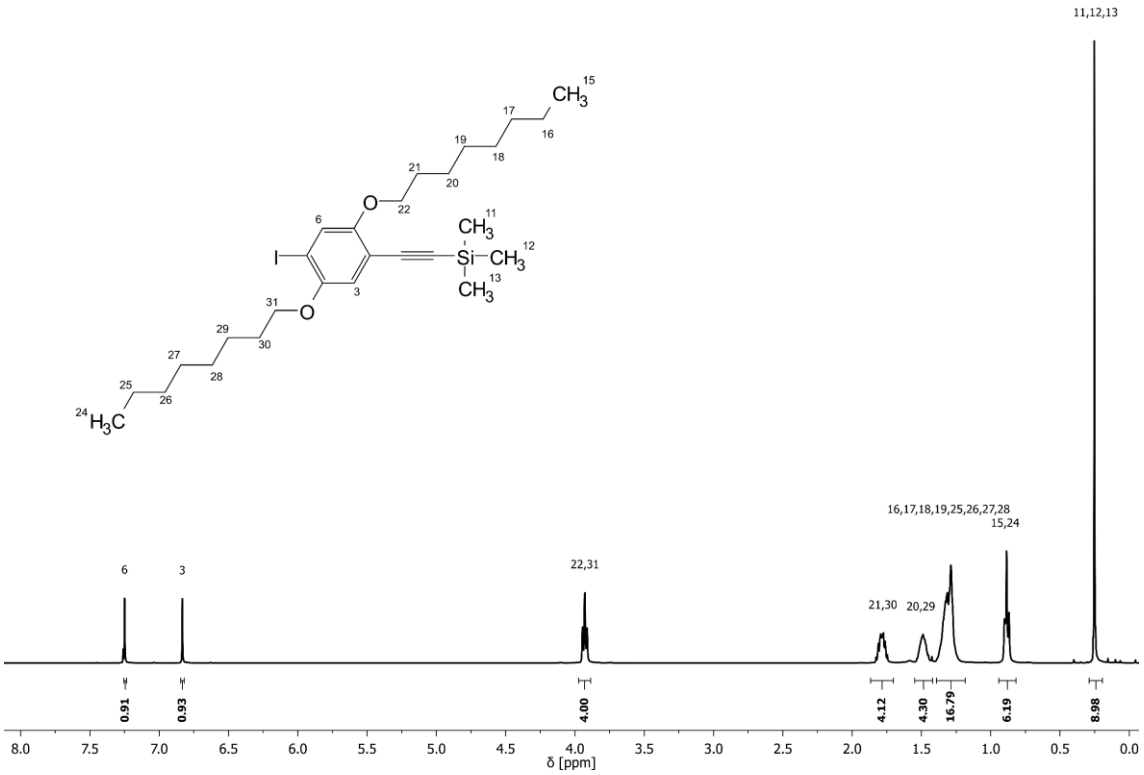
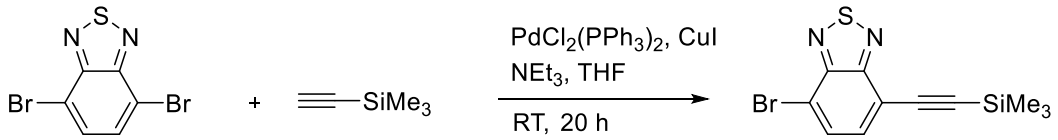


Figure 55: ^{1}H NMR spectrum of building block **B5** with assigned signals.

6.3.2 Syntheses of Building Blocks with Electron Accepting Properties

Synthesis of 4-Bromo-7-((trimethylsilyl)ethynyl)benzo[*c*][1,2,5]thiadiazole **B6**



B6

4,7-Dibromobenzo[c][1,2,5]thiadiazole (500 mg, 1.70 mmol, 1.00 eq.), 2.5 mol% *bis*(triphenylphosphine)palladium(II) dichloride (29.8 mg, 42.5 µmol) and 5 mol% copper(I) iodide (16.2 mg, 8.50 µmol) were placed into a Schlenk flask and degassed. Under continuous argon flow, 20 mL dry THF and 2.36 mL dry triethylamine were added, and the mixture was stirred for 10 minutes. Subsequently, 267 µL trimethylsilylacetylene (184 mg, 1.87 mmol, 1.10 eq.) with 5 mL dry THF were added dropwise with a syringe. The reaction mixture was stirred for 20 hours at room temperature, taken up in dichloromethane and washed with saturated NH_4Cl solution. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (cyclohexane/dichloromethane 9:1) to yield the product as a white solid (150 mg, 28%). TLC (cyclohexane/ dichloromethane 9:1) R_f = 0.13; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.79 (d, J = 7.6 Hz, 1 H, 1 C**H**$_{aromatic}$CBr), 7.62 (d, J = 7.6 Hz, 1 H, 1 C**H**$_{aromatic}$C≡C), 0.33 (s, 9 H, 3 C**H**$_3$Si); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 154.22, 153.09, 133.79, 131.90, 116.55, 115.16, 103.08, 99.50, -0.01; FAB of $C_{11}H_{11}BrN_2SSi$ ($M+H^+$ = 313.0); HRMS (FAB) of $C_{11}H_{11}BrN_2SSi$ [$M+H^+$] calc. 309.9596, found 309.9597; IR (ATR) v = 2958.05, 2145.56, 1849.79, 1575.25, 1521.24, 1477.70, 1367.04, 1324.61, 1303.45, 1246.08, 1229.82, 1045.75, 937.71, 882.55, 840.93, 821.57, 754.86, 701.58, 683.95, 630.35, 618.53, 546.93, 517.29, 504.19, 436.08, 412.00 cm^{-1}.

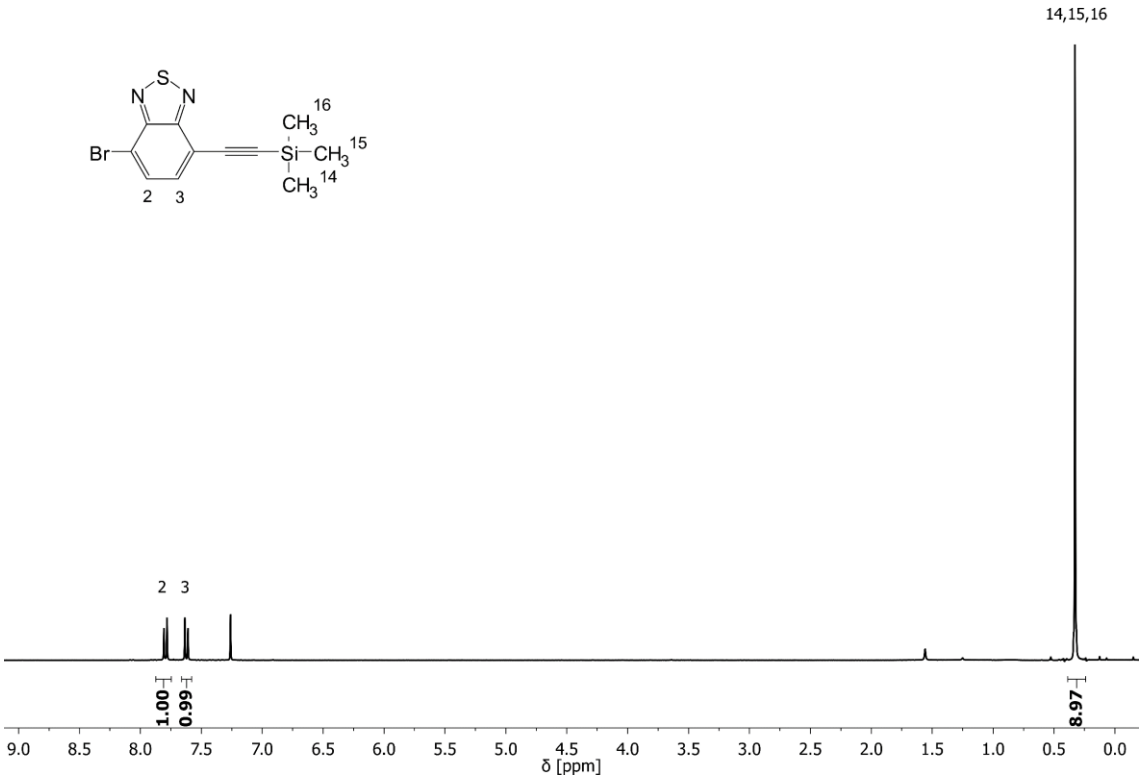
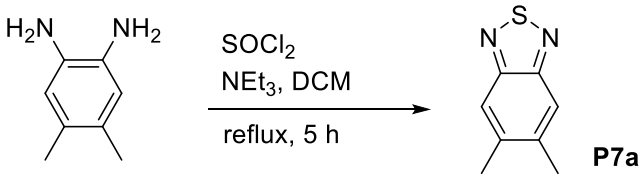


Figure 56: ^{1}H NMR of building block **B6** with assigned signals.

Synthesis of 5,6-dimethylbenzo[c][1,2,5]thiadiazole **P7a**

This synthesis was performed according to a procedure published in a patent.[222]



P7a

4,5-Dimethyl-1,2-phenyldiamine monohydrate (2.27 g, 14.7 mmol, 1.00 eq.) was dissolved in 50 mL dichloromethane and 8.50 mL triethylamine were added. Subsequently, thionyl chloride (2.18 mL, 3.57 g, 30.0 mmol, 2.04 eq.) was added slowly and the reaction mixture was heated under reflux for 5 hours. The reaction mixture was concentrated under reduced pressure; then, dichloromethane was added and washed with distilled water. The organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (dry load, cyclohexane/ethyl acetate 4:1) to yield the product as a yellow solid (2.18 g, 90%). TLC (cyclohexane/ dichloromethane 9:1) R_f = 0.21; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.70 (s, 2 H, 2 C**H**$_{\textbf{aromatic}}$), 2.41 (s, 6 H, 2 C**H**$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 154.34, 140.59, 119.85, 20.90; ESI-MS of $C_8H_8N_2S$ ($M+H^+$ = 165.05); IR (ATR) v = 2975.4, 1716.5, 1498.0, 1474.7, 1447.3, 1371.7, 1271.3, 1025.0, 1005.6, 851.3, 821.0, 767.1, 731.5, 664.2, 539.0, 428.9, 419.5 cm^{-1}.

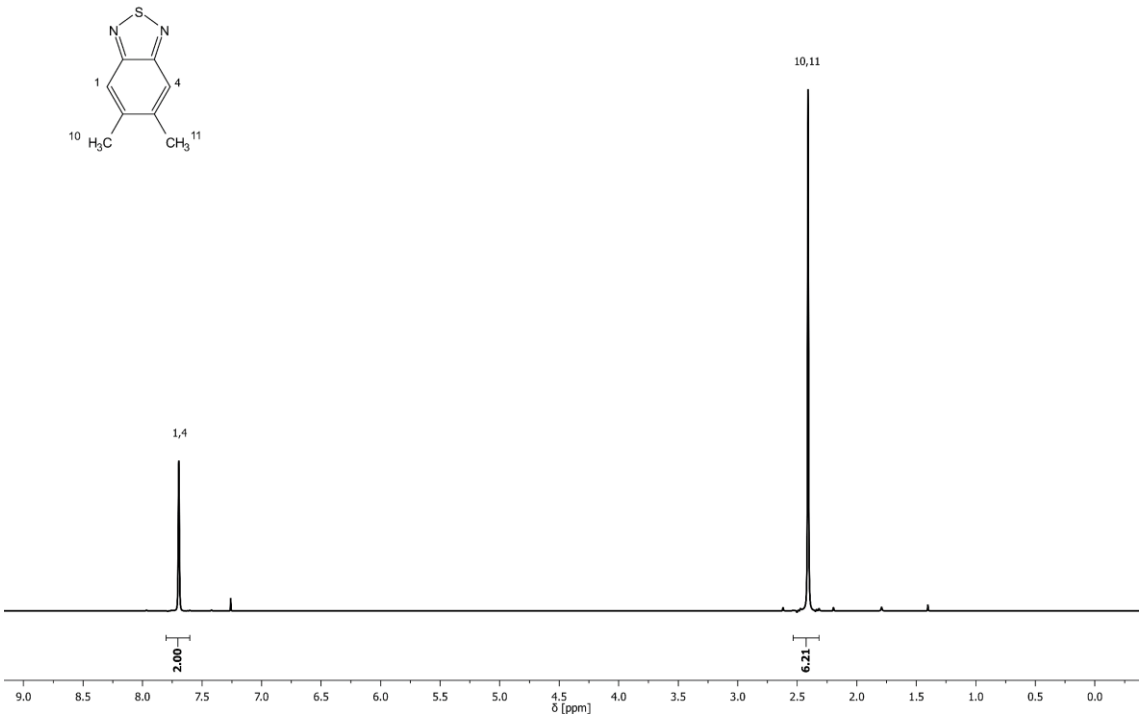
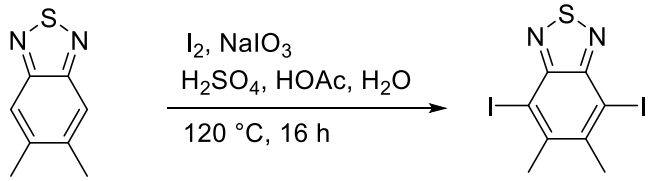


Figure 57: ^{1}H NMR spectrum of precursor **P7a** with assigned signals.

Synthesis of 4,7-diiodo-5,6-dimethylbenzo[c][1,2,5]thiadiazole **P7b**

This synthesis was performed according to a procedure published in a patent.[222]



P7b

5,6-Dimethylbenzo[c][1,2,5]thiadiazole (1.50 g, 9.13 mmol, 1.00 eq.), iodine (2.55 g, 10.0 mmol, 1.10 eq.), sodium iodate (904 mg, 4.57 mmol, 0.500 eq.), 1.9 mL sulfuric acid, 31 mL acetic acid and 0.2 mL distilled water were stirred at 120 °C for 16 hours. The chilled reaction mixture was transferred to aqueous Na_2SO_3 solution and dichloromethane was added. The aqueous phase was extracted three times with dichloromethane and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (dry load, cyclohexane/ethyl acetate 9:1) to yield the product as a yellow solid (1.70 g, 45%). TLC (cyclohexane/dichloromethane 9:1) R_f = 0.24; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 2.80 (s, 6 H, 2 C**H$_3$**); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 153.24, 144.25, 93.66, 28.59; ESI-MS of $C_8H_6I_2N_2S$ ($M+Na^+$ = 438.82); IR (ATR) v = 1537.8, 1435.2, 1377.2, 1268.5, 1250.2, 1114.7, 1021.1, 914.7, 873.0, 840.1, 793.0, 755.0, 698.0, 594.3, 579.8, 553.5, 496.8, 480.6, 447.6, 404.3, 381.0 cm^{-1}.

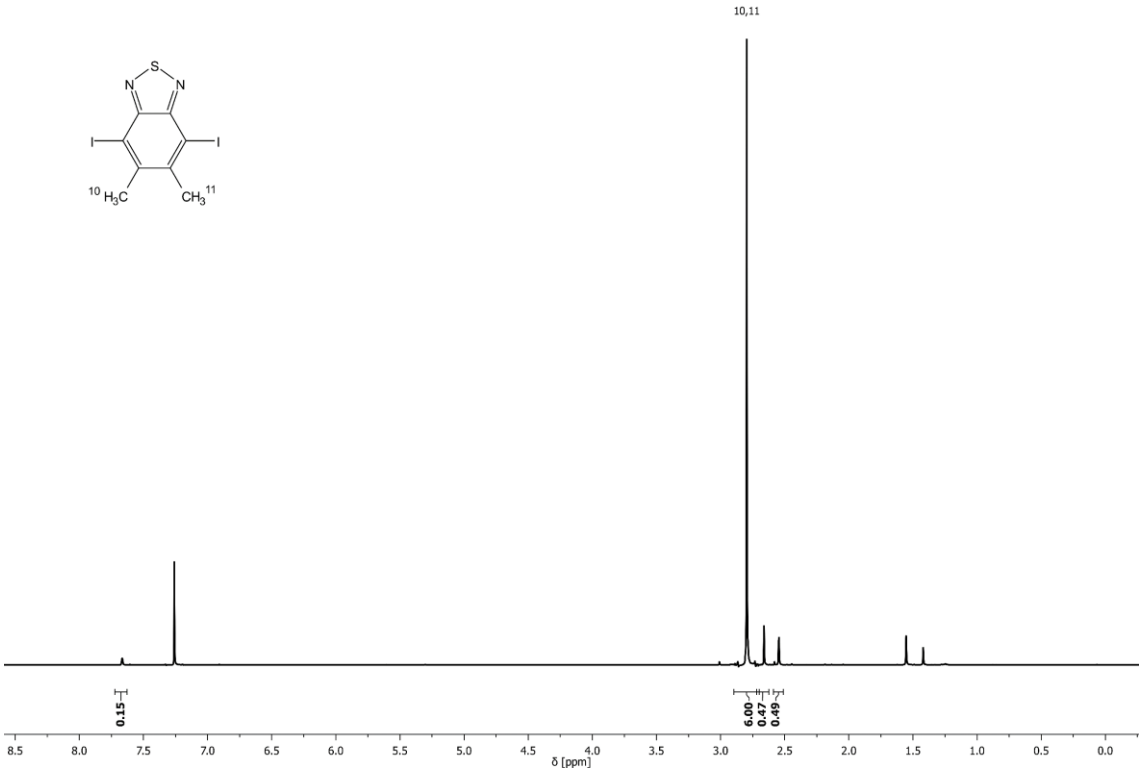
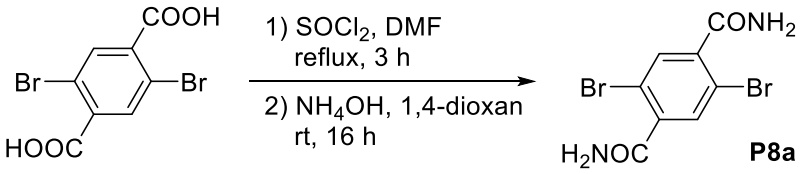


Figure 58: ^{1}H NMR spectrum of precursor **P7b** with assigned signals.

Synthesis of 2,5-dibromoterephthalamide **P8a**

This synthesis was performed according to a procedure by Chou and Wong *et al*.[223]



2.5-Dibromoterephthalic acid (1.50 g, 4.63 mmol, 1.00 eq.), 20 mL thionyl chloride and five drops of DMF were refluxed for 3 hours. The solvent was removed under reduced pressure by co-evaporation with 20 mL toluene. The residue was dissolved in 20 mL 1,4-dioxane and 20 mL concentrated ammonium hydroxide was added dropwise. The mixture was stirred overnight at room temperature. Subsequently, the precipitate was filtered and washed with 1,4-dioxane to yield the product as a white solid (910 mg, 61%). TLC (methanol) R_f = 0; ^{1}H NMR (DMSO-d$_6$, 300 MHz): δ (ppm) = 8.00, 7.73 (s, 4 H, 2 NH$_2$), 7.64 (s, 2 H, 2 C**H**$_{\text{aromatic}}$); ^{13}C NMR (DMSO-d$_6$, 125 MHz): δ (ppm) = 167.16, 140.89, 132.29, 117.66; ESI-MS of $C_8H_6Br_2N_2O_2$ ($M+Na^+$ = 344.87); IR (ATR) v =3381.3, 3174.5, 1645.2, 1613.8, 1482.9, 1391.4, 1318.6, 1123.9, 1056.5, 886.2, 797.2, 725.1, 659.8, 599.0, 500.9, 449.5, 394.6 cm^{-1}.

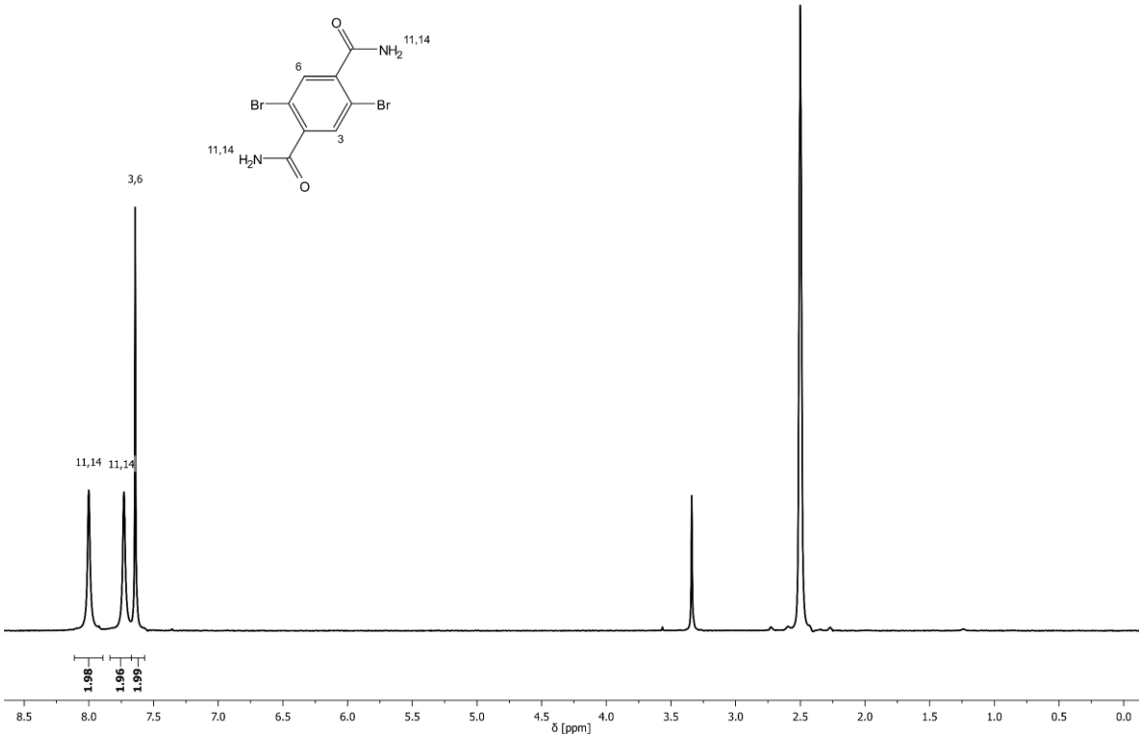
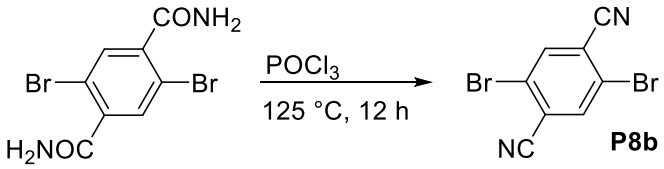


Figure 59: ^{1}H NMR spectrum of precursor **P8a** with assigned signals.

