The effect of fluorine substituents in conjugated polymers

Lvenich, Peter Wilfried

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The Effect of Fluorine Substituents in Conjugated Polymers

Peter Wilfried Lövenich

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A thesis submitted for the degree of Doctor of Philosophy at the University of Durham

Department of Chemistry
University of Durham
October 2001
Abstract

The Effect of Fluorine Substituents in Conjugated Polymers

Peter Wilfried Lövenich  Ph.D. Thesis  October 2001

A new route to a well-defined block copolymer with alternating PEO-solubilising groups and fluorinated distyrylbenzene units was established. The Horner Wittig reaction was used as the polycondensation reaction. The non-fluorinated analogue of this block copolymer was prepared via the Wittig reaction. Both polymers were soluble in chloroform and free-standing films could be cast from solution. The position of the HOMO and LUMO energy levels of these two materials were determined by a combination of cyclic voltammetry, UV photoelectron spectroscopy and UV/Vis absorption spectroscopy. The presence of fluorine substituents on the distyrylbenzene unit had no influence on the HOMO-LUMO band-gap (3.0 eV). However, the position of these two energy levels relative to the vacuum level was shifted to higher energies (0.85 eV shift) in the case of the fluorinated block copolymer. The photoluminescence quantum efficiency of the fluorinated block copolymer was 17%, that of the non-fluorinated block copolymer was 34%. The former was used as the electron conducting layer in a light emitting diode with poly(p-phenylene vinylene) as the emissive layer. The latter was used as the emissive layer in light emitting diodes. Luminances over 2000 cd/m² were observed for devices based on the non-fluorinated block copolymer using indium tin oxide as the anode and aluminium as the cathode. The luminescence efficiency of such devices was as high as 0.5 cd/A, corresponding to an internal quantum efficiency of 1.1%.

Furthermore, an oligo(p-phenylene vinylene) was synthesised that contained two terminal fluorinated benzene rings and two central non-fluorinated benzene rings, all connected by vinylene bridges. This material aggregated in a ‘brickwall’ motif, where each molecule overlaps with two halves of molecules in the row above and below. The structure of this J aggregate is due to aryl-fluoroaryl-interactions and was demonstrated by X-ray crystal structure analysis.
Memorandum

The work reported in this thesis has been carried out in the Interdisciplinary Research Centre in Polymer Science and Technology in the Department of Chemistry at the University of Durham, between October 1998 and October 2001. This work has not been submitted for any other degree and is the original work of the author, except where acknowledged by reference.

Some parts of this work have been published as joint publications:


Statement of Copyright

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Financial support

I gratefully acknowledge the funding provided by the European Union Research Training Networks SELOA and LAMINATE.
Acknowledgements

In 1998, when I left Germany to start a Ph.D. in Britain, some people were sceptical. However, the last three years at the Department of Chemistry at the University of Durham have been a very successful – both on a scientific and on a personal basis. I can recommend the experience to anybody who is considering this option. To a great extent this success has been due to the support of my supervisor Professor W. James Feast, of whom many have expressed their envy of my opportunity to work in his group! Also, I would like to acknowledge the support of all the members of the IRC in Polymer Science and Technology at Durham; many of them have become friends and I hope to stay in contact with them. I am grateful to many members of staff at the Chemistry department in particular Dr. Alan Kenwright, Dr. Horst Puschmann, Prof. Randal Richards, Dr. Lian Hutchings, Dr. Dave Parker and Mrs Jarika Dostal.

I am grateful to many collaborators in the LAMINATE network, in particular, Dr. Franco Cacialli and Prof. Richard Friend at the Cavendish Laboratory, Cambridge, for their help with device fabrication. I am also grateful to Dr. Michele de Jong and Prof. William R. Salaneck at Linköping University, Sweden, for the photoelectron spectroscopy measurements and Prof. Carlo Taliani at the Institute for Molecular Spectroscopy, Bologna, for fruitful discussions.

I would like to thank my parents; meinen Eltern danke ich für die Unterstützung während der letzten neun Jahre.