Synthesis of 2,5-dibromoterephthalonitrile **P8b**

This synthesis was performed according to a procedure by Chou and Wong *et al*.[223]



2.5-Dibromoterephthalamide (1.67 g, 5.19 mmol, 1.00 eq.) and 12 mL phosphorus oxychloride were heated at 125 °C for 12 hours. Subsequently, the reaction mixture was poured into ice water and the precipitate was filtered and washed with water to yield the product as a white solid (1.38 g, 93%). TLC (cyclohexane / ethyl acetate 9:1) R_f = 0.49; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.96 (s, 2 H, 2 C**H**$_{\text{aromatic}}$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 138.03, 124.38, 121.30, 114.69; IR (ATR) v = 3080.6, 3011.9, 2921.7, 2851.9, 2235.0, 1811.6, 1459.2, 1331.7, 1256.0, 1184.2, 1149.8, 1082.0, 911.7, 739.1, 680.2, 641.9, 455.9, 383.2 cm^{-1}.

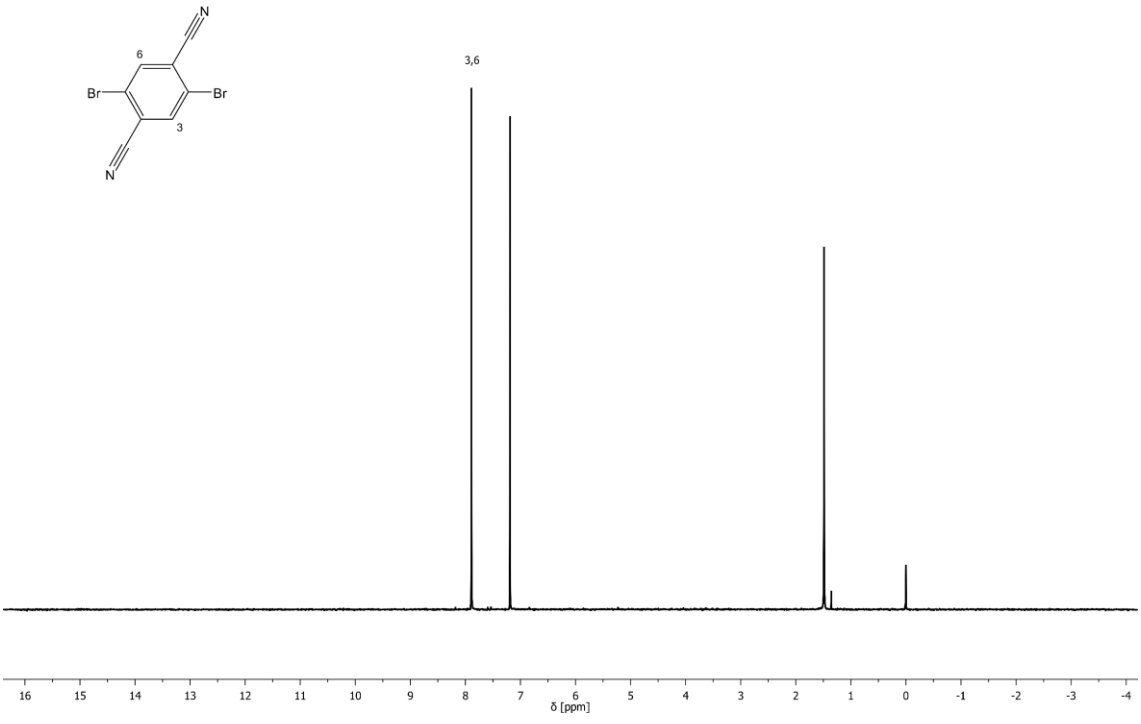
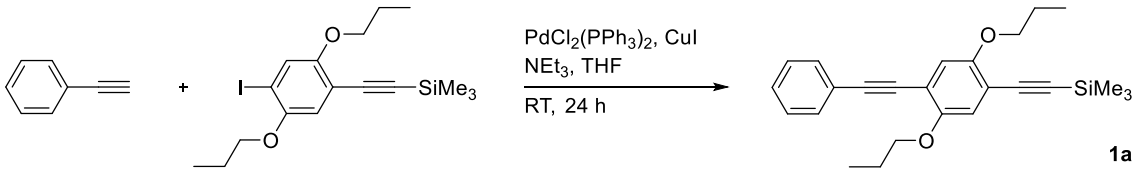


Figure 60: ^{1}H NMR spectrum of precursor **P8b** with assigned signals.

6.3.3 Syntheses of Monodisperse Rod-Like Oligomers

Synthesis of trimethyl((4-(phenylethynyl)-2,5-dipropoxyphenyl)ethynyl)silane **1a**



1,4-*Bis*(propyloxy)-2-iodo-5-trimethylsilylacetylenebenzene **B1** (5.00 g, 12.0 mmol, 1.00 eq.), 2.5 mol% *bis*(triphenylphosphine) palladium(II) dichloride (210 mg, 0.300 mmol) and 5 mol% copper(I) iodide (114 mg, 0.600 mmol) were placed into a Schlenk flask and degassed three times. Under continuous argon flow, 150 mL dry THF and 16.6 mL dry triethylamine (12.2 g, 120 mmol, 10.0 eq.) were added and the mixture was stirred for 10 minutes. Subsequently, 3.96 mL phenylacetylene (3.68 g, 36.0 mmol, 3.00 eq.) in 5 mL THF were added dropwise with a syringe. The reaction mixture was stirred for 48 hours (2 days) at room temperature, taken up in dichloromethane and washed with saturated NH_4Cl solution. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography twice (cyclohexane/dichloromethane 4:1 and cyclohexane/ethyl acetate 20:1) to yield the product as a yellow solid (4.63 g, 99%). TLC (cyclohexane/dichloromethane 4:1) R_f = 0.31; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.58-7.46 (m, 2 H, 2 C**H**$_{aromatic}$C-C≡C), 7.42-7.28 (m, 3 H, 3 C**H**$_{aromatic}$), 6.97, 6.95 (2 s, 2 H, 2 C**H**$_{aromatic}$CO), 3.96 (dt, *J* = 6.4, 4.0 Hz, 4 H, 2 C**H**$_2$O), 1.96-1.71 (m, 4 H, 2 C**H**$_2$CH$_3$),), 1.09 (dt, *J* = 7.4, 2.7 Hz, 6 H, 2 C**H**$_3$), 0.26 (s, 9 H, 3 CH_3Si); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 154.33, 153.63, 131.67, 128.44, 128.38, 123.58, 117.50, 117.21, 114.48, 113.93, 101.30, 100.15, 94.97, 85.98, 71.22, 71.18, 22.84, 10.67, 10.63, 0.08; FAB of $C_{25}H_{30}O_2Si$ ($M+H^+$ = 391.2); HRMS (FAB) of $C_{25}H_{30}O_2Si$ [$M+H^+$] calc. 390.2010, found 390.2011; IR (ATR) v = 2958.6, 2875.0, 2153.4, 1503.5, 1468.9, 1409.2, 1389.4, 1273.6, 1245.6, 1214.7, 1041.6, 1021.1, 889.1, 836.8, 752.4, 687.3, 627.0, 547.5, 526.5, 471.8, 384.5 cm^{-1}.

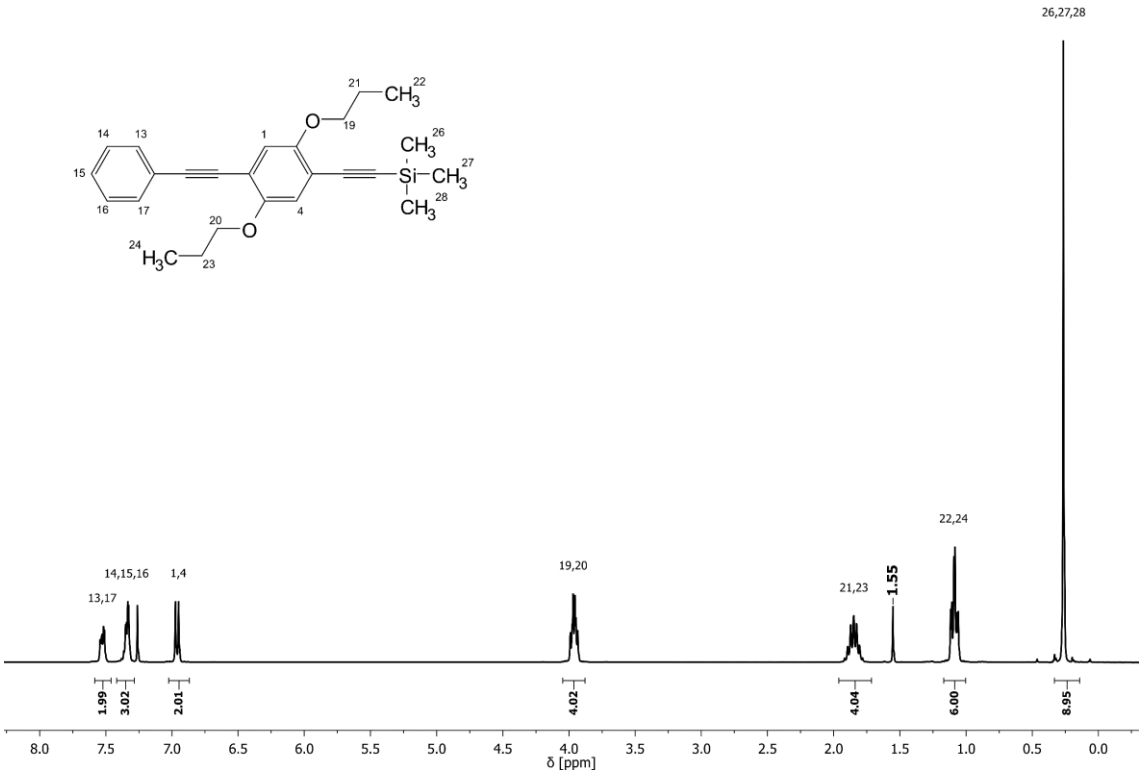
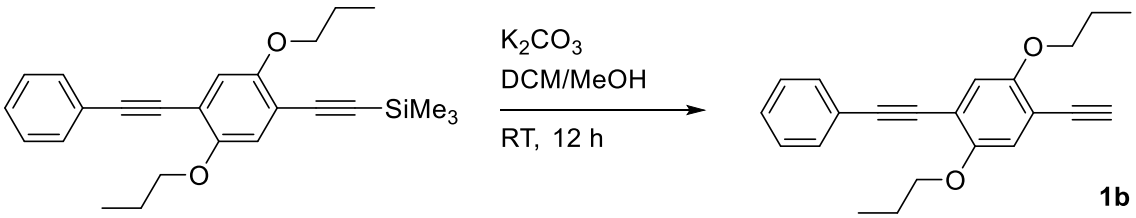


Figure 61: ^{1}H NMR spectrum of protected monomer **1a** with assigned signals.

Synthesis of 1-ethynyl-4-(phenylethynyl)-2,5-dipropoxybenzene **1b**



Trimethyl((4-(phenylethynyl)-2,5-dipropoxyphenyl)ethynyl)silane **1a** (4.00 g, 10.2 mmol, 1.00 eq.) and two equivalents of potassium carbonate (2.83 g, 20.5 mmol) were placed into a Schlenk flask and degassed three times. Under continuous argon flow, 200 mL dry dichloromethane and 200 mL dry methanol were added. The reaction mixture was stirred overnight at room temperature under argon atmosphere and quenched with distilled water. The aqueous phase was extracted three times with dichloromethane, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash silica column chromatography (cyclohexane/ethyl acetate 20:1) to yield the product as an orange solid (3.15 g, 97%). TLC (cyclohexane/dichloromethane 4:1) R_f = 0.22; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.60-7.47 (m, 2 H, 2 C**H**$_{aromatic}$C-C≡C), 7.43-7.28 (m, 3 H, 3 C**H**$_{aromatic}$), 7.00, 6.98 (2 s, 2 H, 2 C**H**$_{aromatic}$CO), 3.98 (dt, J = 6.5, 4.3 Hz, 4 H, 2 C**H**$_2$O), 3.35 (s, 1 H, 1 C≡C-**H**), 1.96-1.75 (m, 4 H, 2 C**H**$_2$CH$_3$), 1.08 (dt, J = 9.8, 7.4 Hz, 6 H, 2 C**H**$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 154.33, 153.63, 131.72, 128.47, 123.55, 118.14, 117.18, 114.95, 112.81, 95.04, 85.83, 82.38, 80.15, 71.34, 71.29, 22.85, 22.72, 10.67, 10.59; FAB of $C_{22}H_{22}O_2$ ($M+H^+$ = 319.2); HRMS (FAB) of $C_{22}H_{22}O_2$ [$M+H^+$] calc. 318.1614, found 318.1614; IR (ATR) v = 3259.6, 2960.2, 2936.7, 2876.7, 1593.3, 1501.4, 1469.4, 1440.3, 1389.9, 1275.5, 1212.1, 1065.9, 1042.0, 1013.4, 967.0, 911.1, 873.5, 857.7, 751.2, 687.3, 629.1, 527.1, 467.8, 387.4 cm^{-1}.

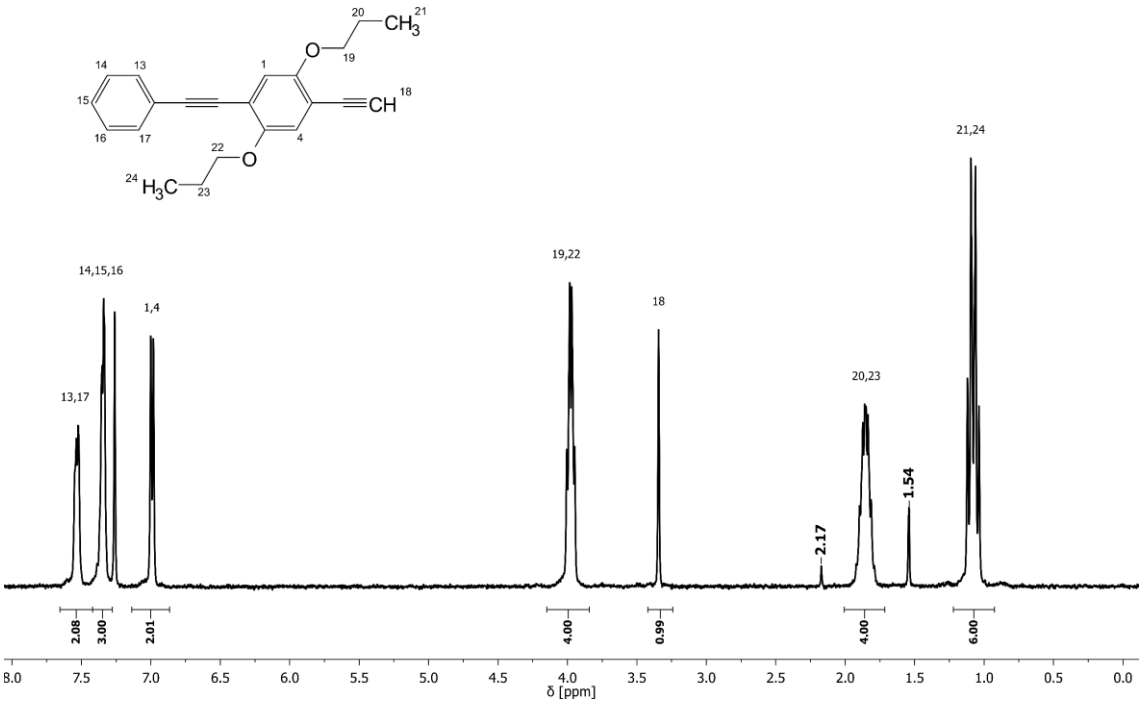
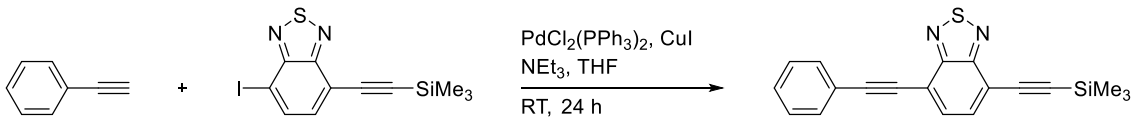


Figure 62: ^{1}H NMR spectrum of deprotected monomer **1b** with assigned signals.

Synthesis of 4-(phenylethynyl)-7-((trimethylsilyl)ethynyl)benzo[c][1,2,5]thiadiazole **1c**



1c

4-iodo-7-((Trimethylsilyl)ethynyl)benzo[c][1,2,5]thiadiazole **B6** (500 mg, 1.61 mmol, 1.00 eq.), 2.5 mol% *bis*(triphenylphosphine)palladium(II) dichloride (28.2 mg, 40.2 µmol) and 5 mol% copper(I) iodide (15.3 mg, 80.3 µmol) were placed into a Schlenk flask and evacuated three times. Under continuous argon flow, 20 mL dry THF and 2.23 mL dry triethylamine (1.63 g, 16.1 mmol, 10.0 eq.) were added and the mixture was stirred for 10 minutes. Subsequently, 529 µL phenylacetylene (492 mg, 4.82 mmol, 3.00 eq.) in 5 mL THF were added dropwise with a syringe. The reaction mixture was stirred for 48 hours (2 days) at room temperature, taken up in dichloromethane and washed with saturated NH_4Cl solution. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (cyclohexane/dichloromethane 4:1 → 3:2) to yield the product as a yellow solid (492 mg, 92%). TLC (cyclohexane/dichloromethane 9:1) R_f = 0.21; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.75 (s, 2 H, 2 C**H**$_{aromatic}$ benzothiadiazole unit), 7.71-7.61 (2 H, 2 C**H**$_{aromatic}$C-C≡C), 7.44-7.35 (m, 3 H, 3 C**H**$_{aromatic}$), 0.34 (s, 9 H, 3 C**H**$_3$Si); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 154.30, 154.24, 133.30, 132.22, 131.99, 129.10, 128.44, 122.46, 117.57, 116.85, 103.46, 100.23, 97.63, 85.30, 0.00, ESI-MS of $C_{19}H_{16}N_2SSi$ ($M+Na^+$ = 355.07); IR (ATR) v = 3055.6, 2959.7, 2209.8, 2153.8, 1597.3, 1560.0, 1539.6, 1493.8, 1440.1, 1347.0, 1273.5, 1254.1, 1240.2, 1127.9, 1056.9, 1028.6, 920.3, 887.8, 841.1, 753.1, 700.1, 687.0, 637.4, 586.2, 527.6, 508.6, 461.9 cm^{-1}.

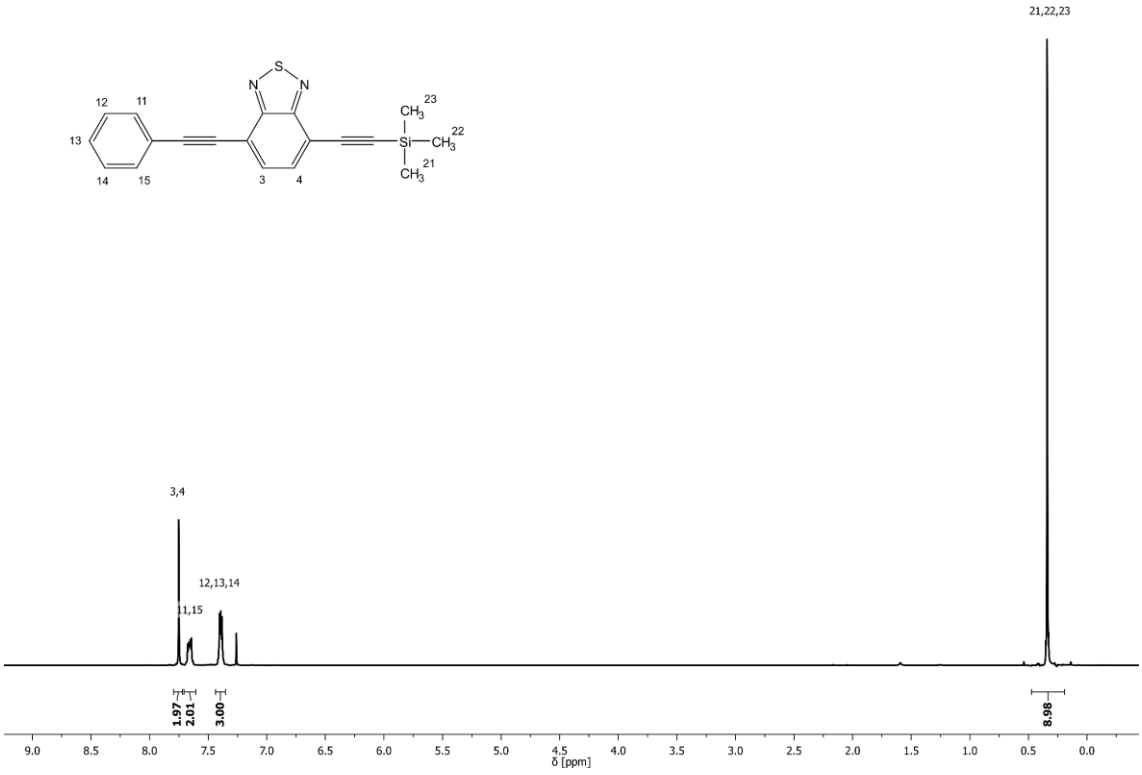
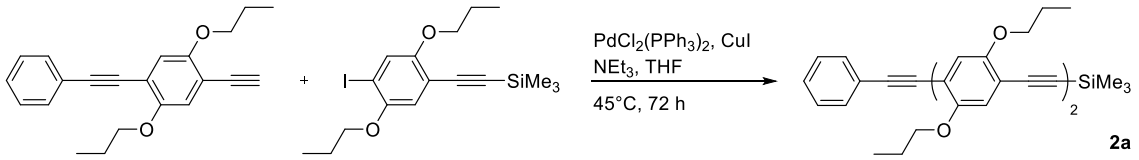


Figure 63: ^{1}H NMR spectrum of protected monomer **1c** with assigned signals.

Synthesis of trimethyl((4-((4-(phenylethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)silane **2a**



1,4-*Bis*(propyloxy)-2-iodo-5-trimethylsilylacetylenebenzene **B1** (7.50 g, 18.0 mmol, 2.87 eq.), 5 mol% *bis*(triphenylphosphine) palladium(II) dichloride (220 mg, 314 µmol) and 5 mol% copper(I) iodide (59.8 mg, 314 µmol) were placed into a Schlenk flask and degassed three times. Under continuous argon flow, 100 mL dry THF and 8.71 mL dry triethylamine (6.36 g, 62.8 mmol, 10.0 eq.) were added and the mixture was stirred for 10 minutes. Subsequently, 1-ethynyl-4-(phenylethynyl)-2,5-dipropoxybenzene **1b** (2.00 g, 6.28 mmol, 1.00 eq.) in 20 mL dry THF was added dropwise with a syringe. The reaction mixture was stirred for 72 hours (3 days) at 45 °C, taken up in dichloromethane and washed with saturated NH_4Cl solution. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (cyclohexane/dichloromethane 3:1 → 3:2) and a flash silica column (cyclohexane/ethyl acetate 20:1) to yield the product as a yellow-orange solid (3.20 g, 84%). TLC (cyclohexane/ dichloromethane 2:1) R_f = 0.35; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.58-7.48 (m, 2 H, 2 C**H**$_{aromatic}$C-C≡C), 7.40-7.30 (m, 3 H, 3 C**H**$_{aromatic}$), 7.01 (s, 2 H, 2 C**H**$_{aromatic}$CO), 6.97 (s, 1 H, 1 C**H**$_{aromatic}$COC-C≡C-Si), 6.94 (s, 1 H, 1 C**H**$_{aromatic}$C-C≡C-Si), 4.14–3.82 (m, 8 H, 4 C**H**$_2$O), 1.71-1.99 (m, 8 H, 4 C**H**$_2$CH$_3$), 1.20-0.94 (m, 12 H, 4 C**H**$_3$), 0.26 (s, 9 H, 3 C**H**$_3$Si); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 154.26, 153.70, 153.57, 153.42, 131.63, 128.42, 128.34, 123.58, 117.56, 117.36, 117.28, 114.72, 114.37, 114.20, 113.89, 101.31, 100.18, 94.98, 91.62, 91.47, 86.09, 71.27, 71.24, 71.15, 71.08, 22.81, 22.79, 22.76, 10.63, 10.59, 0.04; FAB of $C_{39}H_{46}O_4Si$ ($M+H^+$ = 607.3); HRMS (FAB) of $C_{39}H_{46}O_4Si$ [$M+H^+$] calc. 606.3160, found 606.3161; IR (ATR) v = 2961.3, 2873.4, 2150.4, 1596.0, 1506.0, 1466.0, 1420.3, 1384.1, 1271.6, 1248.3, 1205.1, 1060.8, 1010.7, 983.0, 892.2, 838.8, 754.7, 689.3, 637.4, 528.2 cm^{-1}.

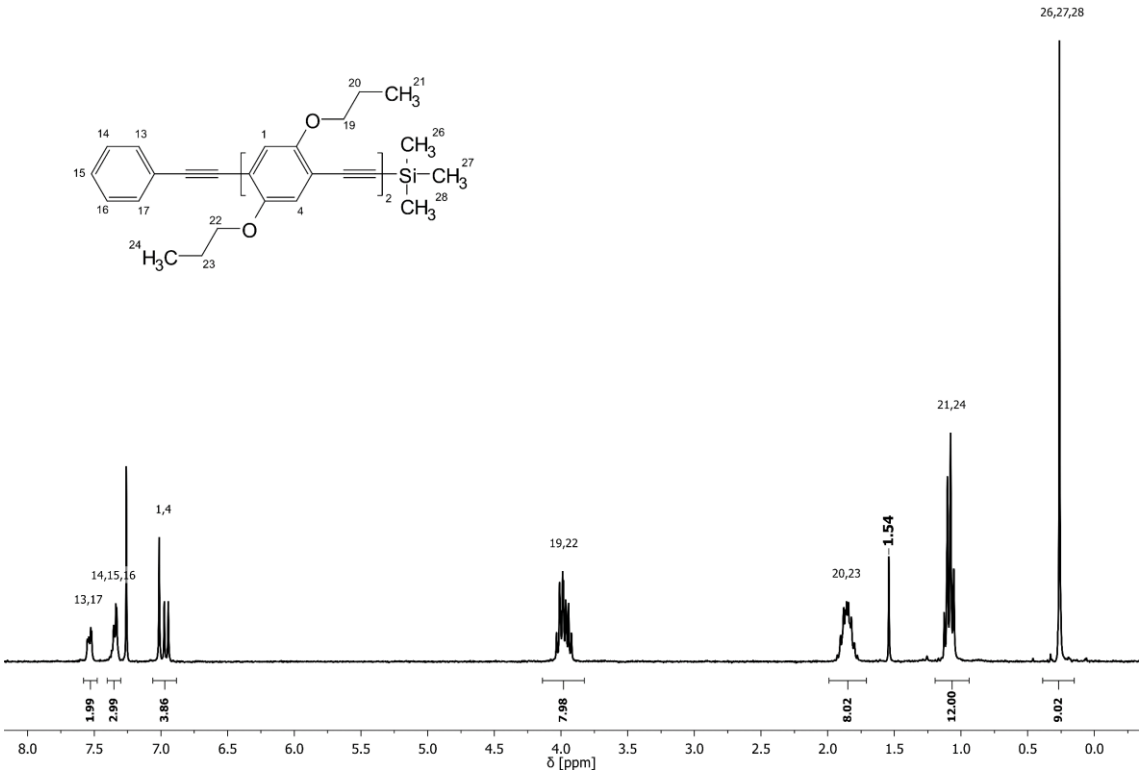
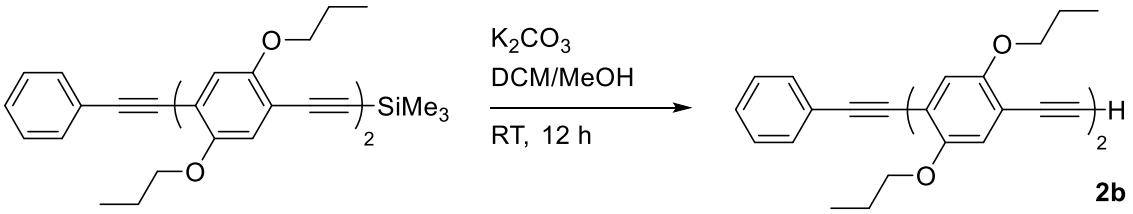


Figure 64: ^{1}H NMR spectrum of protected dimer **2a** with assigned signals.

Synthesis of 1-ethynyl-4-((4-(phenylethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxybenzene **2b**



Compound **2a** (3.00 g, 4.94 mmol, 1.00 eq.) and two equivalents of potassium carbonate (1.37 g, 9.89 mmol) were placed in a Schlenk flask and degassed three times. Under continuous argon flow, 150 mL dichloromethane and 150 mL methanol were added. The reaction mixture was stirred overnight at room temperature under argon atmosphere and quenched with distilled water. The aqueous phase was extracted three times with dichloromethane, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (cyclohexane/ethyl acetate 20:1) to yield the product as a yellow solid (2.63 g, 100%). TLC (cyclohexane/ dichloromethane 4:1) R_f = 0.33; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.62-7.47 (m, 2 H, 2 C**H**$_{aromatic}$C-C≡C), 7.43-7.28 (m, 3 H, 3 C**H**$_{aromatic}$), 7.12-6.88 (m, 4 H, 4 C**H**$_{aromatic}$CO), 4.16-3.87 (m, 8 H, 4 C**H**$_2$O), 3.34 (s, 1 H, 1 C≡C-**H**), 1.99-1.72 (m, 8 H, 4 C**H**$_2$CH$_3$), 1.21-0.97 (m, 12 H, 4 C**H**$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 154.28, 153.77, 153.67, 153.43, 131.68, 128.45, 128.38, 123.62, 118.24, 117.49, 117.38, 117.34, 115.19, 114.36, 112.79, 95.03, 91.67, 91.29, 86.10, 82.42, 80.17, 71.38, 71.35, 71.27, 71.21, 22.85, 22.81, 22.78, 22.67, 10.66, 10.55; FAB of $C_{36}H_{38}O_4$ ($M+H^+$ = 535.4); HRMS (FAB) of $C_{36}H_{38}O_4$ [$M+H^+$] calc. 534.2765, found 534.2768; IR (ATR) v = 3279.3, 2961.5, 2932.5, 2873.8, 1597.1, 1505.1, 1467.4, 1418.6, 1383.9, 1271.7, 1206.3, 1105.7, 1061.2, 1011.2, 982.5, 859.2, 755.1, 689.7, 660.6, 528.5 cm^{-1}.

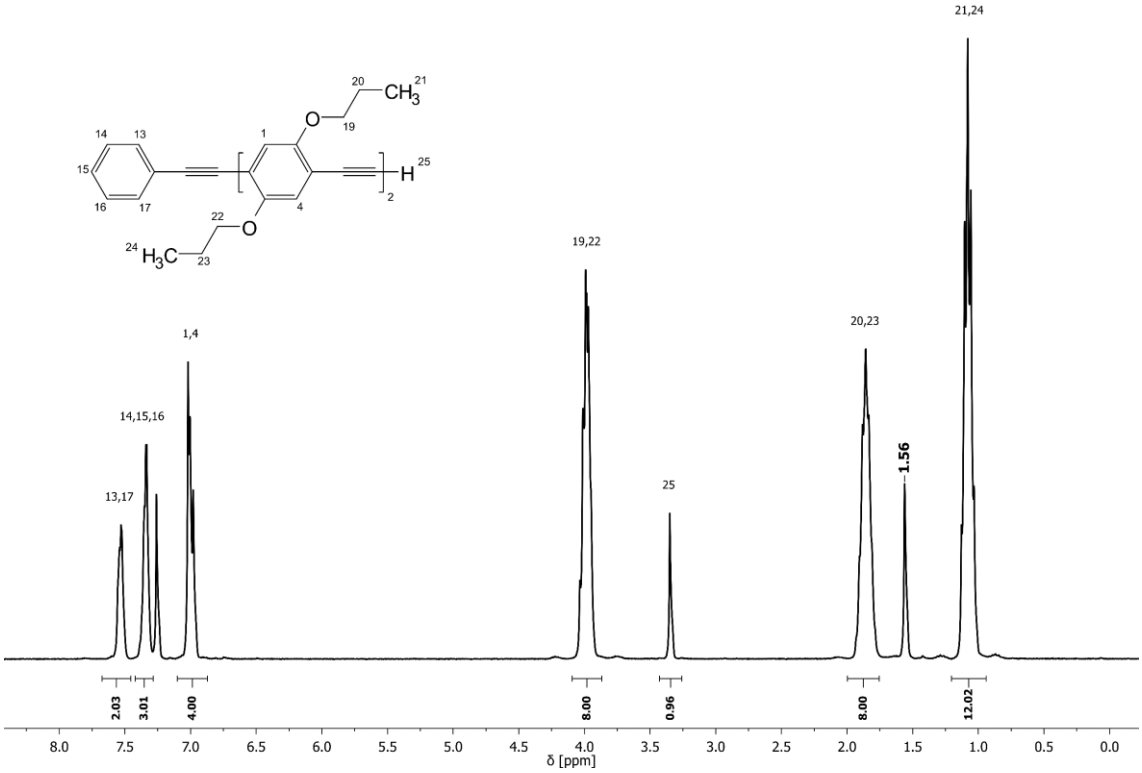
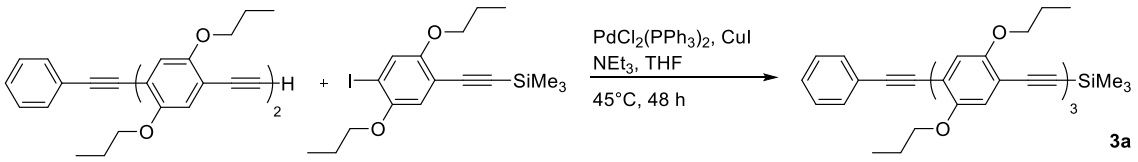


Figure 65: ^{1}H NMR spectrum of deprotected dimer **2b** with assigned signals.

Synthesis of trimethyl((4-((4-((4-(phenylethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)silane **3a**



1,4-*Bis*(propyloxy)-2-iodo-5-trimethylsilylacetylenebenzene **B1** (4.67 g, 11.2 mmol, 3.00 eq.), 5 mol% *bis*(triphenylphosphine) palladium(II) dichloride (131 mg, 187 µmol) and 5 mol% copper(I) iodide (35.6 mg, 187 µmol) were placed into a Schlenk flask. Under continuous argon flow, 130 mL dry THF and 5.20 mL dry triethylamine (3.78 g, 37.4 mmol, 10.0 eq.) were added and the mixture was stirred for 10 minutes. Subsequently, compound **2b** (2.00 g, 3.74 mmol, 1.00 eq.) in 20 mL THF was added dropwise with a syringe. The reaction mixture was stirred for 48 hours (2 days) at 45 °C, taken up in dichloromethane and washed with saturated NH_4Cl solution. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (cyclohexane/dichloromethane 2:1 → 1:1) and a flash silica column (cyclohexane/ethyl acetate 20:1) to yield the product as an orange solid (2.10 g, 68%). TLC (cyclohexane/dichloromethane 2:1) R_f = 0.16; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.65-7.44 (m, 2 H, 2 C**H**$_{aromatic}$C-C≡C), 7.43-7.28 (m, 3 H, 3 C**H**$_{aromatic}$), 7.02 (s, 4 H, 4 C**H**$_{aromatic}$CO), 6.98 (s, 1 H, 1 C**H**$_{aromatic}$COC-C≡C-Si), 6.95 (s, 1 H, 1 C**H**$_{aromatic}$C-C≡C-Si), 3.98 (ddt, J = 12.2, 10.2, 6.5 Hz, 12 H, 6 C**H**$_2$O), 2.03-1.67 (m, 12 H, 6 C**H**$_2$CH$_3$), 1.17-0.98 (m, 18 H, 6 C**H**$_3$), 0.26 (s, 9 H, 3 C**H**$_3$Si); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 154.27, 153.72, 153.59, 153.54, 153.44, 131.68, 126.46, 128.38, 123.60, 117.54, 117.48, 117.34, 117.28, 114.70, 114.46, 114.42, 114.38, 114.17, 101.30, 100.25, 95.00, 91.66, 91.63, 91.55, 86.10, 71.30, 71.25, 71.19, 22.85, 22.78, 10.69, 0.08; FAB of $C_{53}H_{62}O_6Si$ ($M+H^+$ = 823.3); HRMS (FAB) of $C_{53}H_{62}O_6Si$ [$M+H^+$] calc. 822.4310, found 822.4309; IR (ATR) v = 2961.7, 2873.6, 2146.8, 1510.8, 1470.2, 1420.1, 1389.2, 1274.1, 1212.3, 1042.8, 1024.3, 902.8, 837.5, 751.7, 687.8, 527.3 cm^{-1}.

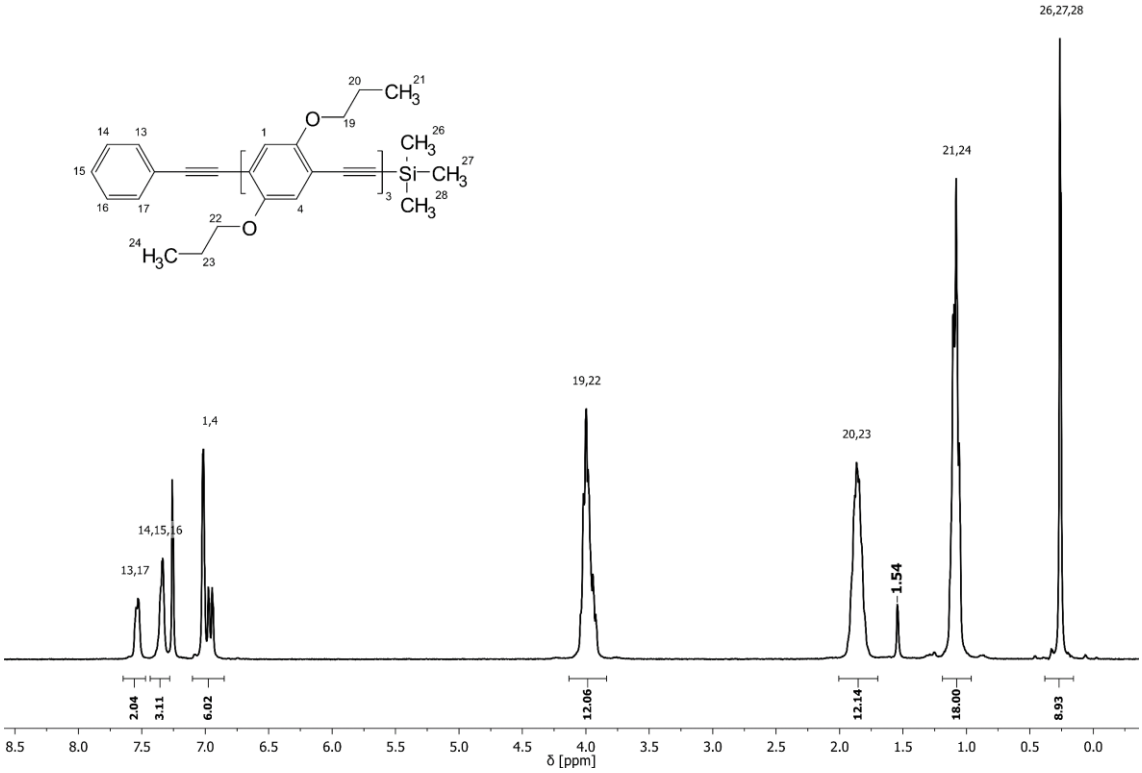
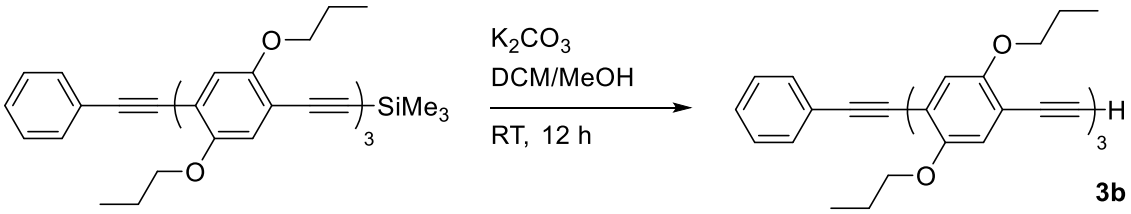


Figure 66: ^{1}H NMR spectrum of protected trimer **3a** with assigned signals.

Synthesis of 1-ethynyl-4-((4-((4-(phenylethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxybenzene **3b**



Compound **3a** (1.90 g, 2.31 mmol, 1.00 eq.) and two equivalents of potassium carbonate (639 mg, 4.62 mmol) were added to 100 mL dichloromethane and 100 mL methanol. The reaction mixture was degassed with argon and stirred overnight at room temperature and quenched with distilled water. The aqueous phase was extracted three times with dichloromethane, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (cyclohexane/ethyl acetate 20:1) to yield the product as a yellow solid (1.74 g, 98%). TLC (cyclohexane/dichloromethane 2:1) R_f = 0.14; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.66-7.45 (m, 2 H, 2 C**H**$_{aromatic}$C-C≡C), 7.45-7.29 (m, 3 H, 3 C**H**$_{aromatic}$), 7.11-6.91 (m, 6 H, 6 C**H**$_{aromatic}$CO), 4.14-3.87 (m, 12 H, 6 C**H**$_2$O), 3.35 (s, 1 H, 1 C≡C-**H**), 2.06-1.75 (m, 12 H, 6 C**H**$_2$CH$_3$), 1.23-0.94 (m, 18 H, 6 C**H**$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 154.19, 153.69, 153.55, 153.35, 131.63, 128.42, 128.34, 123.56, 118.08, 117.45, 117.33, 117.23, 117.20, 115.06, 114.52, 114.36, 114.26, 114.16, 112.69, 95.14, 94.98, 91.68, 91.58, 91.33, 86.09, 82.46, 80.11, 71.25, 71.09, 22.80, 22.73, 22.62, 10.62, 10.52; FAB of $C_{50}H_{54}O_6$ ($M+H^+$ = 751.6); HRMS (FAB) of $C_{50}H_{54}O_6$ [$M+H^+$] calc. 750.3915, found 750.3913; IR (ATR) v = 3288.0, 2958.7, 2932.8, 2873.3, 1595.7, 1508.1, 1469.9, 1423.0, 1385.9, 1272.5, 1204.2, 1062.8, 1041.1, 1020.9, 979.3, 906.5, 861.2, 769.9, 754.4, 687.7, 649.4, 528.2, 465.8 cm^{-1}.

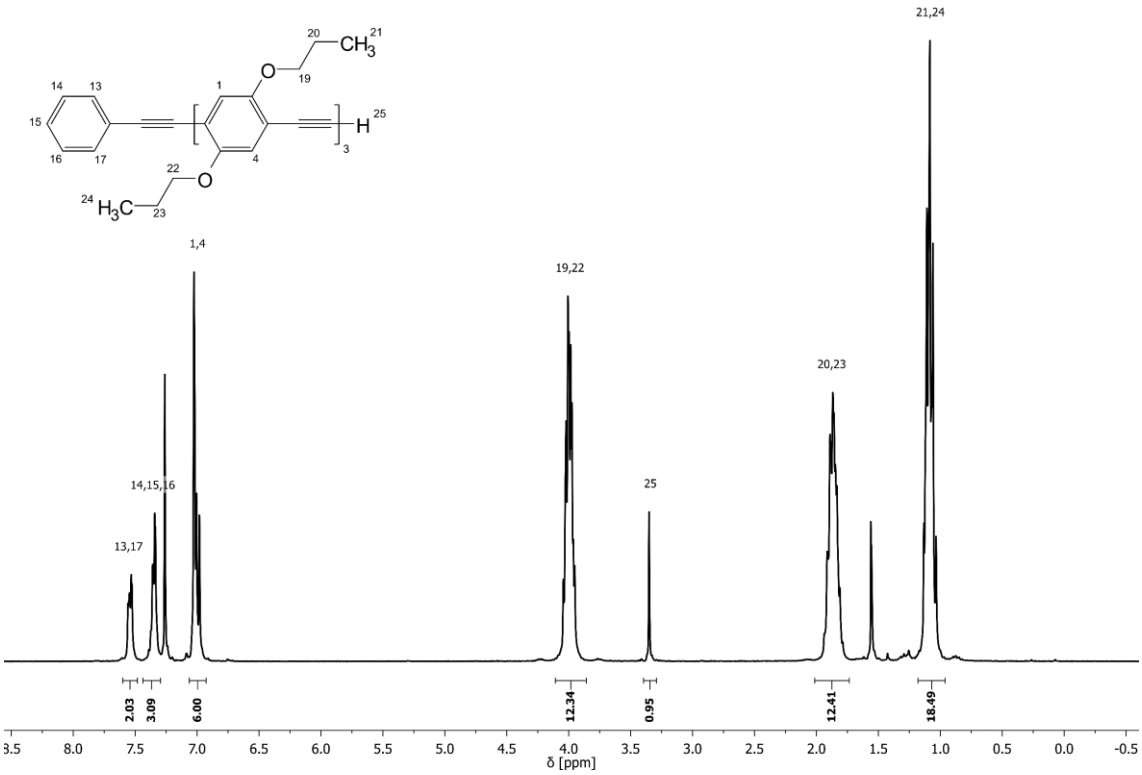
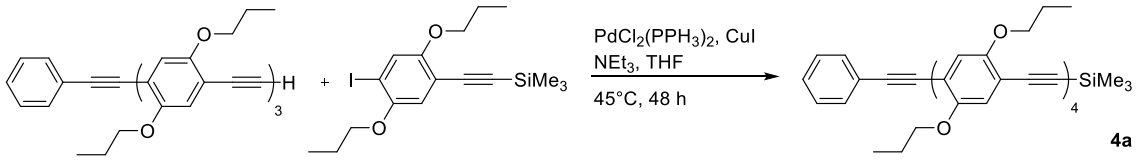


Figure 67: ^{1}H NMR spectrum of deprotected trimer **3b** with assigned signals.