Finally, I would like to thank my girlfriend Catherine who has helped me with the editing of this work.
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1 Introduction

1.1 Conjugated Polymers

Traditionally, organic polymers have been considered as insulators. They are used in the electronics industry for the insulation of metallic conductors, since conventional polymers have a large band gap between the valence band and the conducting band. However, polymers with a conjugated backbone have a much smaller band gap. This is due to the delocalisation of $\pi$-bonding and $\pi^*$-antibonding electron orbitals along the polymer backbone. Conjugated polymers have low ionisation potentials (IPs) and high electron affinities (EAs) and can therefore be oxidised or reduced more easily than conventional polymers. Pure conjugated polymers are usually not conducting but can be converted to highly conducting materials by treatment with an oxidising or reducing agent; in analogy to inorganic semiconductors these conversions are also called p-doping or n-doping, respectively.

The simplest conjugated polymer is polyacetylene (PA) (Figure 1.1.1a). High molecular weight PA was first reported in 1958 by Natta et al. It was prepared in the form of a black powder using an Al(Et)$_3$Ti(OPr)$_4$ initiator system. Berets and Smith reported in 1968 that the doping of PA powder with oxygen or chlorine increases the conductivity. In the 1970’s Shirakawa et al. developed a synthesis for PA films using high concentrations of the Al(Et)$_3$Ti(OPr)$_4$ type catalyst. They were able to show that treatment of such films with halogens increased the conductivity by eight orders of magnitude.

![Chemical structures](image)

*Figure 1.1.1 Conjugated polymers. a) polyacetylene, b) poly(p-phenylene), c) poly(p-phenylene vinylene), d) polythiophene, e) polyaniline*
In 1980 Edwards and Feast reported the synthesis of a soluble and well defined precursor polymer via the ring opening metathesis polymerisation (ROMP) which could be converted to PA films by thermal treatment (Figure 1.1.2). In the so-called Durham precursor route, the precursor polymer could be purified and processed by conventional solution methods. During the thermal conversion hexafluoro-o-xylene was released and PA formed. The initially generated cis double bonds were isomerised to trans double bonds.

Poly(p-phenylene vinylene) (PPV) was first prepared in 1960 by McDonald and Campbell via the Wittig reaction (Figure 1.1.3). A 1:1 mixture of terephtalaldehyde and p-xylylene-bis(triphenylphosphonium chloride) was treated with base and gave a yellow powder. The molecular weight of PPV prepared by this route was low and the polymer insoluble.

In 1966, Wessling and Zimmermann developed a precursor route, which allowed the preparation of oriented high molecular weight polymer films (Figure 1.1.4). A bis-sulfonium salt was treated with base giving rise to a quinodimethane intermediate. The presence of radical trapping agents lowered the molecular weight of the precursor polymer, suggesting that the polymerisation proceeds radically but anionic propagation can not be excluded. The precursor polymer with one sulfonium group per repeat unit could be isolated and purified by dialysis. The number average molecular weight of this precursor was determined to be at least 100,000 g/mol. The precursor could be oriented and converted thermally to PPV films. This route is generally referred to as the Wessling route.
Also in 1966 Gilch and Wheelwright reported the synthesis of PPV based on the dehydrohalogenation of α,α’-dichloro-p-xylylene (Figure 1.1.5).\textsuperscript{12} The reaction also proceeded \textit{via} a quinodimethane intermediate, which polymerised to give poly(α-chloro-xylylene). This polymer intermediate could be isolated if a dilute solution of base is added slowly to an excess of α,α’-dichloro-p-xylylene. Using an excess of base or thermal treatment led to the fully conjugated polymer. This route is generally referred to as the Gilch route.

A large number of different conjugated polymers have been prepared including hydrocarbon polymers such as PA, poly(p-phenylene) (PPP) and PPV as well as heterocyclic polymers such as polythiophenes or polyaniline (Figure 1.1.1).\textsuperscript{13} A range of applications for conjugated polymers are being investigated including their use in batteries, non-linear optics, field effect transistors and in photovoltaic and electroluminescent devices.\textsuperscript{14}

\section*{1.2 Light emitting diodes}

In 1990 Burroughes \textit{et al.} demonstrated that conjugated polymers such as PPV are electroluminescent.\textsuperscript{15} Since then much attention has been given to the synthesis and properties of PPV and the use of conjugated polymers in light emitting diodes (LEDs).\textsuperscript{16} Today, LEDs based on polymers offer an alternative to the established
display technologies based on cathode-ray tubes and liquid-crystal displays, since polymer coating techniques are cheap and can be applied to large areas.