Synthesis of trimethyl((4-((4-((4-(phenylethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)silane **4a**



1,4-*Bis*(propyloxy)-2-iodo-5-trimethylsilylacetylenebenzene **B1** (3.74 g, 9.00 mmol, 5.00 eq.), 5 mol% *bis*(triphenylphosphine) palladium(II) dichloride (63.1 mg, 90.0 µmol) and 5 mol% copper(I) iodide (17.1 mg, 90.0 µmol) were placed into a Schlenk flask and degassed three times. Under continuous argon flow, 70 mL dry THF and 2.49 mL dry triethylamine (1.82 g, 18.0 mmol, 10.0 eq.) were added and the mixture was stirred for 30 minutes. Subsequently, compound **3b** (1.35 g, 1.80 mmol, 1.00 eq.) in 25 mL THF was added dropwise with a syringe under continuous argon flow. The reaction mixture was stirred for 48 hours (2 days) at 45 °C, taken up in dichloromethane and washed with saturated NH_4Cl solution. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (cyclohexane/dichloromethane 2:1→1:2) and recrystallization from *n*-hexane to yield the product as a yellow solid (1.22 g, 65%). TLC (cyclohexane/dichloromethane 2:3) R_f = 0.34; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.64-7.47 (m, 2 H, 2 C**H**$_{aromatic}$C-C≡C), 7.44-7.30 (m, 3 H, 3 C**H**$_{aromatic}$), 7.12-6.83 (m, 8 H, 8 C**H**$_{aromatic}$CO), 4.18-3.80 (m, 16 H, 8 C**H**$_2$O), 1.97-1.74 (m, 16 H, 8 C**H**$_2$CH$_3$), 1.20-0.97 (m, 24 H, 8 C**H**$_3$), 0.26 (s, 9 H, 3 C**H**$_3$Si); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 154.29, 153.75, 153.62, 153.57, 153.46, 131.71, 128.47, 128.39, 123.63, 117.58, 117.52, 117.41, 117.38, 117.32, 114.73, 114.50, 114.47, 114.41, 114.19, 113.90, 101.31, 100.27, 95.02, 91.69, 91.66, 91.56, 86.12, 77.36, 71.34, 71.28, 71.23, 71.13, 22.87, 22.82, 22.80, 10.71, 10.69, 10.67, 10.65, 0.10; FAB of $C_{67}H_{78}O_8Si$ ($M+H^+$ = 1039.5); HRMS (FAB) of $C_{67}H_{78}O_8Si$ [$M+H^+$] calc. 1038.5466, found 1038.5463; IR (ATR) v = 2962.11, 2934.63, 2874.83, 2148.77, 1943.89, 1595.96, 1493.76, 1468.98, 1421.24, 1383.35, 1272.49, 1248.71, 1205.75, 1105.78, 1061.34, 1043.86, 1010.75, 981.55, 839.86, 755.09, 689.75, 636.42, 579.20, 527.86, 465.76 cm^{-1}.

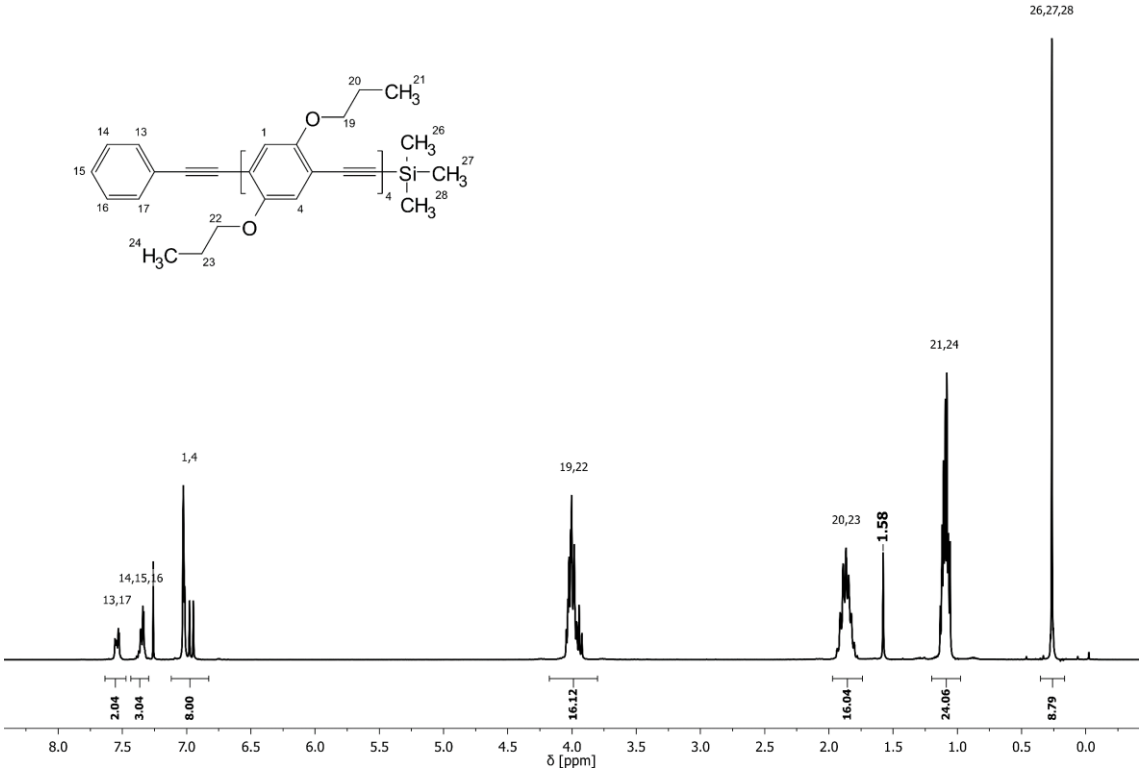
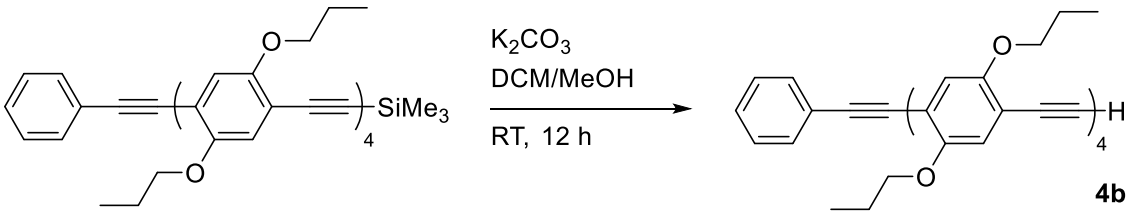


Figure 68: ^{1}H NMR spectrum of protected tetramer **4a** with assigned signals.

Synthesis of 1-ethynyl-4-((4-((4-((4-(phenylethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxybenzene **4b**



Compound **4a** (739 mg, 0.711 mmol, 1.00 eq.) and two equivalents of potassium carbonate (197 mg, 1.42 mmol) were added to 40 mL dichloromethane and 40 mL methanol. The reaction mixture was degassed with argon and stirred overnight at room temperature and quenched with distilled water. The aqueous phase was extracted three times with dichloromethane, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by recrystallization from *n*-hexane to yield the product as a yellow-brown solid (682 mg, 99%). TLC (cyclohexane/dichloromethane 2:3) R_f = 0.31; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.65-7.47 (m, 2 H, 2 C**H**$_{aromatic}$C-C≡C), 7.47-7.29 (m, 3 H, 3 C**H**$_{aromatic}$), 7.11-6.89 (m, 8 H, 8 C**H**$_{aromatic}$CO), 4.11-3.88 (m, 16 H, 8 C**H**$_2$O), 3.35 (s, 1 H, 1 C≡C-**H**), 2.01-1.66 (m, 16 H, 8 C**H**$_2$CH$_3$), 1.23-0.92 (m, 24 H, 8 C**H**$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 154.24, 153.74, 153.60, 153.57, 153.40, 131.70, 128.47, 128.39, 123.61, 118.15, 117.51, 117.39, 117.31, 117.25, 115.13, 114.58, 114.48, 114.43, 114.30, 114.19, 112.70, 95.02, 91.75, 91.72, 91.67, 91.65, 91.34, 86.11, 82.44, 80.16, 77.36, 71.33, 71.28, 71.22, 71.16, 22.86, 22.81, 22.79, 22.67, 10.70, 10.68, 10.57; FAB of $C_{64}H_{70}O_8$ ($M+H^+$ = 967.4); HRMS (FAB) of $C_{64}H_{70}O_8$ [$M+H^+$] calc. 966.5071, found 966.5070; IR (ATR) v = 3279.04, 2962.42, 2934.19, 2873.84, 2196.23, 2098.17, 1595.37, 1497.81, 1471.12, 1421.28, 1385.61, 1272.61, 1205.97, 1105.42, 1061.46, 1042.54, 1012.50, 982.24, 905.52, 857.47, 754.61, 689.37, 527.99, 462.05, 417.67 cm^{-1}.

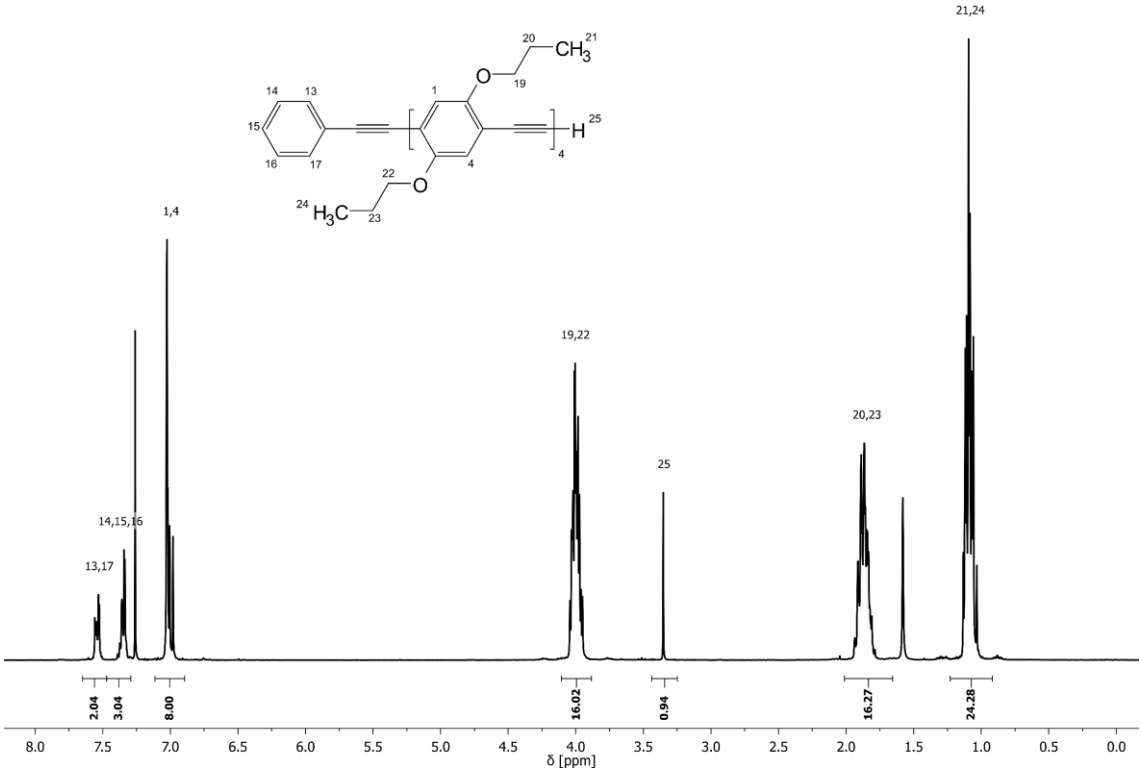
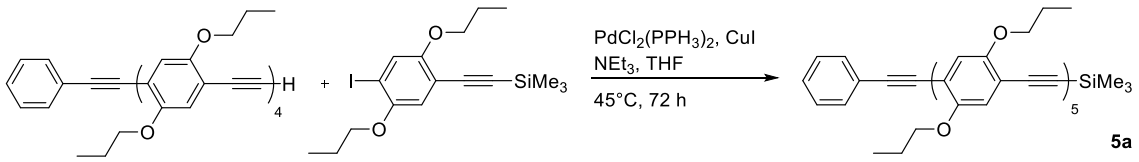


Figure 69: ^{1}H NMR spectrum of deprotected tetramer **4b** with assigned signals.

Synthesis of trimethyl((4-((4-((4-((4-((4-(phenylethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)silane **5a**



1,4-*Bis*(propyloxy)-2-iodo-5-trimethylsilylacetylenebenzene **B1** (968 mg, 2.33 mmol, 5.00 eq.), 5 mol% *bis*(triphenylphosphine) palladium(II) dichloride (16.3 mg, 23.3 µmol) and 5 mol% copper(I) iodide (4.4 mg, 23.3 µmol) were placed into a Schlenk flask and degassed three times. Under continuous argon flow, 20 mL dry THF and 645 µL dry triethylamine (471 mg, 4.65 mmol, 10.0 eq.) were added and the mixture was stirred for 30 minutes. Subsequently, compound **4b** (450 mg, 0.465 mmol, 1.00 eq.) in 15 mL THF was added dropwise with a syringe under continuous argon flow. The reaction mixture was stirred for 72 hours (3 days) at 45 °C, taken up in dichloromethane and washed with saturated NH_4Cl solution. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (cyclohexane/dichloromethane 1:1→1:3) and recrystallization from cyclohexane/ethyl acetate (10:1) to yield the product as a yellow solid (307 mg, 53%). TLC (dichloromethane/cyclohexane 2:1) R_f = 0.27; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.58-7.50 (m, 2 H, 2 C**H**$_{aromatic}$C-C≡C), 7.42-7.31 (m, 3 H, 3 C**H**$_{aromatic}$), 7.07-6.91 (m, 10 H, 10 C**H**$_{aromatic}$CO), 4.09-3.79 (m, 20 H, 10 C**H**$_2$O), 2.05-1.71 (m, 20 H, 10 C**H**$_2$CH$_3$), 1.23-0.88 (m, 30 H, 10 C**H**$_3$), 0.26 (s, 9 H, 3 C**H**$_3$Si); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 154.27, 153.72, 153.59, 153.56, 153.44, 131.68, 128.45, 128.38, 123.60, 117.55, 117.49, 117.37, 117.35, 117.28, 114.70, 114.45, 114.39, 114.17, 113.88, 101.30, 100.24, 95.00, 91.71, 91.55, 86.10, 77.48, 77.16, 76.84, 71.30, 71.25, 71.20, 71.10, 22.84, 22.80, 22.78, 10.67, 10.65, 10.63, 0.07; FAB of $C_{81}H_{94}O_{10}Si$ ($M+H^+$ = 1256.2); IR (ATR) v = 2960.00, 2934.39, 2870.20, 2148.20, 1594.34, 1511.03, 1463.82, 1423.93, 1383.07, 1270.73, 1247.60, 1204.43, 1062.33,

1040.10, 1012.94, 982.26, 902.26, 860.46, 839.41, 751.72, 685.88, 626.99, 527.44, 468.07 cm^{-1}.

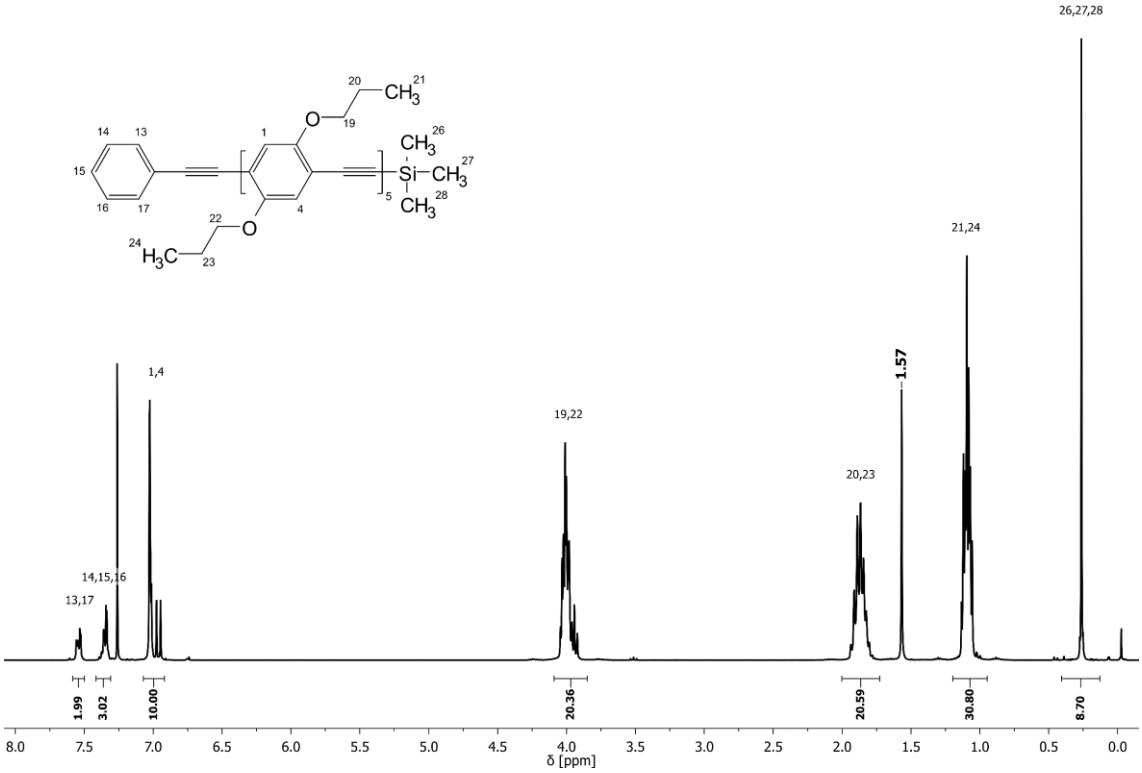
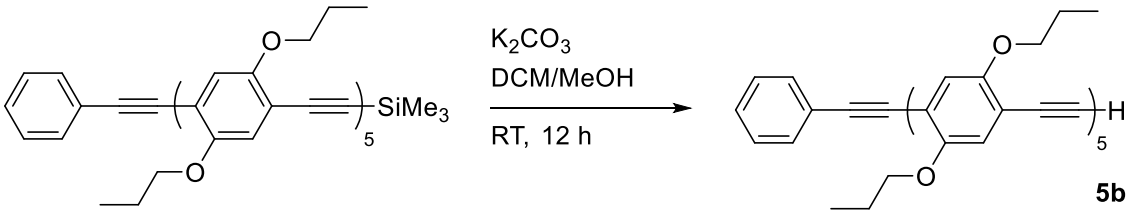


Figure 70: ^{1}H NMR spectrum of protected pentamer **5a** with assigned signals.

Synthesis of 1-ethynyl-4-((4-((4-((4-(phenylethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxybenzene **5b**



Compound **5a** (125 mg, 99.5 µmol, 1.00 eq.) and two equivalents of potassium carbonate (27.5 mg, 0.199 mmol) were added to 12 mL dichloromethane and 6 mL methanol. The reaction mixture was degassed with argon and stirred overnight at room temperature and quenched with distilled water. The aqueous phase was extracted three times with dichloromethane, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (dichloromethane/cyclohexane 3:1) to yield the product as a yellow solid (116 mg, 98%). TLC (dichloromethane/cyclohexane 2:1) R_f = 0.16; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.63-7.47 (m, 2 H, 2 C**H**$_{aromatic}$C-C≡C), 7.43-7.32 (m, 3 H, 3 C**H**$_{aromatic}$), 7.11-6.91 (m, 10 H, 10 C**H**$_{aromatic}$CO), 4.15-3.87 (m, 20 H, 10 C**H**$_2$O), 3.35 (s, 1 H, 1 C≡C-**H**), 2.01-1.75 (m, 20 H, 10 C**H**$_2$CH$_3$), 1.19-0.92 (m, 30 H, 10 C**H**$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 154.23, 153.74, 153.60, 153.58, 153.39, 131.69, 128.46, 128.38, 123.61, 118.15, 117.51, 117.39, 117.31, 117.25, 115.13, 114.58, 114.49, 114.44, 114.31, 114.19, 112.71, 95.01, 91.72, 91.67, 91.34, 86.11, 82.44, 80.16, 71.32, 71.27, 71.22, 71.16, 22.85, 22.79, 22.66, 10.67, 10.57; FAB of $C_{78}H_{86}O_{10}$ ($M+H^+$ = 1184.3); IR (ATR) v = 3288.46, 2959.22, 2933.08, 2873.56, 1595.35, 1511.17, 1470.04, 1424.66, 1385.03, 1273.01, 1204.34, 1104.57, 1062.42, 1039.80, 1019.72, 979.46, 905.22, 860.98, 768.48, 754.29, 688.02, 648.90, 527.53, 464.63 cm^{-1}.

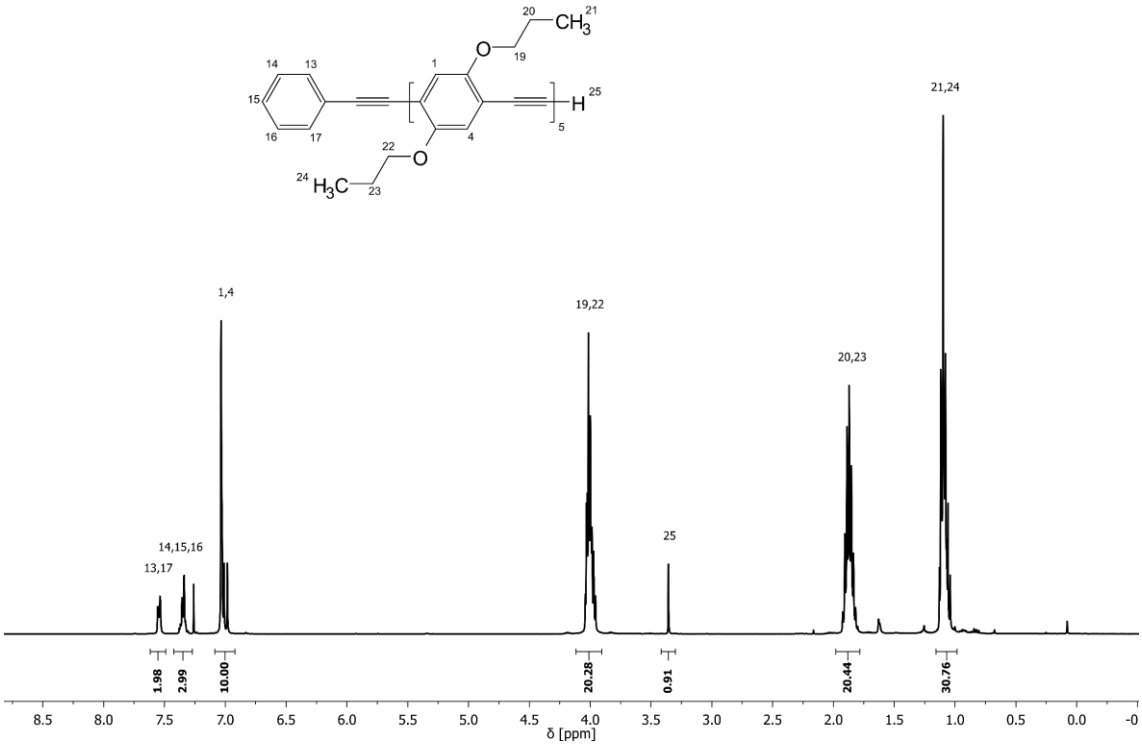
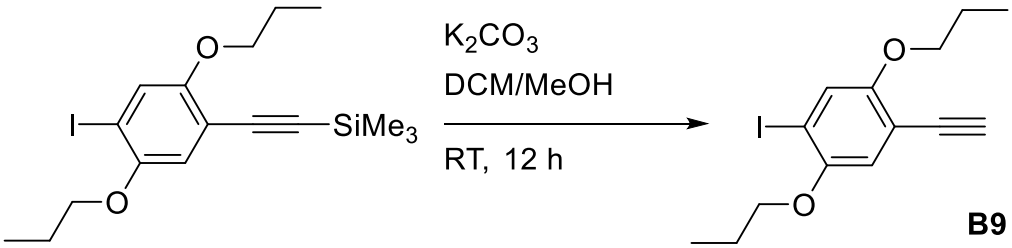


Figure 71: ^{1}H NMR spectrum of deprotected pentamer **5b** with assigned signals.

6.3.4 Oligomerization Approach

Synthesis of 1-ethynyl-4-iodo-2,5-dipropoxybenzene **B9**



1,4-*Bis*(propyloxy)-2-iodo-5-trimethylsilylacetylenebenzene (1.00 g, 2.40 mmol, 1.00 eq.) and two equivalents of potassium carbonate (1.65 g, 4.81 mmol) were added to 50 mL dichloromethane and 50 mL methanol. The reaction mixture was degassed with argon and stirred overnight at room temperature and quenched with distilled water. The aqueous phase was extracted three times with dichloromethane, dried over Na_2SO_4, filtered and concentrated under reduced pressure to yield the product as a yellow solid (818 mg, 99%). TLC (cyclohexane/ dichloromethane 4:1) R_f = 0.43; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.29, 6.87 (2 s, 2 H, 2 C**H**$_{aromatic}$), 3.92 (dt, J = 8.6, 6.5 Hz, 4 H, 2 C**H$_2$**O), 3.30 (s, 1 H, 1 C≡C-**H**), 1.95-1.73 (m, 4 H, 2 C**H$_2$**CH_3), 1.07, 1.06 (2 t, J = 7.6 Hz, 6 H, 2 C**H$_3$**); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 154.91, 151.78, 123.97, 116.82, 112.42, 88.42, 81.91, 79.76, 71.66, 71.43, 22.68, 22.64, 10.81, 10.54; FAB of $C_{14}H_{17}IO_2$ ($M+H^+$ = 345.1); HRMS (FAB) of $C_{14}H_{17}IO_2$ [$M+H^+$] calc. 344.0268, found 344.0266; IR (ATR) v = 3267.6, 2953.8, 2907.9, 2870.5, 1587.3, 1485.3, 1456.5, 1367.5, 1264.8, 1208.8, 1147.4, 1011.4, 907.2, 857.6, 818.7, 767.0, 722.2, 685.8, 658.7, 643.0, 441.9, 416.8 cm^{-1}.

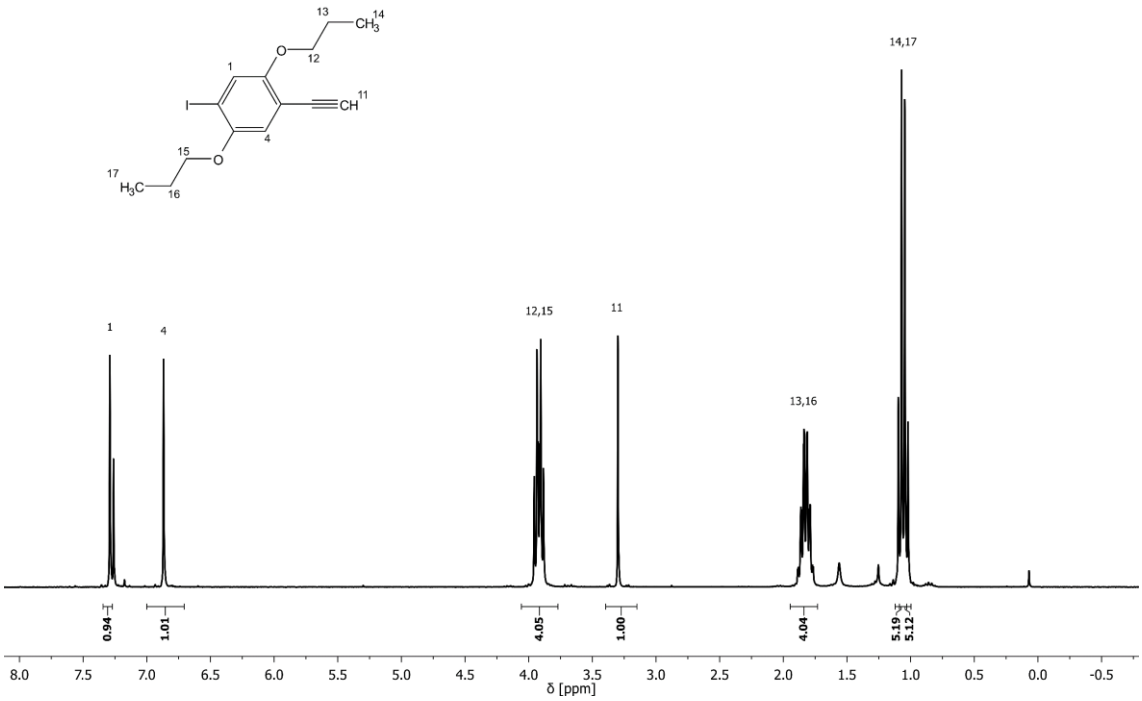
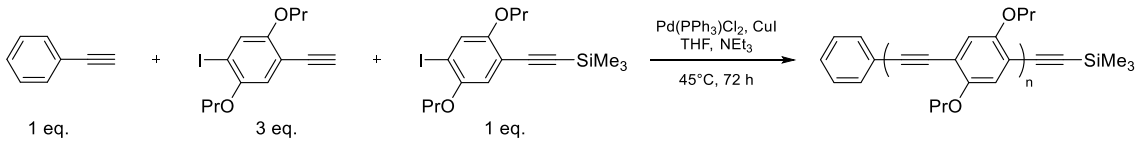


Figure 72: ^{1}H NMR spectrum of building block **B9** with assigned signals.

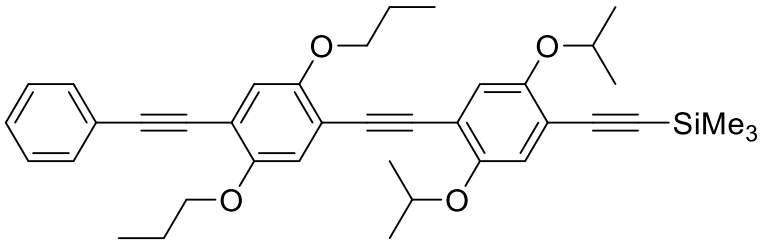
<u>The direct oligomerization approach to **O1**</u>



Phenylacetylene (106 µL, 98.9 mg, 0.968 mmol, 1.00 eq.), deprotected building block **B9** (1.00 g, 2.91 mmol, 3.00 eq.) and building block **B1** (403 mg, 0.968 mmol, 1.00 eq.) were introduced in a Sonogashira reaction with 5 mol% *bis*(triphenylphosphine) palladium(II)dichloride (34.0 mg, 48.4 µmol) and 5 mol% copper(I)iodide (9.2 mg, 48.4 µmol). They were placed into a Schlenk flask and degassed. Under continuous argon flow, 50 mL dry THF and 0.88 mL dry triethylamine (650 mg, 6.40 mmol, 10.0 eq.) were added and the mixture was stirred for 72 hours (3 days) at 45 °C. The reaction mixture was taken up in dichloromethane and washed with saturated NH_4Cl solution. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was analyzed by SEC (Figure 27).

6.3.5. Syntheses of Sequence-Defined Rod-Like Oligomers

Synthesis of ((2,5-diisopropoxy-4-((4-(phenylethynyl)-2,5-dipropoxyphenyl) ethynyl)phenyl)ethynyl)trimethylsilane **2c**



1,4-*Bis*(isopropyloxy)-2-iodo-5-trimethylsilylacetylenebenzene **B2** (5.88 g, 14.1 mmol, 3.00 eq.), 5 mol% *bis*(triphenylphosphine) palladium(II) dichloride (165 mg, 0.236 mmol) and 5 mol% copper(I) iodide (44.9 mg, 0.236 mmol) were placed into a Schlenk flask and degassed three times. Under continuous argon flow, 100 mL dry THF and 6.57 mL (4.77 g, 47.1 mmol, 10.0 eq.) dry triethylamine were added and the mixture was stirred for 10 minutes. Subsequently, 1-ethynyl-4-(phenylethynyl)-2,5-dipropoxybenzene **1b** (1.50 g, 4.71 mmol, 1.00 eq.) in 50 mL THF was added dropwise with a syringe. The reaction mixture was stirred for 72 hours (3 days) at 45 °C, taken up in dichloromethane and washed with saturated NH_4Cl solution. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (cyclohexane/dichloromethane 3:1 → 3:2) and a flash silica column (cyclohexane/ethyl acetate 20:1) to yield the product as a yellow solid (1.84 g, 64%). TLC (cyclohexane/dichloromethane 2:1) R_f = 0.31; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) =7.61-7.46 (m, 2 H, 2 C**H**$_{aromatic}$C-C≡C), 7.43-7.29 (m, 3 H, 3 C**H**$_{aromatic}$), 7.08-6.91 (m, 4 H, 4 C**H**$_{aromatic}$CO), 4.50 (dhept, *J* = 18.4, 6.2 Hz, 2 H, 2 C**H(**$CH_3)_2$), 4.00 (dt, *J* = 6.5, 4.7 Hz, 4 H, 2 C**H$_2$**O), 1.86 (dp, *J* = 6.9, 1.9 Hz, 4 H, 2 C**H$_2$**CH_3), 1.36 (dd, *J* = 7.1, 6.0 Hz, 12 H, 4 C**H$_3$**CH), 1.10, 1.08 (2 t, *J* = 7.2 Hz, 6 H, 2 C**H$_3$**CH_2), 0.26 (s, 9 H, 3 C**H$_3$**Si); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 153.71, 153.61, 152.92, 131.66, 128.44, 123.60, 121.86, 121.09, 117.45, 117.25, 116.57, 116.15, 114.36, 114.25, 101.61, 100.04, 94.99, 91.65, 91.38, 86.08, 73.54, 73.11, 71.27, 22.83, 22.34, 10.70, 0.06; FAB of $C_{39}H_{46}O_4Si$ ($M+H^+$ = 607.3); HRMS (FAB) of $C_{39}H_{46}O_4Si$ [$M+H^+$] calc. 606.3165,

found 606.3164; IR (ATR) v = 2965.3, 2932.5, 2875.7, 2150.2, 1595.6, 1505.1, 1488.3, 1418.1, 1382.8, 1330.7, 1271.0, 1249.1, 1204.2, 1137.2, 1105.3, 1060.6, 1010.0, 962.1, 889.0, 839.6, 756.8, 690.7, 637.6, 527.7, 466.2 cm^{-1}.

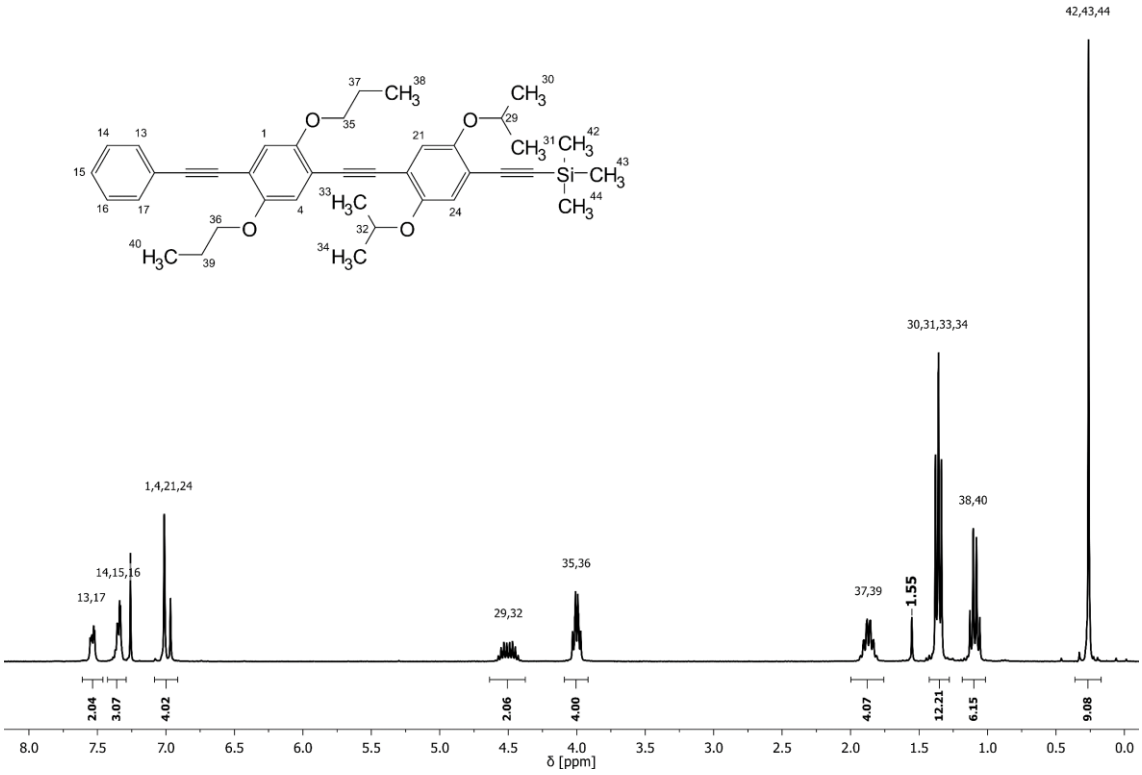
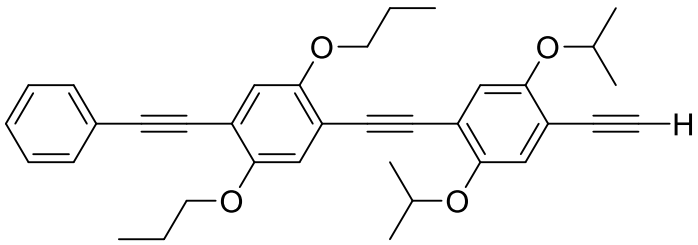


Figure 73: ^{1}H NMR spectrum of protected sequence-defined dimer **2c** with assigned signals.

Synthesis of 1-ethynyl-2,5-diisopropoxy-4-((4-(phenylethynyl)-2,5-dipropoxyphenyl)ethynyl)benzene **2d**



Compound **2c** (800 mg, 1.32 mmol, 1.00 eq.) and two equivalents of potassium carbonate (365 mg, 2.64 mmol) were placed in a Schlenk flask and degassed three times. Under continuous argon flow 40 mL dichloromethane and 40 mL methanol were added. The reaction mixture was stirred overnight at room temperature under argon atmosphere and quenched with distilled water. The aqueous phase was extracted three times with dichloromethane, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (cyclohexane/ethyl acetate 20:1) to yield the product as an orange solid (688 mg, 98%). TLC (cyclohexane/ dichloromethane 2:1) R_f = 0.28; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.60-7.46 (m, 2 H, 2 C**H**$_{aromatic}$C-C≡C), 7.46-7.30 (m, 3 H, 3 C**H**$_{aromatic}$), 7.11-6.91 (m, 4 H, 4 C**H**$_{aromatic}$CO), 4.66-4.41 (m, 2 H, 2 C**H(**$CH_3)_2$)), 4.11-3.90 (m, 4 H, 2 C**H**$_2$O), 3.32 (s, 1 H, 1 C≡C-**H**), 2.00-1.77 (m, 4 H, 4 C**H**$_2$$CH_3$), 1.37 (dd, J = 6.1, 2.2 Hz, 12 H, 4 C**H**$_3$CH), 1.23-0.97 (m,6 H, 2 C**H**$_3$$CH_2$), ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 153.47, 153.37, 153.30, 152.30, 131.35, 128.26, 128.19, 123.34, 121.30, 120.13, 117.05, 116.87, 116.61, 114.34, 114.05, 113.98, 94.86, 91.42, 91.35, 86.04, 82.51, 80.11, 72.78, 72.54, 70.85, 70.82, 22.58, 22.55, 22.03, 21.94, 10.47, 10.42, FAB of $C_{36}H_{38}O_4$ ($M+H^+$ = 535.3); HRMS (FAB) of $C_{36}H_{38}O_4$ [$M+H^+$] calc. 534.2770, found 534.2771; IR (ATR) v = 3285.7, 2970.9, 2932.2, 2874.6, 1596.1, 1505.2, 1487.3, 1417.5, 1383.0, 1330.5, 1271.3, 1203.5, 1135.2, 1105.6, 1060.5, 1011.7, 957.6, 862.6, 754.6, 689.4, 664.0, 611.7, 527.8, 459.1 cm^{-1}.

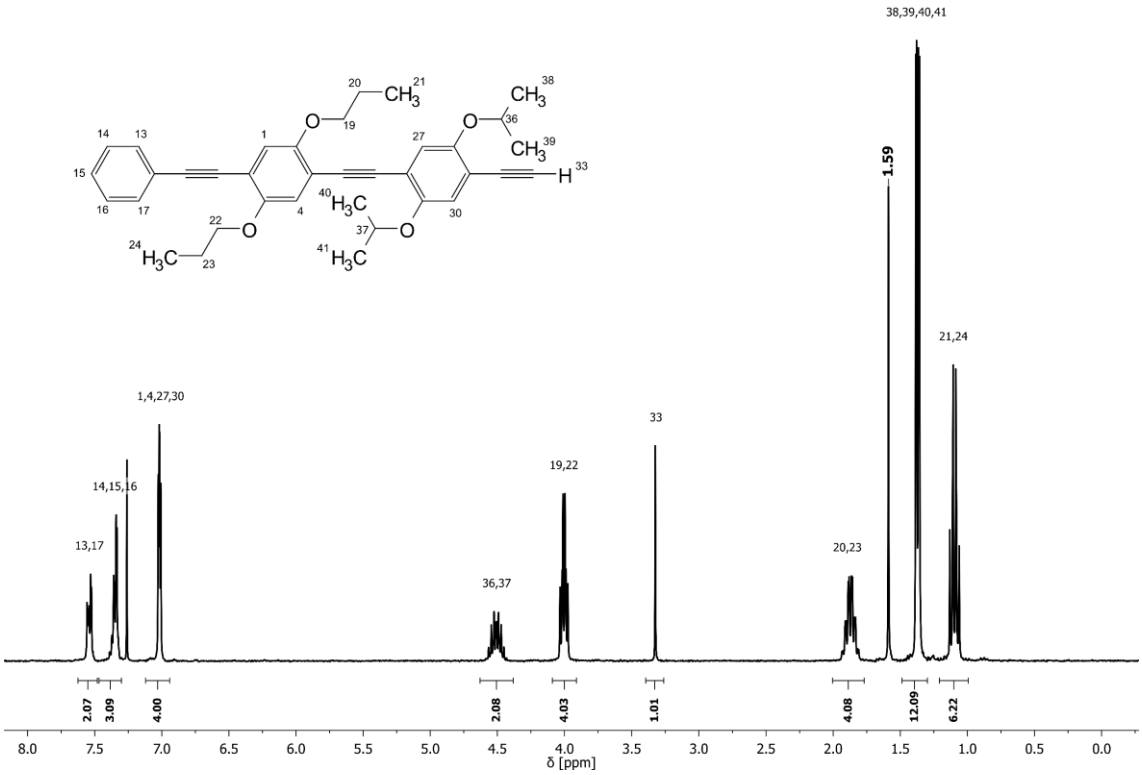
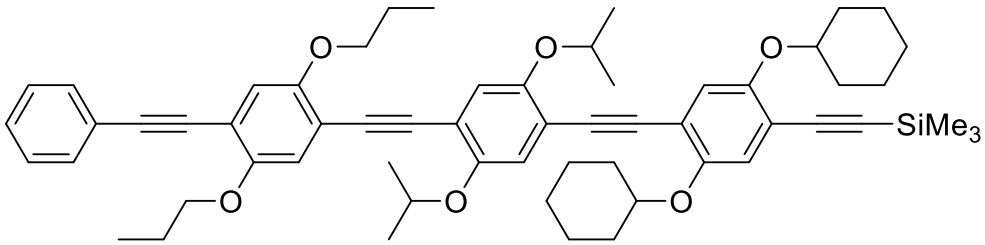


Figure 74: ^{1}H NMR spectrum of deprotected sequence-defined dimer **2d** with assigned signals.

Synthesis of ((2,5-*bis*(cyclohexyloxy)-4-((2,5-diisopropoxy-4-((4-(phenylethynyl)-2,5-dipropoxyphenyl)ethynyl)phenyl)ethynyl)phenyl)ethynyl)trimethylsilane **3c**



1,4-*Bis*(cyclohexyloxy)-2-iodo-5-trimethylsilylacetylenebenzene **B3** (6.76 g, 14.4 mmol, 5.00 eq.), 10 mol% *bis*(triphenylphosphine) palladium(II) dichloride (202 mg, 288 µmol) and 2.5 mol% copper(I) iodide (13.7 mg, 72.0 µmol) were placed into a Schlenk flask and degassed three times. Under continuous argon flow, 60 mL dry THF and 3.99 mL dry triethylamine (2.91 g, 28.8 mmol, 10.0 eq.) were added and the mixture was stirred for 10 minutes. Subsequently, compound **2d** (1.54 g, 2.88 mmol, 1.00 eq.) in 50 mL THF was added dropwise with a syringe. The reaction mixture was stirred for 72 hours (3 days) at 45 °C, taken up in dichloromethane and washed with saturated NH_4Cl solution. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (dichloromethane/ cyclohexane 2:1) and a further silica column (cyclohexane/ethyl acetate 20:1 → 15:1) to yield the product as a yellow solid (1.40 g, 54%). TLC (cyclohexane/ dichloromethane 2:1) R_f = 0.17; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.58-7.51 (m, 2 H, 2 C**H**$_{aromatic}$C-C≡C), 7.41-7.30 (m, 3 H, 3 C**H**$_{aromatic}$), 7.08–6.99 (m, 5 H, 5 C**H**$_{aromatic}$CO), 6.97 (s, 1 H, 1 C**H**$_{aromatic}$C-C≡C-Si), 4.66-4.44 (m, 2 H, 2 C**H(**$CH_3)_2$)), 4.37-4.17 (m, 2 H, 2 C**H**CH_2), 4.10-3.91 (m, 4 H, 2 C**H$_2$**O), 2.02-1.75 (m, 12 H, 2 C**H$_2$**CH_3, 4 C**H**$_{equatorial}$CHO, 4 C**H**$_{equatorial}$$CH_2$CHO), 1.75-1.56 (m, 6 H, 4 C**H**$_{axial}$CHO, 2 C**H**$_{equatorial}$$CH_2CH_2$CHO), 1.46-1.31 (m, 18 H, 4 C**H$_3$**CH, 4 C**H**$_{axial}$$CH_2$CHO, 2 C**H**$_{axial}$$CH_2CH_2$CHO), 1.10 (dt, J = 7.4, 4.9 Hz, 6 H, 2 C**H$_3$**CH_2), 0.26 (s, 9 H, 3 C**H$_3$**Si), ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 153.71, 153.60, 153.30, 152.87, 152.85, 152.65, 131.68, 128.45, 128.38, 123.58, 121.57, 121.19, 121.04, 120.91, 117.41, 117.23, 116.52, 116.30, 116.24, 116.03, 114.39, 114.20, 101.66, 99.93, 95.00, 91.81, 91.62, 91.53, 91.41, 86.09, 77.89, 77.37, 73.19, 73.14, 71.27, 71.23, 31.90, 31.77, 25.84, 25.82, 23.60, 23.35, 22.85, 22.81, 22.39, 22.36,

10.74, 10.70, 0.08; FAB of $C_{59}H_{70}O_6Si$ ($M+H^+ = 903.6$); HRMS (FAB) of $C_{59}H_{70}O_6Si$ [$M+H^+$] calc. 902.4942, found 902.4943; IR (ATR) v = 2931.5, 2856.4, 2149.7, 1595.6, 1485.6, 1414.3, 1383.9, 1270.8, 1248.4, 1197.6, 1106.1, 1040.2, 1015.8, 963.2, 887.7, 839.1, 755.1, 689.2, 646.8, 524.7, 460.8 cm^{-1}.