In a simple LED the fluorescent polymer is sandwiched between two electrodes.\textsuperscript{17} A metal of low work function, such as aluminium or calcium, is usually used as the cathode. The work function of a solid describes the minimum energy that is required to remove an electron from the surface of the solid into the vacuum. The work functions of aluminium and calcium are 4.3 eV and 2.9 eV, respectively. These metals can donate electrons readily into the lowest unoccupied molecular orbital (LUMO) of the conjugated polymer. Indium-tin-oxide (ITO) is the most prevalent material used as the anode because of its high work function (4.5-5.1 eV) and its transparency in the visible region.

![Figure 1.2.1 Schematic representation of a light emitting diode.](image)

When the diode is biased sufficiently, positive and negative charges are injected from opposite electrodes. PPV is oxidised at the anode where radical cations ('holes') are created and it is reduced at the anode where radical anions ('electrons') are created. These radical cations and radical anions move towards the oppositely charged electrode. They can capture one another within one polymer chain and form a neutral bound electronically exited state. This so-called exciton is confined to the polymer chain. The spin wave-function of the exciton can be a singlet or a triplet. Spin allowed radiative emission is only from the singlet exited state.\textsuperscript{2} Since the exchange energy between the singlet and the triplet state is large due to the confinement of the exciton the triplet excitons do not produce light emission. Only the singlet excitons give rise to electroluminescence.

A simple single layer device consisting of an emissive polymer sandwiched between an ITO glass substrate and a metal is denoted as ITO/polymer/metal. Offsets between the work function of the anode and the highest occupied molecular orbital (HOMO) of the polymer or between the work function of the cathode and the lowest unoccupied molecular orbital (LUMO) of the polymer lead to barriers for
hole-injection or electron-injection, respectively. Figure 1.2.2 (left) shows energy levels in the device ITO/PPV/Al. The levels are measured relative to the vacuum level. The values for these energy levels recorded in the literature vary slightly and errors of ±0.2 eV should be kept in mind. However, it becomes clear that the HOMO of PPV aligns fairly well with the work function of ITO, whereas a large offset is found between the work function of aluminium and the LUMO of PPV. Therefore, the injection of holes predominates over the injection of electrons. If the injection rates of holes and electrons are unequal, the excess carriers of one sign pass through the polymer without recombination, contributing to the current but not to the emission. The efficiency of the LEDs based on PPV with aluminium as cathode, as it was recorded in 1990, is of the order of $5 \times 10^{-4}$ photons generated per electron injected. This corresponds to an internal quantum efficiency of 0.05%.

![Energy levels](image)

*Figure 1.2.2 Energy levels for the device ITO/PPV/Ca (left) and ITO/PPV/CN-PPV/Ca (right). All values contain an error of ±0.2 eV.*

To increase the efficiency of such a device, electron injection has to be boosted. This can be achieved by the introduction of an additional layer. For example the LUMO of a cyano-substituted PPV (CN-PPV, which will be explained in more detail in the next section) matches well with the work function of Ca. Very high efficiencies of 4% have been achieved for double layer devices such as ITO/PPV/CN-PPV/Ca. Figure 1.2.2 (right) shows the energy levels of the two polymers and the work functions of the electrodes. The good match of the energy levels at the cathode and the anode becomes apparent. The use of a double layer
structure can have a further beneficial effect; recombination of the holes and electrons is likely to occur near the interface of the two polymers since one is a good hole carrier and the other one a good electron carrier and high densities of carriers are created on each side of the interface. This reduces the probability of exciton quenching by dissociation near the electrodes, which can reduce the efficiency of the device.\textsuperscript{17}

Polymer LEDs are described in terms of the following characteristics:

- The electroluminescence (EL) spectrum together with the solid-state absorption and emission spectra of the polymer give an indication of the energy levels of the polymer. The colour of the emission is obviously an important factor for LEDs. The human eye has three sets of cells in the retina responding to blue (446 nm), green (555 nm) and red light (599 nm).\textsuperscript{17} These three colours are required for a full-colour display.

- The photoluminescence (PL) quantum efficiency of the polymer is the ratio of emitted to absorbed photons when the polymer is irradiated with light.