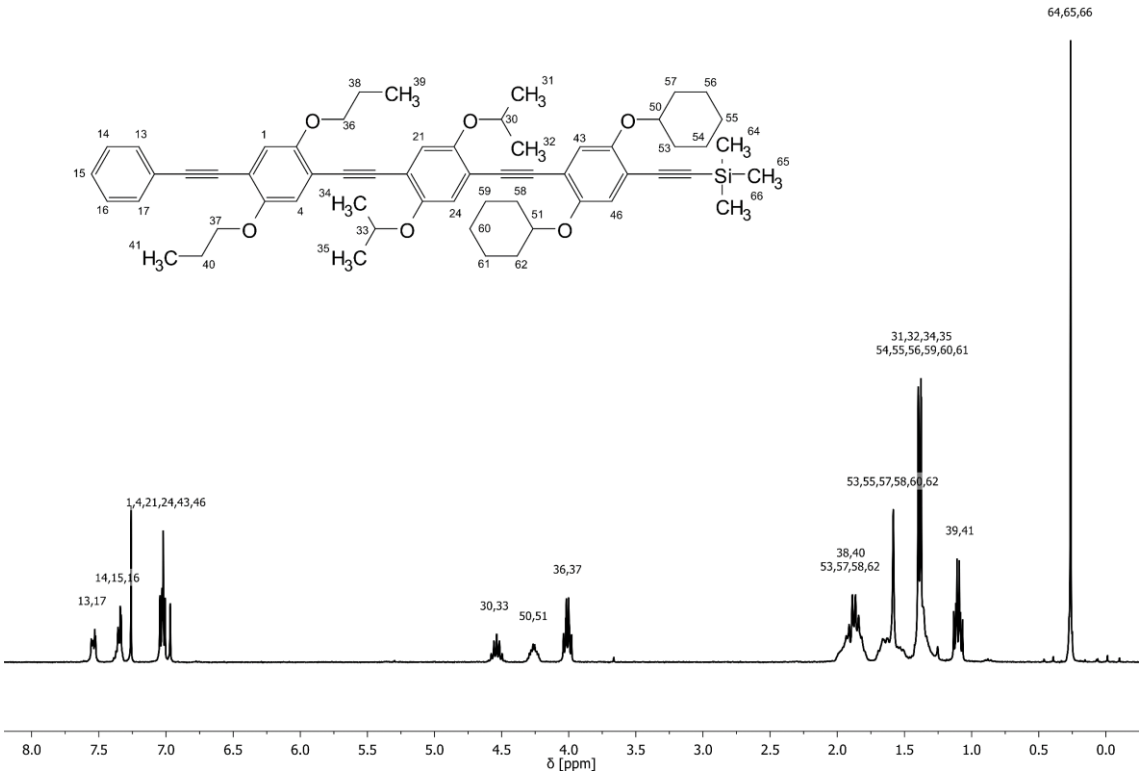
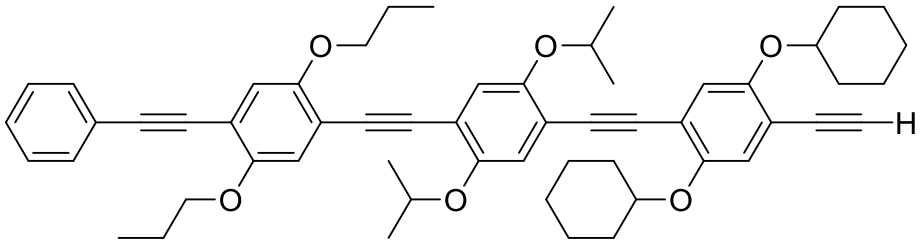


Figure 75: ^1H NMR spectrum of protected sequence-defined trimer **3c** with assigned signals.

Synthesis of sequence-defined, deprotected trimer **3d**



Compound **3c** (1.35 g, 1.49 mmol, 1.00 eq.) and two equivalents of potassium carbonate (413 mg, 2.99 mmol) were placed in a Schlenk flask and degassed three times. Under continuous argon flow 70 mL dichloromethane and 70 mL methanol were added. The reaction mixture was stirred overnight at room temperature under argon atmosphere and quenched with distilled water. The aqueous phase was extracted three times with dichloromethane, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (cyclohexane/ethyl acetate 8:1) to yield the product as an orange solid (1.22 g, 98%). TLC (cyclohexane/ dichloromethane 2:1) R_f = 0.29; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.59-7.49 (m, 2 H, 2 C**H**$_{aromatic}$C-C≡C), 7.43-7.30 (m, 3 H, 3 C**H**$_{aromatic}$), 7.10-6.97 (m, 6 H, 6 C**H**$_{aromatic}$CO), 4.65-4.45 (m, 2 H, 2 C**H(**$CH_3)_2$)), 4.35-4.14 (m, 2 H, 2 C**H**CH_2), 4.10-3.92 (m, 4 H, 2 C**H$_2$**O), 3.32 (s, 1 H, 1 C≡C-**H**), 2.10-1.75 (m, 12 H, 2 C**H$_2$**CH_3, 4 C**H**$_{equatorial}$CHO, 4 C**H**$_{equatorial}$$CH_2$CHO), 1.73-1.48 (m, 6 H, 4 C**H**$_{axial}$CHO, 2 C**H**$_{equatorial}$$CH_2CH_2$CHO), 1.47-1.23 (m, 18 H, 4 C**H$_3$**CH, 4 C**H**$_{axial}$$CH_2$CHO, 2 C**H**$_{axial}$$CH_2CH_2$CHO), 1.10 (dt, J = 7.4, 4.8 Hz, 6 H, 2 C**H$_3$**CH_2), ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 153.73, 153.63, 153.38, 152.91, 152.39, 131.70, 128.47, 128.40, 123.60, 121.55, 121.25, 121.07, 120.46, 117.46, 117.26, 116.90, 116.35, 116.25, 114.47, 114.39, 114.25, 95.02, 91.79, 91.57, 91.47, 86.10, 82.22, 80.44, 78.03, 77.36, 73.24, 73.19, 71.30, 71.27, 31.91, 25.82, 25.76, 23.75, 23.61, 22.86, 22.83, 22.41, 22.38, 10.75, 10.71; FAB of $C_{56}H_{62}O_6$ (M+H$^+$ = 831.5); HRMS (FAB) of $C_{56}H_{62}O_6$ [M+H$^+$] calc. 830.4546, found 830.4547; IR (ATR) v = 3279.97, 2931.27, 2856.32, 1596.03, 1485.92, 1450.30, 1415.15, 1383.81, 1370.35, 1270.94, 1197.47, 1137.72, 1105.86, 1040.21, 1015.97, 962.78, 886.50, 859.45, 754.92, 689.36, 645.52, 527.72, 457.80 cm^{-1}.

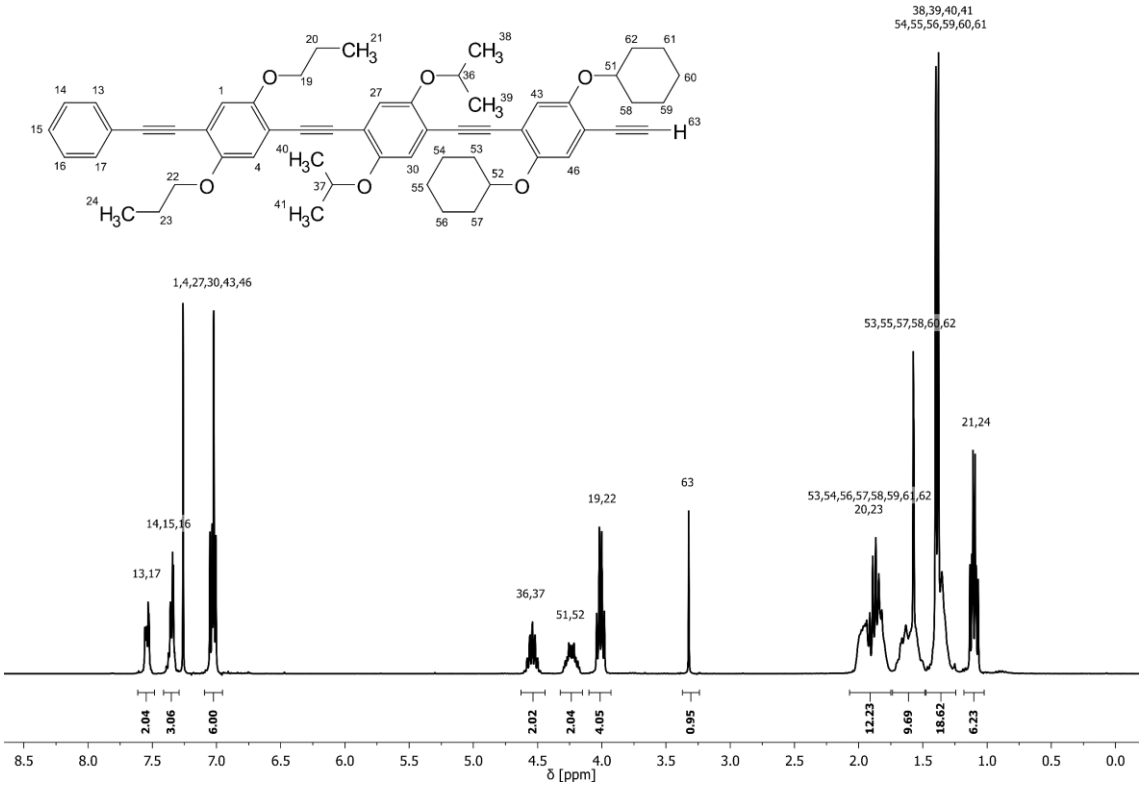
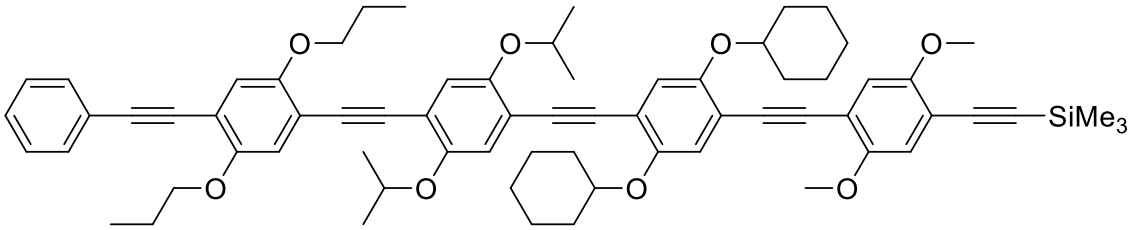


Figure 76: ^{1}H NMR spectrum of deprotected sequence-defined trimer **3d** with assigned signals.

Synthesis of ((4-((2,5-*bis*(cyclohexyloxy)-4-((2,5-diisopropoxy-4-((4-(phenylethynyl)-2,5-dipropoxyphenyl)ethynyl)phenyl)ethynyl)phenyl)ethynyl)-2,5-dimethoxyphenyl)ethynyl)trimethylsilane **4c**



1,4-*Bis*(methoxy)-2-iodo-5-trimethylsilylacetylenebenzene **B4** (2.60 g, 7.22 mmol, 5.00 eq.), 10 mol% *bis*(triphenylphosphine) palladium(II) dichloride (101 mg, 0 144 mmol) and 2.5 mol% copper(I) iodide (6.9 mg, 36.1 µmol) were placed into a Schlenk flask and degassed three times. Under continuous argon flow, 60 mL dry THF and 2.00 mL dry triethylamine (1.46 g, 14.4 mmol, 10.0 eq.) were added and the mixture was stirred for 10 minutes. Subsequently, compound **3d** (1.20 g, 1.44 mmol, 1.00 eq.) in 40 mL THF was added dropwise with a syringe. The reaction mixture was stirred for 72 hours (3 days) at 45 °C, taken up in dichloromethane and washed with saturated NH_4Cl solution. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (dichloromethane/ cyclohexane 1:1 → 9:1) to yield the product as a yellow solid (568 mg, 37%). TLC (dichloromethane/cyclohexane 3:1) R_f = 0.15; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.58-7.49 (m, 2 H, 2 C**H**$_{aromatic}$C-C≡C), 7.39-7.31 (m, 3 H, 3 C**H**$_{aromatic}$), 7.11-6.90 (m, 8 H, 8 C**H**$_{aromatic}$CO), 4.55 (hept, J = 6.1 Hz, 2 H, 2 C**H**$(CH_3)_2$)), 4.38-4.23 (m, 2 H, 2 C**H**CH_2), 4.08-3.95 (m, 4 H, 2 C**H**$_2$O), 3.88, 3.86 (s, 6 H, 2 C**H**$_3$O), 2.07-1.79 (m, 12 H, 2 C**H**$_2CH_3$, 4 C**H**$_{equatorial}$CHO, 4 C**H**$_{equatorial}CH_2$CHO), 1.77-1.48 (m, 6 H, 4 C**H**$_{axial}$CHO, 2 C**H**$_{equatorial}CH_2CH_2$CHO), 1.48-1.27 (m, 18 H, 4 C**H**$_3$CH, 4 C**H**$_{axial}CH_2$CHO, 2 C**H**$_{axial}CH_2CH_2$CHO), 1.10 (dt, J = 7.4, 4.5 Hz, 6 H, 2 C**H**$_3CH_2$), 0.28 (s, 9 H, 3 C**H**$_3$Si); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 154.43, 153.80, 153.74, 153.63, 152.91, 152.89, 152.81, 152.66, 131.70, 128.46, 128.39, 123.61, 121.24, 121.08, 121.00, 120.72, 117.47, 117.28, 116.47, 116.36, 116.27, 116.24, 115.98, 115.80, 114.43, 114.24, 114.12, 113.18, 101.10, 100.58, 95.01, 92.24, 91.83, 91.77, 91.68, 91.43, 91.07, 86.11, 77.95, 77.91, 73.22, 73.18, 71.31, 71.27, 56.52,

56.49, 31.95, 31.86, 25.90, 25.85, 23.64, 23.53, 22.86, 22.83, 22.43, 22.39, 10.75, 10.71, 0.16; FAB of $C_{69}H_{78}O_8Si$ ($M+H^+$ = 1064.3); IR (ATR) v = 2931.1, 2855.7, 2148.8, 1717.1, 1595.9, 1505.5, 1486.7, 1464.4, 1415.4, 1384.5, 1272.2, 1248.7, 1207.1, 1106.3, 1038.6, 1017.0, 963.5, 856.5, 840.5, 755.4, 690.1, 633.0, 527.4, 457.4 cm^{-1}.

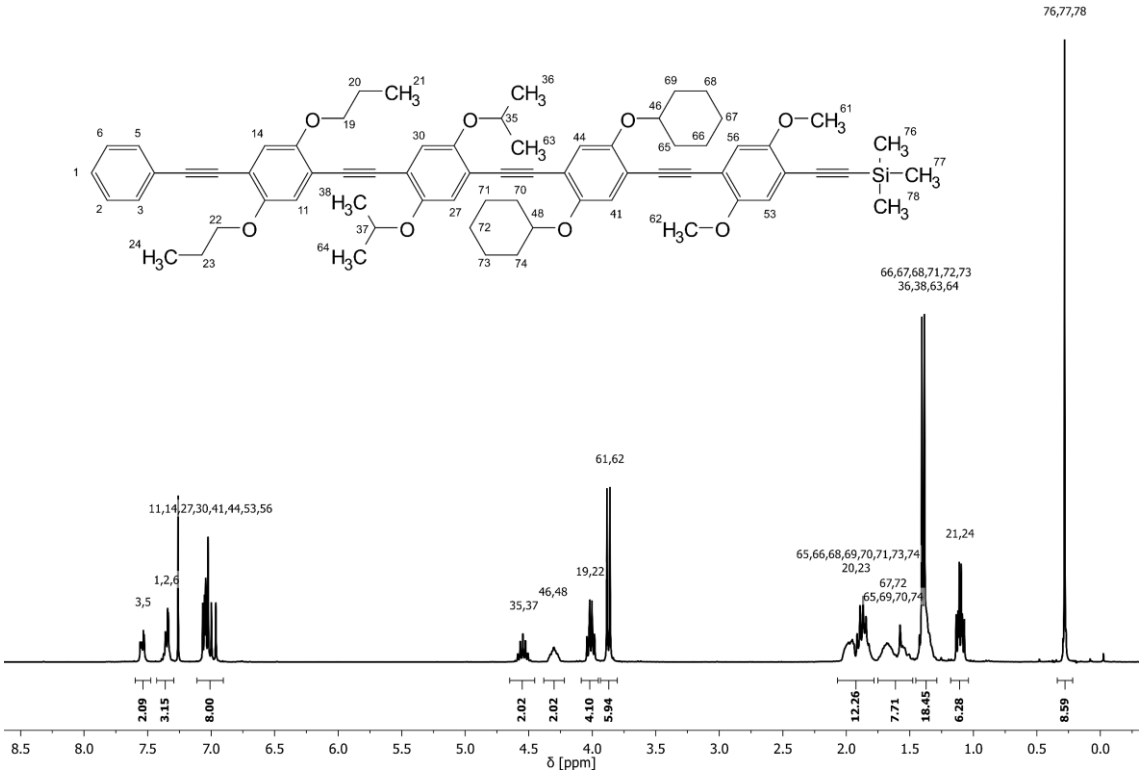
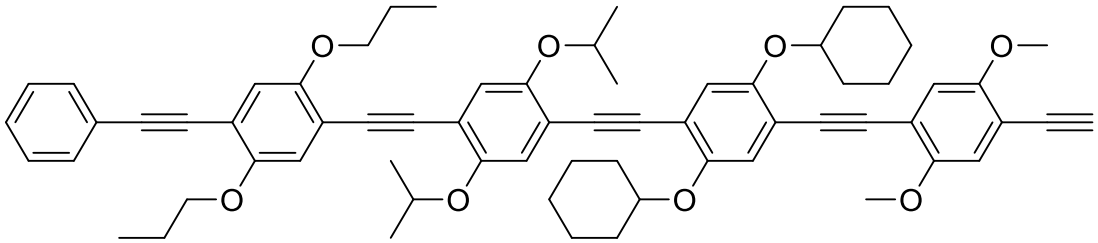


Figure 77: ^1H NMR spectrum of protected sequence-defined tetramer **4c** with assigned signals.

Synthesis of sequence-defined, deprotected tetramer **4d**



Compound **4c** (500 mg, 0.470 mmol, 1.00 eq.) and two equivalents of potassium carbonate (130 mg, 0.940 mmol) were placed in a Schlenk flask and degassed three times. Under continuous argon flow 25 mL dichloromethane and 25 mL methanol were added. The reaction mixture was stirred overnight at room temperature under argon atmosphere and quenched with distilled water. The aqueous phase was extracted three times with dichloromethane, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (dichloromethane/cyclohexane 12:1) to yield the product as a yellow solid (397 mg, 85%). TLC (dichloromethane/ cyclohexane 3:1) R_f = 0.11; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.60-7.48 (m, 2 H, 2 C**H**$_{aromatic}$C-C≡C), 7.42-7.29 (m, 3 H, 3 C**H**$_{aromatic}$), 7.12-6.95 (m, 8 H, 8 C**H**$_{aromatic}$CO), 4.55 (hept, J = 6.1 Hz, 2 H, 2 C**H(**$CH_3)_2$)), 4.40-4.22 (m, 2 H, 2 C**H**CH_2), 4.08-3.94 (m, 4 H, 2 C**H**$_2$O), 3.89, 3.88 (2 s, 6 H, 2 C**H**$_3$O), 3.42 (s, 1 H, 1 C≡C-**H**), 2.09-1.77 (m, 12 H, 2 C**H**$_2CH_3$, 4 C**H**$_{equatorial}$CHO, 4 C**H**$_{equatorial}CH_2$CHO), 1.77-1.48 (m, 6 H, 4 C**H**$_{axial}$CHO, 2 C**H**$_{equatorial}CH_2CH_2$CHO), 1.48-1.27 (m, 18 H, 4 C**H**$_3$CH, 4 C**H**$_{axial}CH_2$CHO, 2 C**H**$_{axial}CH_2CH_2$CHO), 1.10 (dt, J = 7.4, 4.5 Hz, 6 H, 2 C**H**$_3CH_2$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 154.65, 153.83, 153.75, 153.64, 152.90, 152.84, 152.66, 131.71, 128.47, 128.40, 123.61, 121.23, 121.09, 120.96, 120.78, 117.47, 117.28, 116.58, 116.37, 116.34, 116.30, 115.87, 115.66, 114.57, 114.42, 114.25, 111.93, 95.02, 92.35, 91.83, 91.75, 91.72, 91.45, 90.83, 86.11, 82.75, 80.10, 77.98, 77.88, 73.22, 73.19, 71.32, 71.28, 56.54, 56.49, 31.96, 31.87, 25.90, 25.85, 23.64, 23.53, 22.87, 22.84, 22.43, 22.39, 10.76, 10.71; ESI-MS of $C_{66}H_{70}O_8$ ($M+H^+$ = 991.51); HRMS (FAB) of $C_{66}H_{70}O_8$ [$M+H^+$] calc. 990.5071, found 990.5068; IR (ATR) ν = 3277.4, 2930.3, 2855.9, 2209.2, 2104.2, 1716.0, 1596.1, 1504.9, 1486.5, 1463.9, 1415.1, 1384.4, 1272.3, 1204.5, 1138.1, 1106.1, 1038.0, 1016.5, 962.4, 861.0, 754.2, 689.9, 644.5, 527.9, 458.0 cm^{-1}.

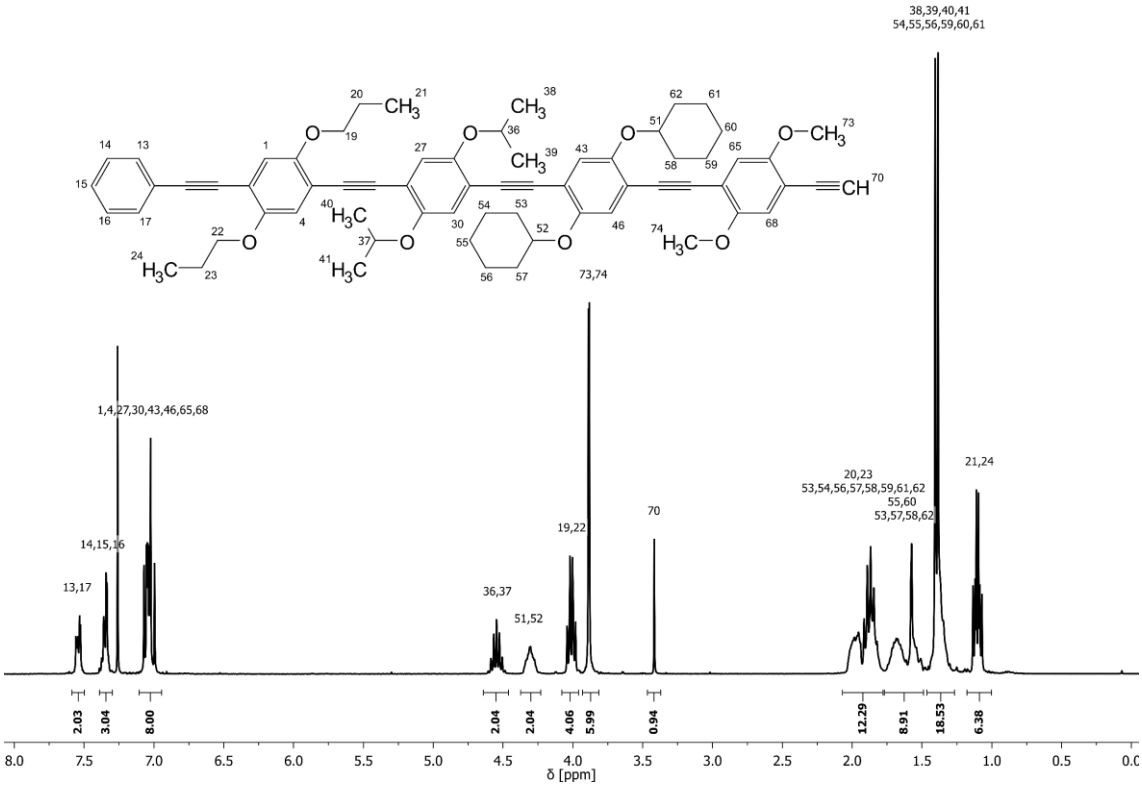
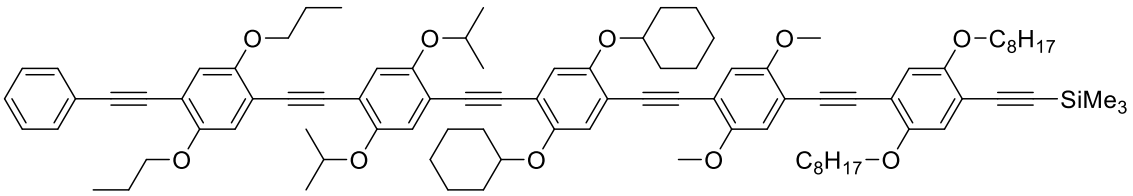


Figure 78: ^{1}H NMR spectrum of deprotected sequence-defined tetramer **4d** with assigned signals.

Synthesis of ((4-((4-((2,5-*bis*(cyclohexyloxy)-4-((2,5-diisopropoxy-4-((4-(phenylethynyl)-2,5-dipropoxyphenyl)ethynyl)phenyl)ethynyl)phenyl)ethynyl)-2,5-dimethoxyphenyl)ethynyl)-2,5-*bis*(octyloxy)phenyl)ethynyl)trimethylsilane **5c**



1,4-*Bis*(octyloxy)-2-iodo-5-trimethylsilylacetylenebenzene **B5** (841 mg, 1.51 mmol, 5.00 eq.), 10 mol% *bis*(triphenylphosphine) palladium(II) dichloride (21.2 mg, 30.3 µmol) and 2.5 mol% copper(I) iodide (1.4 mg, 7.56 µmol) were placed into a Schlenk flask and degassed three times. Under continuous argon flow, 20 mL dry THF and 420 µL dry triethylamine (306 mg, 3.03 mmol, 10.0 eq.) were added and the mixture was stirred for 10 minutes. Subsequently, compound **4d** (300 mg, 0.303 mmol, 1.00 eq.) in 20 mL THF was added dropwise with a syringe. The reaction mixture was stirred for 72 hours (3 days) at 45 °C, taken up in dichloromethane and washed with saturated NH_4Cl solution. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (dichloromethane/ cyclohexane 1:1 → 49:1) to yield the product as a yellow solid (140 mg, 33%). TLC (dichloromethane/cyclohexane 3:1) R_f = 0.25; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.59–7.47 (m, 2 H, 2 C**H**$_{aromatic}$C-C≡C), 7.40-7.29 (m, 3 H, 3 C**H**$_{aromatic}$), 7.21-6.85 (m, 10 H, 10 C**H**$_{aromatic}$CO), 4.55 (hept, J = 6.1 Hz, 2 H, 2 C**H**$(CH_3)_2$), 4.38-4.22 (m, 2 H, 2 C**H**CH_2), 4.09-3.93 (m, 8 H, 4 C**H**$_2$O), 3.90, 3.89 (s, 6 H, 2 C**H**$_3$O), 2.13-1.77 (m, 16 H, 4 C**H**$_2CH_3$, 4 C**H**$_{equatorial}CHO$, 4 C**H**$_{equatorial}CH_2CHO$), 1.75-1.61 (m, 4 H, 4 C**H**$_{axial}CHO$), 1.60-1.45 (m, 6 H, 2 C**H**$_{equatorial}CH_2CH_2CHO$, 2 C**H**$_2CH_2CH_2O$), 1.45-1.18 (m, 34 H, 4 C**H**$_3CH$, 4 C**H**$_{axial}CH_2CHO$, 2 C**H**$_{axial}CH_2CH_2CHO$, 8 C**H**$_2(CH_2)_n$), 1.10 (dt, J = 7.4, 4.4 Hz, 6 H, 2 C**H**$_3CH_2$), 0.88 (dt, J = 10.0, 6.8 Hz, 6 H, 2 C**H**$_3(CH_2)_n$), 0.26 (s, 9 H, 3 C**H**$_3$Si); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) = 154.25, 153.94, 153.90, 153.71, 153.62, 153.60, 152.89, 152.86, 152.77, 152.64, 131.69, 128.46, 128.39, 123.59, 121.21, 121.04, 120.97, 120.70, 117.40, 117.25, 117.21, 116.92, 116.41, 116.34, 116.24, 116.01, 115.66, 114.38, 114.26, 114.19, 113.86, 113.79,

113.63, 101.29, 100.33, 95.01, 92.29, 91.83, 91.78, 91.67, 91.45, 91.42, 91.22, 86.09, 77.94, 77.88, 73.20, 73.16, 71.27, 71.23, 69.65, 69.56, 56.50, 56.44, 31.99, 31.97, 31.95, 31.87, 29.55, 29.53, 29.51, 29.47, 29.45, 29.43, 26.19, 26.07, 25.91, 25.85, 23.65, 23.55, 22.86, 22.83, 22.82, 22.80, 22.43, 22.39, 14.25, 14.23, 10.77, 10.72, 0.11; ESI-MS of $C_{93}H_{114}O_{10}Si$ ($M+H^+$ = 1419.82); IR (ATR) v = 2926.5, 2853.8, 2149.1, 1595.5, 1486.5, 1465.2, 1413.9, 1383.3, 1272.7, 1208.4, 1106.7, 1038.5, 963.4, 840.8, 754.9, 689.2, 628.7, 461 cm^{-1}.

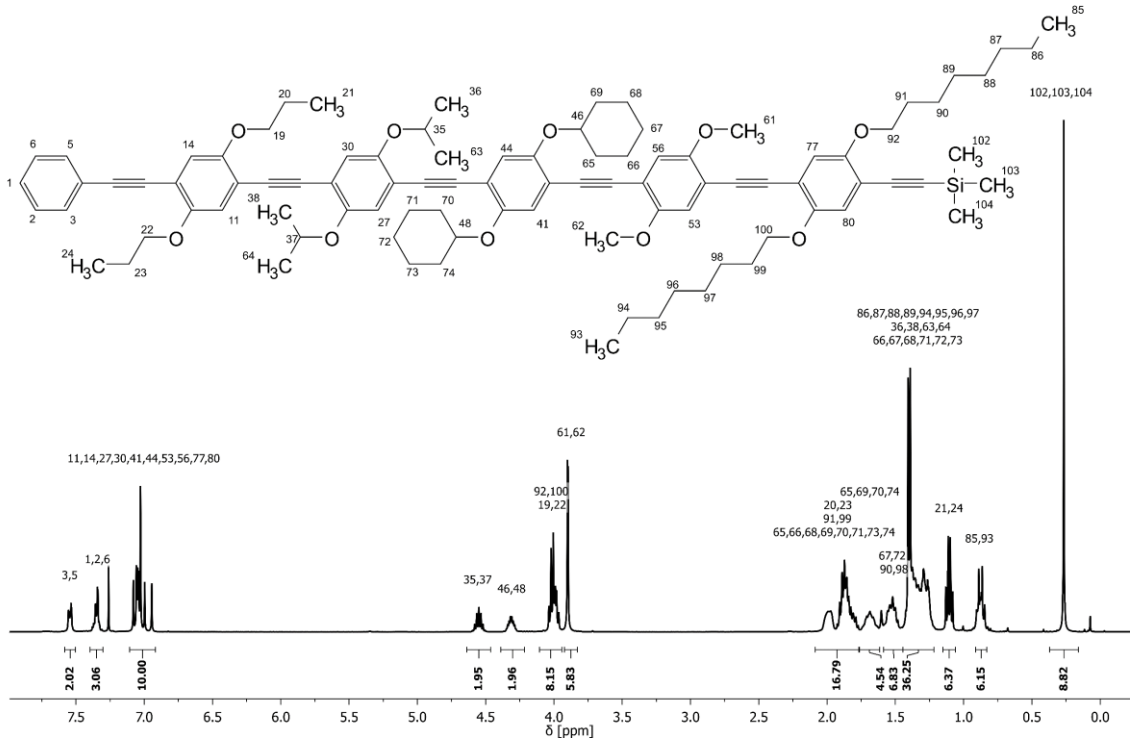
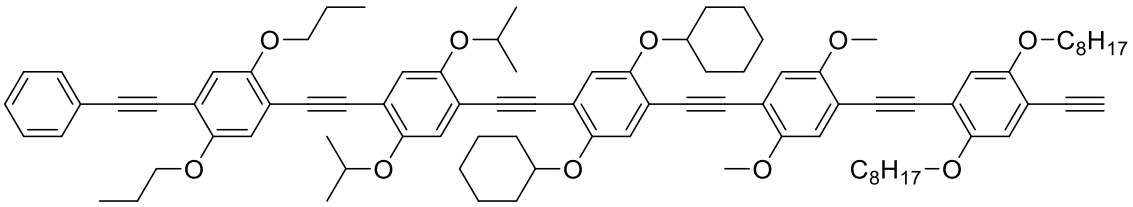


Figure 79: ^1H NMR spectrum of protected sequence-defined pentamer **5c** with assigned signals.

Synthesis of sequence-defined, deprotected pentamer **5d**



Compound **5c** (80.0 mg, 56.3 µmol, 1.00 eq) and two equivalents of potassium carbonate (15.6 mg, 0.113 mmol) were placed in a Schlenk flask and degassed three times. Under continuous argon flow 8 mL dichloromethane and 4 mL methanol were added. The reaction mixture was stirred overnight at room temperature under argon atmosphere and quenched with distilled water. The aqueous phase was extracted three times with dichloromethane, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (dichloromethane/cyclohexane 4:1→8:1) to yield the product as a yellow solid (73.6 mg, 97%). TLC (dichloromethane/cyclohexane 3:1) R_f = 0.19; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) =7.54 (dd, J = 7.6, 2.0 Hz, 2 H, 2 C**H**$_{aromatic}$C-C≡C), 7.43-7.28 (m, 3 H, 3 C**H**$_{aromatic}$), 7.14-6.90 (m, 10 H, 10 C**H**$_{aromatic}$CO), 4.55 (hept, J = 6.1 Hz, 2 H, 2 C**H(**$CH_3)_2$)), 4.40-4.22 (m, 2 H, 2 C**H**CH_2), 4.01 (dt, J = 7.9, 6.4 Hz, 8 H, 4 C**H**$_2$O), 3.90 (s, 6 H, 2 C**H**$_3$O), 3.35 (s, 1 H, 1 C≡C-**H**), 2.07-1.95 (m, 4 H, 4 C**H**$_{equatorial}$CHO), 1.85 (ddp, J = 21.5, 14.4, 6.9 Hz, 12 H, 4 C**H**$_{equatorial}$$CH_2$CHO, 2 C**H**$_2$$CH_2$O, 2 C**H**$_2$$CH_3$), 1.76-1.62 (m, 4 H, 2 C**H**$_2$$CH_2$$CH_2$O), 1.58-1.46 (m, 6 H, 4 C**H**$_{axial}$CHO, 2 C**H**$_{equatorial}$$CH_2$$CH_2$CHO), 1.41-1.19 (m, 34 H, 4 C**H**$_3$CH, 4 C**H**$_{axial}$$CH_2$CHO, 2 C**H**$_{axial}$$CH_2$$CH_2$CHO, 8 C**H**$_2$), 1.11, 1.10 (2 t, J = 7.3 Hz, 6 H, 2 C**H**$_3$$CH_2$), 0.88 (dt, J = 13.0, 6.8 Hz, 6 H, 2 C**H**$_3$$(CH_2)_n$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) = 154.23, 153.97, 153.91, 153.71, 153.60, 152.88, 152.86, 152.78, 152.64, 131.69, 128.46, 128.39, 123.59, 121.20, 121.04, 120.96, 120.70, 117.80, 117.40, 117.21, 116.94, 116.43, 116.33, 116.24, 115.99, 115.69, 115.68, 114.68, 114.38, 114.19, 113.88, 113.54, 112.75, 95.01, 92.32, 91.83, 91.77, 91.68, 91.61, 91.50, 91.43, 91.19, 86.09, 82.53, 80.17, 77.94, 77.87, 73.20, 73.16, 71.27, 71.23, 69.73, 69.72, 56.51, 56.45, 31.97, 31.94, 31.87, 29.53, 29.45, 29.42, 29.37, 29.29, 26.07, 26.06, 25.91, 25.85, 23.65, 23.54, 22.86, 22.83, 22.80, 22.43, 22.39, 14.26, 14.23, 10.77, 10.72; ESI-MS of $C_{90}H_{106}O_{10}$ ($M+H^+$ = 1347.78); IR (ATR) v = 3276.5, 2925.8, 2853.4, 1596.0, 1486.5, 1465.2,

1413.2, 1383.2, 1272.4, 1208.0, 1106.4, 1038.1, 962.9, 860.9, 754.5, 689.4, 528.1 cm^{-1}.

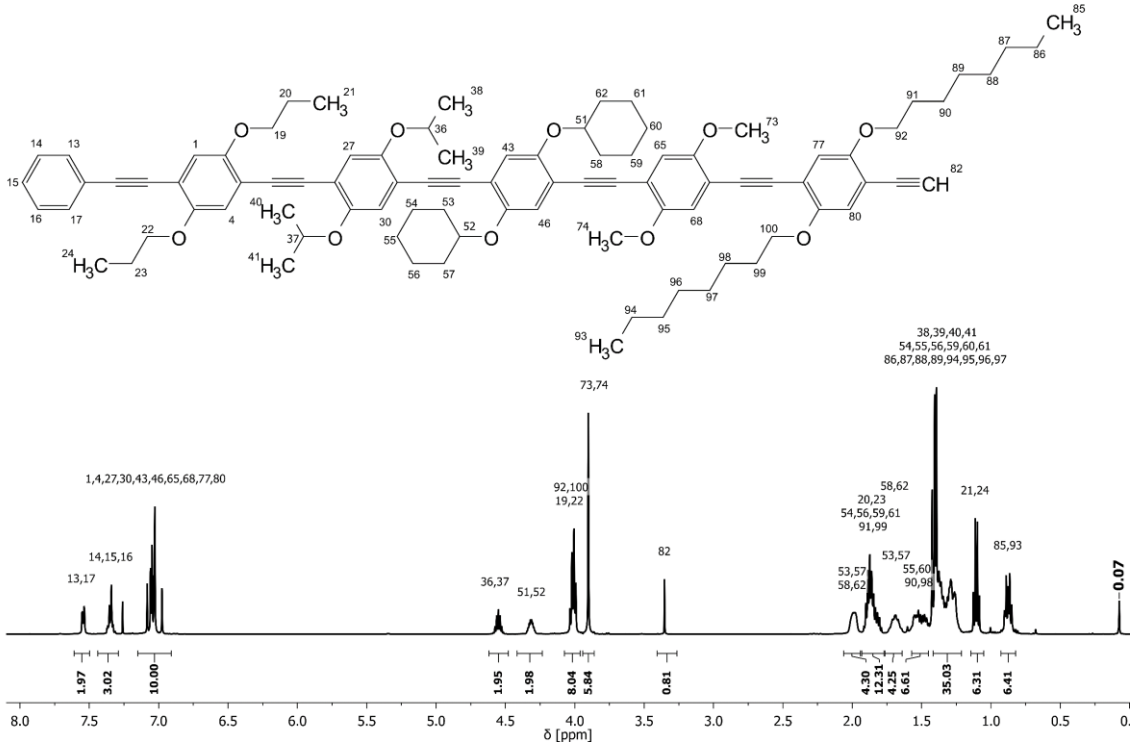
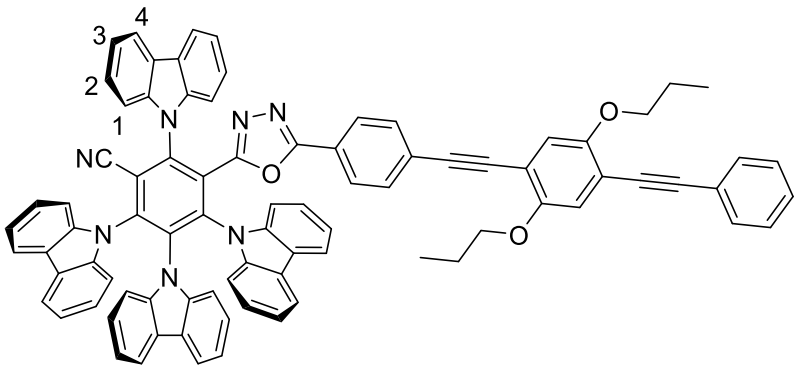


Figure 80: ^{1}H NMR spectrum of deprotected sequence-defined pentamer **5d** with assigned signals.

6.3.6 Syntheses of TADF-Oligomer Conjugates

Synthesis of (2r,3s,4s,6s)-2,3,4,6-tetra(9H-carbazol-9-yl)-5-(5-(4-((4-(phenylethynyl)-2,5-dipropoxyphenyl)ethynyl)phenyl)-1,3,4-oxadiazol-2-yl)benzonitrile **T1**



(2r,3s,4s,6s)-2,3,4,6-Tetra(9H-carbazol-9-yl)-5-(5-(4-iodophenyl)-1,3,4-oxadiazol-2-yl)benzonitrile **T** (50.0 mg, 48.4 µmol, 1.00 eq.), 1-ethynyl-4-(phenylethynyl)-2,5-dipropoxybenzene **1b** (61.6 mg, 0.194 mmol, 4.00 eq.), 10 mol% *bis*(triphenylphosphine) palladium(II) dichloride (3.4 mg, 4.84 µmol) and 2.5 mol% copper(I) iodide (0.2 mg, 1.21 µmol) were placed into a Schlenk flask and evacuated three times. Under continuous argon flow, 20 mL dry THF and 100 µL dry triethylamine were added. The reaction mixture was stirred for 72 hours (3 days) at 45 °C, taken up in dichloromethane and washed with saturated NH_4Cl solution. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (dichloromethane/cyclohexane 2:3→8:1) to yield the product as a yellow solid (53.6 mg, 90%). TLC (dichloromethane/cyclohexane 3:1) R_f = 0.32; ^{1}H NMR (CD_2Cl_2, 500 MHz): δ (ppm) = 8.18 (d, J = 7.8 Hz, 2 H, carbazole 4), 7.89-7.76 (m, 2 H, carbazole 4), 7.70 (dd, J = 6.3, 2.2 Hz, 2 H, carbazole 4), 7.66-7.53 (m, 6 H, 2 C**H**$_{aromatic}$C-C≡C benzene end unit, carbazole 1, carbazole 2), 7.51-7.36 (m, 7 H, 3 C**H**$_{aromatic}$ benzene end unit, carbazole 3, carbazole 4), 7.36-7.28 (m, 4 H, 2 C**H**$_{aromatic}$C-C≡C, carbazole 1), 7.26 (dd, J = 6.8, 1.7 Hz, 2 H, carbazole 1), 7.21-7.11 (m, 6 H, 2 C**H**$_{aromatic}$C-C=N, carbazole 3, carbazole 1), 7.11-7.01 (m, 6 H, 2 C**H**$_{aromatic}$CO, carbazole 2, carbazole 3), 6.90 (t, J = 7.4 Hz, 2 H, carbazole 3), 6.83-6.69 (m, J = 16.1, 8.1 Hz, 4 H, carbazole 2, carbazole 2), 4.02 (td, J = 6.4, 1.9 Hz, 4 H, 2 C**H**$_2$O), 1.99-1.78

(m, 4 H, 2 C**H**$_2$CH$_3$), 1.13 (t, *J* = 7.4 Hz, 6 H, 2 C**H**$_3$); ^{13}C NMR (CD_2Cl_2, 125 MHz): *δ* (ppm) = 164.62, 157.32, 154.35, 154.10, 144.18, 143.37, 142.53, 141.70, 139.78, 139.01, 138.30, 137.73, 132.02, 129.01, 128.57, 127.59, 127.42, 126.91, 126.45, 126.24, 125.44, 124.70, 124.51, 124.25, 123.79, 122.20, 122.13, 121.86, 121.76, 121.55, 121.41, 120.84, 120.80, 120.18, 118.74, 117.37, 117.31, 115.19, 113.51, 112.71, 110.76, 110.56, 110.02, 109.96, 95.58, 94.09, 89.82, 86.33, 71.61, 71.52, 23.26, 23.23, 10.90, 10.89; FAB of $C_{85}H_{57}N_7O_3$ ($M+H^+$ = 1224.5); IR (ATR) v = 2960.6, 1599.9, 1479.5, 1443.9, 1333.0, 1309.0, 1216.3, 1150.7, 1013.8, 843.5, 741.8, 720.9, 688.9, 617.4, 527.6, 421.1, 385.0 cm^{-1}.