- The internal quantum efficiency $q_{\text{int}}$ is the ratio of the number of photons produced to the number of electrons flowing through the external circuit and is given by

$$q_{\text{int}} = \gamma r \eta,$$

where $\gamma$ is the ratio of excitons formed to the electrons flowing in the external circuit, $r$ is the fraction of excitons formed as singlets and $\eta$ is the efficiency of the radiative decay of the singlet excitons and therefore identical with the photoluminescence quantum efficiency.\textsuperscript{19}

- The external quantum efficiency takes into account the fact that not all photons leave the device but some are internally reflected depending on the angle at which they hit the interface.\textsuperscript{20} External efficiencies are therefore approximately a factor $2n^2$ smaller than internal efficiencies, where $n$ is the refractive index of the polymer. In order to avoid the confusion between the two efficiencies and the uncertainty that is included when internal efficiencies are calculated from the measured external efficiencies, the value of brightness per unit of current (cd/A) instead of efficiencies is generally quoted in recent years, as it can be measured more reliably.
- The energy levels of the HOMO and the LUMO of the polymer together with the work functions of the electrodes determine the barriers for electron and hole injection.
- The brightness of the device is measured in candelas per square meters (cd/m²). A television screen typically has a brightness of about 100 cd/m².
- The turn-on voltage is the minimal voltage required to observe electroluminescence.
- The stability of LEDs is an important factor for consumer products. The shelf lifetime should be many years and the operational lifetime between 100 h and 10,000 h depending on the application.

1.3 Derivatives of PPV

Changes in the chemical structure of PPV and its derivatives give rise to changes in the physical properties described in the previous section. The ability to tune these physical properties by manipulating the chemical structure of PPV has resulted in the synthesis of a great number of derivatives. Some examples of the different synthetic approaches to PPV derivatives and the resulting changes in the physical properties are given below.

PPV has an optical band gap of about 2.7 eV and emits in the yellow-green region of the visible spectrum with an emission maximum at 560 nm (2.2 eV). The solid state PL quantum efficiency of PPV is 27%.\(^2\) The first report of electroluminescence by Burroughes \emph{et al.} gives a quantum efficiency of 0.05%. Since then efficiencies of 0.1% have been reported for an ITO/PPV/Ca device.\(^3\)

Shortly after the discovery of the electroluminescence of PPV in Cambridge, Heeger and Braun reported the use of a dialkoxy substituted PPV derivative in LEDs.\(^4\) Poly[2-(2'ethylhexyloxy)-5-methoxy-1,4-phenylene vinylene] (MEH-PPV) was prepared via the Gilch route (\textit{Figure 1.3.1}).\(^5\) MEH-PPV is soluble in the conjugated form in organic solvents such as chloroform, THF or xylene. The EL and PL maxima of MEH-PPV are at 590 nm and therefore red-shifted relative to PPV. This is due to the electron-donating effect of the two alkoxy-groups. The PL
efficiency is 10 - 15%.\textsuperscript{22} The authors report an internal quantum efficiency of 1% for a device of the form ITO/MEH-PPV/ Ca. This is a tenfold increase compared to the efficiency of PPV.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{synthesis_mehppv_gilch}
\caption{Synthesis of MEH-PPV via the Gilch-route.}
\end{figure}

A cyano-substituted PPV (CN-PPV) was first prepared by Hörhold et al. via the Knoevenagel reaction.\textsuperscript{26} A terephthalaldehyde derivative is reacted with a benzene-1,4-diacetonitrile derivative. The resulting polymer is soluble due to the alkoxy side chains. The polymer has a much higher PL efficiency (48\%) than PPV itself (27\%).\textsuperscript{22} The cyano-groups increase the electron affinity and the ionisation potential of the polymer (see Figure 1.2.2). Double layer ITO/PPV/CN-PPV/Ca devices of the form ITO/PPV/CN-PPV/Ca show the highest internal efficiencies (4\%) recorded so far.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{synthesis_cnnppv_knoevenagel}
\caption{Synthesis of CN-PPV via the Knoevenagel reaction.}
\end{figure}

Processability of conjugated polymers can be achieved in several ways. So far the precursor route or the introduction of solubilising side chains on the conjugated polymer backbone have been discussed. It is also possible to use isolated chromophores in an otherwise non-conjugated polymer.\textsuperscript{27} Such chromophores can be incorporated as side chains or within the polymer backbone. Fully conjugated polymers often contain a small amount of randomly distributed defects interrupting the conjugation and leading to a statistical distribution of conjugation lengths. In contrast, isolated chromophores have a precisely defined uniform length, which can be tailored to a specific emission wavelength. Polymers with isolated chromophores
are, strictly speaking, not conjugated polymers but they have similar characteristics such as a low band gap and good film forming properties; they have also been used successfully as the emissive layer in LEDs.

A very well defined polymer with oligo(phenylene vinylene) units as side chains was prepared by Lee et al. using ring opening metathesis polymerisation.\textsuperscript{28} The polymer proved to be efficient as the emissive layer in a light emitting diode and a quantum yield of 0.3\% was obtained when Ca was used as the cathode and ITO as the anode. The PL and EL maximum is at 475 nm. This is blue shifted relative to PPV due to the shorter conjugation length.

![Figure 1.3.3 Synthesis of a well defined polymer with distyrylbenzene units in side chains (DSB Side) via ring opening metathesis polymerisation.](image1)

A variety of different approaches have been used to prepare polymers with isolated chromophores within the polymer backbone. In 1993 Karasz et al. reported the first block copolymer with alternating distyrylbenzene (DSB) units and non-conjugated flexible linkers.\textsuperscript{29} The polymer is one of the first examples of a polymer emitting blue light. The EL maximum is at 465 nm. The Wittig reaction was used as the polycondensation reaction and the polymer consists of alternating DSB units and octane-1,8-diol units.

![Figure 1.3.4 Synthesis of a block copolymer with DSB units and flexible linker units (DSB Block-A) via the Wittig reaction.](image2)
Benfaremo et al. have prepared a block copolymer of DSB and polyethylene oxide (PEO).\textsuperscript{30} PEO with an average molecular weight of 900 (PEO\textsubscript{900}) was activated as mesylate (methanesulfonate) and reacted with 4,4'-bis(4-hydroxystyryl)benzene. Due to the good solubility properties of the PEO unit no additional solubilising groups on the chromophore were required. The polymer is soluble in a range of organic solvents (THF, DMF, chloroform and acetonitrile). The polymer emits blue light but devices based on this polymer were not stable.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.3.5.png}
\caption{Synthesis of a block copolymer with DSB units and PEO units (DSB Block-B).}
\end{figure}

Li et al. have prepared a similar block copolymer based on DSB and oligo(ethylene oxide).\textsuperscript{31} The Wittig reaction was used as the polycondensation reaction. The oligo(ethylene oxide) chain is much shorter than in the polymer prepared by Benfaremo et al. (DSB Block A) and two additional methyl groups on the central ring of the DSB unit aid solubility. The polymer is soluble in chloroform and shows blue photoluminescence. However, as in the previous case, LEDs based on this polymer were unstable.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.3.6.png}
\caption{Synthesis of a block copolymer with DSB units and PEO units via the Wittig reaction (DSB-Block-C).}
\end{figure}

Recently, Karasz et al. have shown that the Heck reaction can be used as the polymerisation reaction to prepare segmented block copolymers (Figure 1.3.7).\textsuperscript{32}
The authors selected the Heck reaction since it gives rise predominantly to trans-double bonds. Depending on the substituent $R$, the EL maximum is between 450 and 470 nm; long substituents lead to torsion of the chromophore and therefore a reduction of the effective conjugation length and a blue shift of the emission maximum. In the case of $R = H$, the polymer (DSB-Block-D) is very similar to Karasz' first block copolymer prepared by the Wittig reaction and only contains two additional methylene groups in the flexible linker. The authors report that yields and molecular weights of the polymers are high, but they do not report any EL quantum efficiencies for devices based on these polymers.

![Figure 1.3.7 Synthesis of a block copolymer with DSB units via the Heck reaction (DSB-Block-D).](image)

The Knoevenagel reaction has also been used to prepare block copolymers. The electroluminescence maximum (505 nm) of the block copolymer with cyano groups is red shifted compared to that of the parent polymer 'DSB Block A' (Figure 1.3.4) since the cyano groups lower the LUMO energy level strongly. However, the authors mention difficulty with side reactions leading to cross-linking of the polymer and no efficiencies are reported.

![Figure 1.3.8 Synthesis of a block copolymer with cyano groups via the Knoevenagel reaction (DSB-CN).](image)
Hay and Klavetter have prepared a block copolymer with alternating flexible linker units and conjugated units. However, in this case the conjugated units have different lengths depending on the feed ratio of the three comonomers used. Figure 1.3.9 shows the three different comonomers; terephtaldehyde, p-xylylene-bis(triphenylphosphonium chloride) and a comonomer with a central non-conjugated unit and two terminal aldehyde groups were cocondensed using the Wittig reaction. The absorption spectrum of the resulting polymer is an intermediate of the absorption spectrum of PPV and DSB-Block-A (Figure 1.3.4), as expected since the polymer contains DSB units as well as longer conjugated oligo(phenylene vinylene) units. However, the PL and EL spectra are very similar to those of PPV and show no resemblance to those of a DSB block copolymer. The authors assign this to an efficient intra- and intermolecular energy transfer from the shorter to the longer chromophores. The EL quantum efficiency for a device using ITO and Ca as electrodes was 0.8%. This increase in the efficiency relative to PPV is due to a better confinement of the exciton.