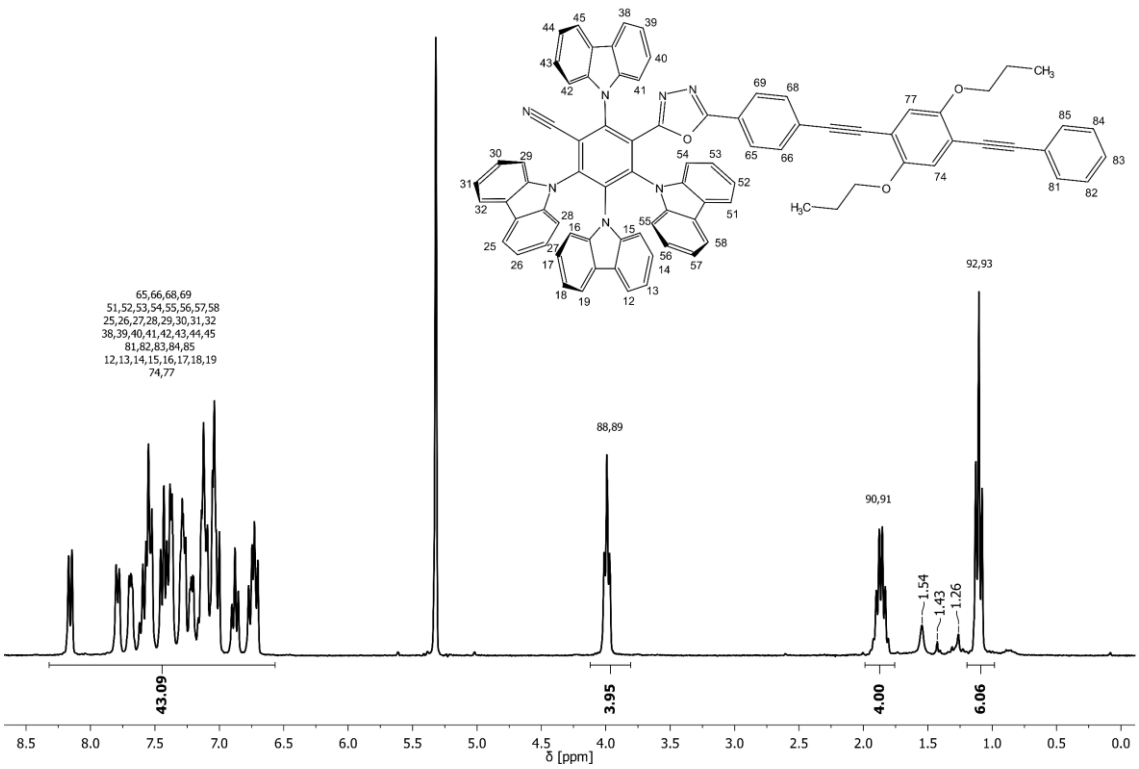
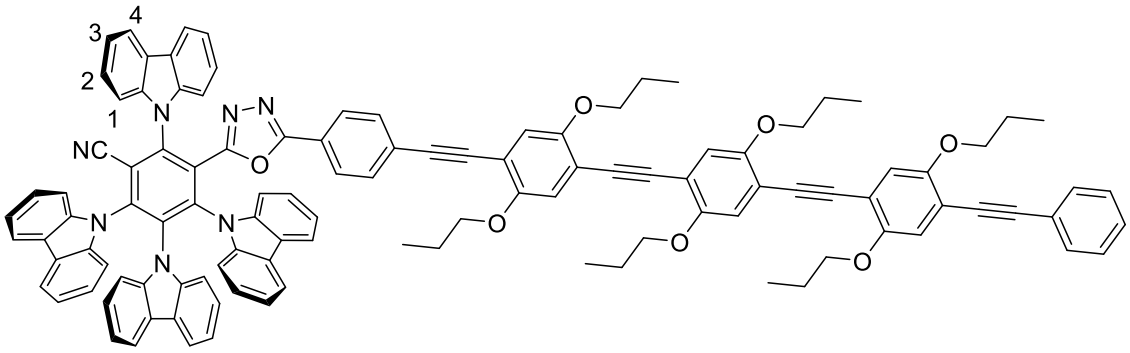


Figure 81: ^{1}H NMR spectrum of monomer-TADF adduct **T1** with assigned signals.

Synthesis of (2r,3s,4s,6s)-2,3,4,6-tetra(9H-carbazol-9-yl)-5-(5-(4-((4-((4-((4-(phenylethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)phenyl)-1,3,4-oxadiazol-2-yl)benzonitrile **T3**



(2r,3s,4s,6s)-2,3,4,6-Tetra(9H-carbazol-9-yl)-5-(5-(4-iodophenyl)-1,3,4-oxadiazol-2-yl)benzonitrile **T** (50.0 mg, 48.4 µmol, 1.00 eq.), 1-ethynyl-4-((4-((4-(phenylethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxybenzene **3b** (72.6 mg, 96.8 µmol, 2.00 eq.), 10 mol% *bis*(triphenylphosphine)palladium(II) dichloride (3.4 mg, 4.84 µmol) and 2.5 mol% copper(I) iodide (0.2 mg, 1.21 µmol) were placed into a Schlenk flask and evacuated three times. Under continuous argon flow, 20 mL dry THF and 100 µL dry triethylamine were added. The reaction mixture was stirred for 66 hours at 45 °C, taken up in dichloromethane and washed with saturated NH_4Cl solution. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (dichloromethane/cyclohexane 3:1→8:1) to yield the product as a yellow solid (70.3 mg, 88%). TLC (dichloromethane/cyclohexane 4:1) R_f = 0.24; ^{1}H NMR (CD_2Cl_2, 500 MHz): δ (ppm) = 8.16 (d, *J* = 7.8 Hz, 2 H, carbazole 4), 7.84-7.75 (m, 2 H, carbazole 4), 7.69 (dt, *J* = 6.4, 2.7 Hz, 2 H, carbazole 4), 7.63-7.57 (m, 2 H, carbazole 2), 7.57-7.51 (m, 4 H, 2 C**H**$_{aromatic}$C-C≡C benzene end unit, carbazole 1), 7.49-7.36 (m, 7H, 3 C**H**$_{aromatic}$ benzene end unit, carbazole 3, carbazole 4), 7.33-7.25 (m, 4 H, 2 C**H**$_{aromatic}$C-C≡C, carbazole 1), 7.25-7.19 (m, 2 H, carbazole 1), 7.17-7.09 (m, 6 H, 2 C**H**$_{aromatic}$C-C=N, carbazole 3, carbazole 1), 7.09-6.99 (m, 10 H, 6 C**H**$_{aromatic}$CO, carbazole 2, carbazole 3), 6.88 (t, *J* = 7.5 Hz, 2 H, carbazole 3), 6.74 (dd, *J* = 16.5, 7.9 Hz, 4 H, carbazole 2, carbazole 2), 4.09-3.95 (m, 12 H, 6 C**H**$_2$O), 1.96-1.79 (m, 12 H,

6 C**H**$_2$CH$_3$), 1.17-1.04 (m, 18 H, 6 C**H**$_3$); ^{13}C NMR (CD_2Cl_2, 125 MHz): *δ* (ppm) = 164.61, 157.31, 154.33, 154.13, 153.97, 153.93, 153.91, 144.17, 143.36, 142.52, 141.70, 139.78, 139.00, 138.30, 137.73, 132.00, 128.99, 128.94, 128.57, 127.58, 127.41, 126.90, 126.45, 126.24, 125.44, 125.38, 124.70, 124.50, 124.25, 123.88, 122.19, 122.12, 121.86, 121.76, 121.55, 121.39, 120.83, 120.78, 120.16, 118.74, 117.67, 117.64, 117.58, 117.49, 117.46, 115.37, 114.80, 114.54, 114.52, 114.49, 113.57, 112.70, 110.76, 110.56, 110.02, 109.96, 95.28, 94.17, 92.41, 92.12, 91.95, 91.88, 89.83, 86.47, 71.68, 71.65, 71.64, 71.61, 71.59, 71.51, 23.28, 23.24, 23.22, 10.89, 10.87; FAB of $C_{113}H_{89}N_7O_7$ ($M+H^+$ = 1658.0); IR (ATR) v = 3049.6, 2961.7, 2872.9, 1599.1, 1489.5, 1444.7, 1421.2, 1381.8, 1333.2, 1309.2, 1273.3, 1209.2, 1150.7, 1119.1, 1060.8, 1012.3, 980.6, 844.1, 742.5, 721.1, 688.5, 617.5, 551.8, 527.9, 421.4 cm^{-1}.

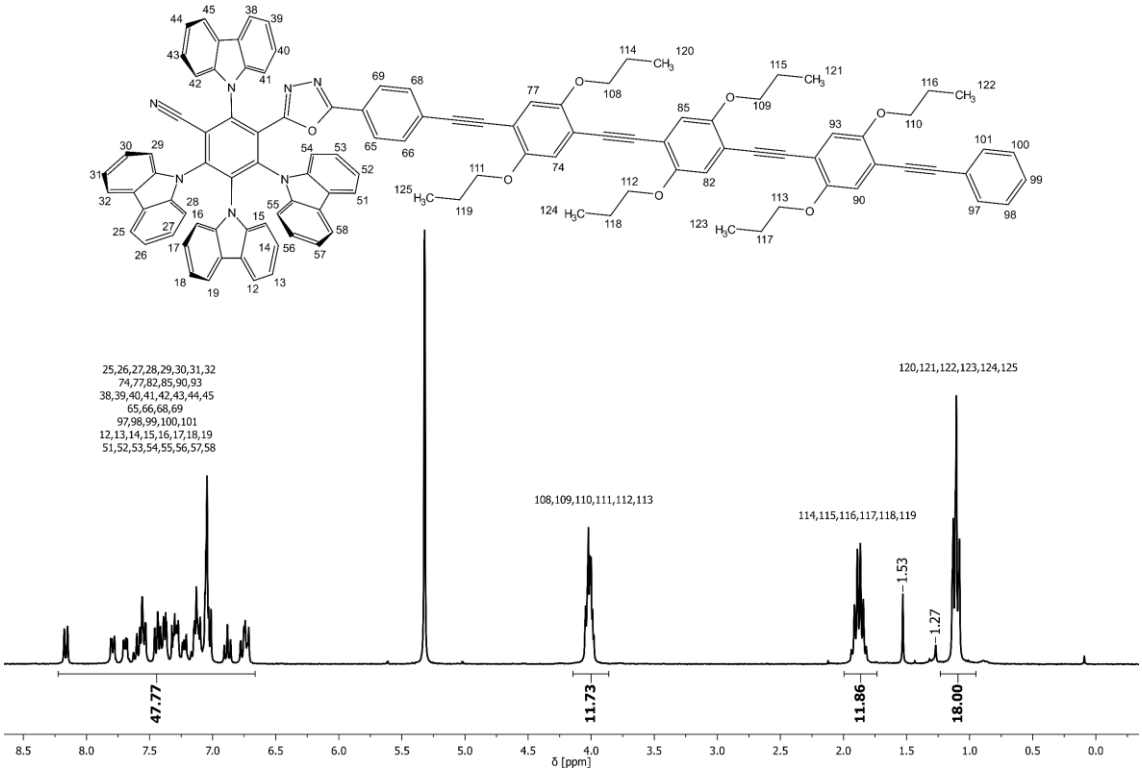
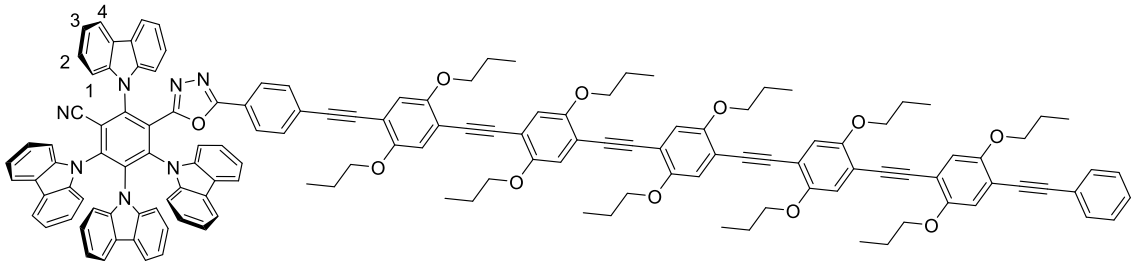


Figure 82: ^{1}H NMR spectrum of trimer-TADF adduct **T3** with assigned signals.

Synthesis of (2r,3s,4s,6s)-2,3,4,6-tetra(9H-carbazol-9-yl)-5-(5-(4-((4-((4-((4-((4-((4-(phenylethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)phenyl)-1,3,4-oxadiazol-2-yl)benzonitrile **T5**



(2r,3s,4s,6s)-2,3,4,6-Tetra(9H-carbazol-9-yl)-5-(5-(4-iodophenyl)-1,3,4-oxadiazol-2-yl)benzonitrile **T** (50.0 mg, 48.4 µmol, 1.00 eq.), 1-ethynyl-4-((4-((4-((4-((4-(phenylethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxyphenyl)ethynyl)-2,5-dipropoxybenzene **5b** (115 mg, 96.8 µmol, 2.00 eq.), 10 mol% *bis*(triphenylphosphine)palladium(II) dichloride (3.4 mg, 4.84 µmol) and 2.5 mol% copper(I) iodide (0.2 mg, 1.21 µmol) were placed into a Schlenk flask and evacuated three times. Under continuous argon flow, 20 mL dry THF and 100 µL dry triethylamine were added. The reaction mixture was stirred for 74 hours at 45 °C, taken up in dichloromethane and washed with saturated NH_4Cl solution. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica column chromatography (dichloromethane/cyclohexane 4:1→1:0) and aluminium oxide column chromatography (pure dichloromethane) to yield the product as a yellow solid (35.5 mg, 35%). TLC (dichloromethane/cyclohexane 4:1) R_f = 0.22; ^{1}H NMR (CD_2Cl_2, 500 MHz): δ (ppm) = 8.16 (d, J = 7.8 Hz, 2 H, carbazole 4), 7.84-7.75 (m, 2 H, carbazole 4), 7.69 (dt, J = 6.4, 2.7 Hz, 2 H, carbazole 4), 7.63-7.57 (m, 2 H, carbazole 2), 7.57-7.51 (m, 4 H, 2 C**H**$_{aromatic}$C-C≡C benzene end unit, carbazole 1), 7.49-7.36 (m, 7H, 3 C**H**$_{aromatic}$ benzene end unit, carbazole 3, carbazole 4), 7.33-7.25 (m, 4 H, 2 C**H**$_{aromatic}$C-C≡C, carbazole 1), 7.25-7.19 (m, 2 H, carbazole 1), 7.17-7.09 (m, 6 H, 2 C**H**$_{aromatic}$C-C=N, carbazole 3, carbazole 1), 7.09-6.99 (m, 14 H, 10 C**H**$_{aromatic}$CO, carbazole 2, carbazole 3), 6.88 (t, J = 7.5 Hz, 2 H, carbazole 3), 6.74 (dd, J = 16.5, 7.9 Hz,

4 H, carbazole 2, carbazole 2), 4.09-3.95 (m, 20 H, 10 C**H**$_2$O), 1.96-1.79 (m, 20 H, 10 C**H**$_2$CH$_3$), 1.17-1.04 (m, 30 H, 10 C**H**$_3$); ^{13}C NMR (CD_2Cl_2, 125 MHz): δ (ppm) = 164.62, 157.32, 154.34, 154.14, 153.96, 153.92, 144.17, 143.37, 142.53, 141.71, 139.78, 139.01, 138.31, 137.74, 132.00, 129.00, 128.94, 128.58, 127.59, 127.42, 126.91, 126.45, 126.25, 125.45, 124.71, 124.51, 124.25, 123.90, 122.20, 122.13, 121.86, 121.77, 121.55, 121.40, 120.84, 120.79, 120.17, 118.75, 117.66, 117.58, 117.50, 117.46, 115.37, 114.80, 114.70, 114.68, 114.64, 114.58, 114.51, 113.57, 112.71, 110.76, 110.56, 110.03, 109.97, 95.27, 94.18, 92.43, 92.18, 92.13, 92.08, 92.00, 91.91, 89.85, 86.50, 71.67, 71.65, 71.63, 71.58, 71.50, 23.28, 23.22, 10.88; ESI-MS of $C_{141}H_{121}N_7O_{11}$ ([M+Na]$^{2+}$/2 = 1067.45); IR (ATR) v = 2919.9, 2850.0, 1721.9, 1599.1, 1490.5, 1453.2, 1422.0, 1384.0, 1334.0, 1310.8, 1273.2, 1209.2, 1061.2, 1013.2, 982.4, 859.3, 801.4, 743.9, 722.1, 617.6, 527.6, 426.2, 389.8 cm^{-1}.

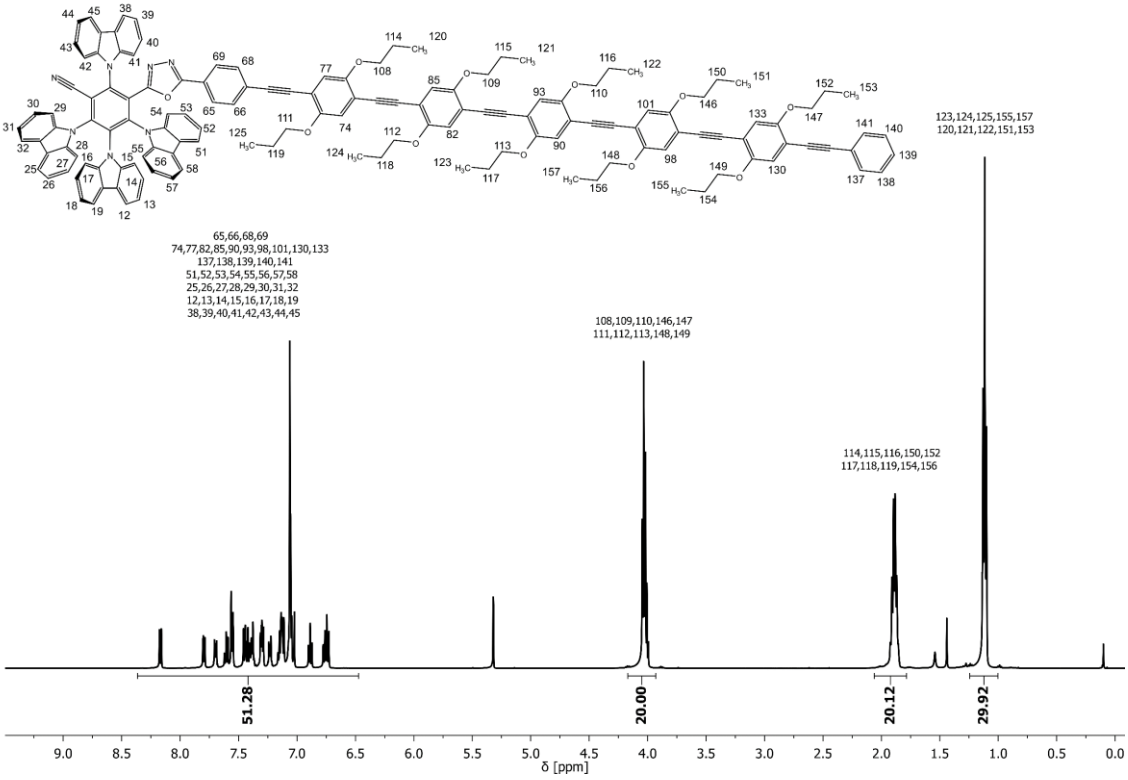


Figure 83: ^{1}H NMR spectrum of pentamer-TADF adduct **T5** with assigned signals.

7. Literature

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Abbreviations

alt	Alternating
ATR	Attenuated Total Reflection
CC	Column Chromatography
CN-PPV	Cyano-Poly(Phenylene Vinylene)
COSY	Correlated Spectroscopy
(dan)BH	1,8-Naphtalenediaminatoboran
DMF	*N*,*N*-Dimethylformamide
DNA	Deoxyribonucleic Acid
DP	Degree of Polymerization
DSC	Differential Scanning Calorimetry
ESI	Electrospray Ionization
FAB	Fast Atom Bombardment
FSPE	Fluorous Solid Phase Extraction
GC	Gas Chromatography
HOMO	Highest Occupied Molecular Orbital
HPLC	High-Performance Liquid Chromatography
HRMS	High Resolution Mass Spectroscopy
HSQC	Heteronuclear Single Quantum Coherence
HWE	Horner-Wadsworth-Emmons Reaction
IR	Infrared
ISC	Intersystem Crossing
ITO	Indium Tin Oxide
IUPAC	International Union of Pure and Applied Chemistry
LUMO	Lowest Unoccupied Molecular Orbital
MALDI	Matrix-Assisted Laser Desorption/Ionization

MCR	Multicomponent Reactions
MEH-PPV	Poly(2-methoxy-5-(2'-ethylhexyloxy)-*para*-phenylene vinylene)
mRNA	Messenger Ribonucleic Acid
MS	Mass Spectrometry
NMR	Nuclear Magnetic Resonance
OHex	Hexyloxy
OAE	Oligo(arylene ethynylene)
OLED	Organic Light-Emitting Diode
OPE	Oligo(phenylene ethynylene)
OPV	Oligo(phenylene vinylene)
P-3CR	Passerini three-component reaction
P3HT	Poly(3-hexylthiophene-2,5-diyl)
PAE	Poly(arylene ethynylene)
PCBM	[6,6]-Phenyl C_{61} butyric acid methyl ester
PG	Protecting Group
PL	Photoluminescence
PPV	Poly(phenylene vinylene)
R_f	Retardation Factor
RISC	Reverse Intersystem Crossing
RNA	Ribonucleic Acid
rRNA	Ribosomal Ribonucleic Acid
RT	Room Temperature
S_1	Singlet Excited State
SEC	Size Exclusion Chromatography
SPOS	Solid Phase Organic Synthesis
SPPS	Solid Phase Peptide Synthesis
T_1	Triplet Excited State

TADF	Thermally Activated Delayed Fluorescence
TBAF	Tetra-*n*-butylammonium fluoride
T_g	Glass Transition Temperature
THF	Tetrahydrofuran
TLC	Thin-Layer Chromatography
T_m	Melting Point (Temperature)
TMEDA	*N*,*N*,*N*',*N*'-Tetramethylethylenediamine
TMS	Trimethylsilyl
TMSA	Trimethylsilylacetylene
TOF	Time of Flight
tRNA	Transfer Ribonucleic Acid
UV/Vis	Ultraviolet-Visible Light (Spectroscopy)

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