The absorption maxima, the PL maxima and the EL maxima of the previously described polymers are compared in Table 1.3.1. In general, fully conjugated polymers have an absorption and emission maxima at higher wavelength than those containing DSB as chromophore, since a longer conjugation length results in a smaller optical band gap. Substituents can be used to tune the optical properties, for example alkoxy substituents on the aromatic rings lead to a red shift in absorption and emission. Some polymerisation methods lead to defects in the polymers and some polymers give rise to unstable LEDs. It is therefore very important that polymerisation method chosen leads to defect-free, well characterised polymers so
that the stable devices can be prepared and the device characteristics are not altered by impurities in the sample.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Figure</th>
<th>( \lambda_{\text{max}}(\text{abs.}) )</th>
<th>( \lambda_{\text{max}}(\text{PL}) )</th>
<th>( \lambda_{\text{max}}(\text{EL}) )</th>
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</thead>
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<tr>
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<td>560 nm</td>
<td>560 nm</td>
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<td>Figure 1.3.1</td>
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<td>Figure 1.3.2</td>
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<td>-</td>
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<td>Figure 1.3.3</td>
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<td>453 nm</td>
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<td>DSB-Block-B</td>
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<td>-</td>
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<tr>
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<td>Figure 1.3.6</td>
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<tr>
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<td>Figure 1.3.9</td>
<td>370 nm*</td>
<td>540 nm*</td>
<td>540 nm*</td>
</tr>
</tbody>
</table>

Table 1.3.1 Solid state absorption maxima, PL maxima and EL maxima of the polymers described in this section. An asterisk * indicates that the value was not mentioned in the text of the corresponding article but was taken from a diagram; a relatively large error (± 5 nm) should therefore be kept in mind for these values.

1.4 Fluorinated conjugated polymers

The fluorine atom is the atom with the second highest electron affinity (3.399 eV) in the periodic table after chlorine (3.617 eV). While the electron affinity describes the energy gain of an atom when binding an electron, the electronegativity is, according to Pauling, the power of an atom in a molecule to attract electrons to itself. The electronegativity is a less accurate measure than the electron affinity and different methods have been designed to determine it. However, all methods show that fluorine has the greatest power to attract electrons within a molecule followed by oxygen and chlorine. The strong electron withdrawing effect changes the character of organic molecules dramatically. For example most aromatic rings react readily under electrophilic attack while
fluorinated aromatic rings are almost inert under such conditions but react readily under nucleophilic attack.\textsuperscript{38}

The fluorine atom is the smallest halogen. The van der Waal’s radius of fluorine (1.35 Å) is only slightly bigger than that of hydrogen (1.2 Å).\textsuperscript{39} Chlorine (1.80 Å) and bromine (1.95 Å) have distinctly larger van der Waal’s radii. A fluorine atom therefore induces little steric effect when replacing a hydrogen atom in an organic molecule. A carbon-fluorine-bond is stronger than a carbon hydrogen bond. The bond strength of a C-F bond in C\textsubscript{2}F\textsubscript{6} is 530 ± 8 kJ/mol compared with the C-H bond strength of 419 ± 8 kJ/mol in C\textsubscript{2}H\textsubscript{6}.\textsuperscript{39} Polymers that are highly or completely fluorinated have properties beyond the limit of conventional polymers; they show stability at high temperatures, toughness and flexibility at low temperatures and non-adhesiveness. Many fluoropolymers are also resistant to corrosive chemicals.\textsuperscript{40} Chemical stability and the high electronegativity are two of the reasons why the effect of fluorine on conjugated polymers has been studied previously. Some examples are given below.

Fluorine-substituted PPVs were first studied by McCoy \textit{et al.}\textsuperscript{41} The authors prepared poly(2-fluoro-1,4-phenylenevinylene) (1F-PPV) and poly(2,5-difluoro-1,4-phenylene vinylene) (2F-PPV) via the Wessling route (Figure 1.4.1). 1F-PPV showed a slight blue shift in the absorption spectrum relative to PPV. The maximum of the EL spectrum of a device using ITO and Al electrodes was unchanged when compared to the parent PPV polymer. However, the turn-on voltage was at least 7 V, whereas it was only 4 V for the corresponding device based on PPV,\textsuperscript{42} which was attributed to an increase in the ionisation potential of 0.17 eV relative to PPV. Furthermore, the devices constructed with 1F-PPV showed an increase in efficiency.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{1F-2F-PPVs.png}
\caption{Poly(2-fluoro-1,4-phenylenevinylene)(1F-PPV) (left) and poly(2,5-difluoro-1,4-phenylene vinylene)(2F-PPV) (right).}
\end{figure}

The PPV derivative with two fluorine atoms per phenylene unit (2F-PPV) showed a red shift in the EL spectrum with a maximum at 600 nm.\textsuperscript{43} The authors
found that such a red shift is typical for PPV derivatives with 2,5 substitution of \( \pi \)-donating, electron withdrawing groups such as chlorine, bromine as well as alkoxy substituents. The authors did not report efficiencies for devices based on 2F-PPV.

Benjamin et al. have prepared PPV analogues containing \( p \)-phenylenevinylene and 2,3,5,6-tetrafluoro-1,4-phenylenevinylene units \textit{via} the Wessling route (Figure 1.4.2). Two comonomers were reacted in different ratios resulting in polymers with a varying fluorine content. The yield of the polymer decreased as the content of fluorinated comonomer was increased; the polymer yield was only 25\% when the reaction was conducted using a mixture of 60\% fluorinated comonomer and 40\% non-fluorinated comonomer. The photoluminescence intensity decreased sharply as the content of fluorinated monomer was increased. The authors were unable to prepare a fully fluorinated analogue of PPV. Also the electroluminescence was blueshifted as the content of fluorinated comonomer was increased. However, it remained unclear whether this was due to the effect of fluorine on the optical band gap of the polymer or to the shortening of the conjugation length of homo-PPV blocks in the polymer, which were stronger emitters than the fluoro-analogues. The turn-on voltage of devices based on these polymers increased with increasing fluorine-content.

\[
\text{Figure 1.4.2 Synthesis of a copolymer with tetratrafluorophenylene vinylene units via the Wessling route (PPV/4F-PPV).}
\]

Holmes \textit{et al.} prepared copolymers \textit{via} the Gilch-route having 2,3,5,6-tetrafluoro-1,4-phenylene vinylene and 2,5-dialkoxy-1,4-phenylene vinylene units (Figure 1.4.3). The authors incorporated between 7 and 19\% of fluorinated monomer into the copolymer. The incorporation of fluorinated monomer led to a decrease in the yield and also a decrease in the solubility of the polymer. The electroluminescence spectra of all these copolymers were unchanged relative to that of the homopolymer MEH-PPV, the maximum emission for all polymers being at 590 nm. However, the photoluminescence efficiencies of the copolymers (4-7\%)
were significantly lower than that of the MEH-PPV (14%). In these systems the EL efficiencies decreased and the turn-on voltages increased with increasing fluorine content.

\[
\text{Figure 1.4.3 Synthesis of a copolymer with tetrafluorophenylene vinylene units via the Gilch route (MEH-PPV/4F-PPV).}
\]

Efforts have been made to introduce fluorine atoms in side chains rather than directly on the aromatic ring. Grimsdale et al. have prepared poly(2-trifluoromethyl-1,4-phenylene vinylene) using the Gilch-route (Figure 1.4.4).\textsuperscript{33,46} For this material absorption and emission spectra were blue shifted with respect to PPV and the solid state PL quantum efficiency was only 5%. The polymer gave poor, non-uniform electroluminescence in single layer devices.

\[
\text{Figure 1.4.4 Synthesis of poly(2-trifluoromethyl-1,4-phenylene vinylene) via the Gilch route (CF}_3\text{-PPV 1).}
\]

Holmes et al. prepared polymers with trifluoromethyl-groups on the vinylene unit via the Horner-Wittig reaction.\textsuperscript{47,48} The PL maximum was slightly red-shifted compared to PPV. The ionisation potential and the electron affinity were increased. The polymer was used in double layer devices in a similar fashion to CN-PPV in order to aid electron-injection and ‘block’ whole-injection.

\[
\text{Figure 1.4.5 Synthesis of a PPV derivative with trifluoromethyl-groups on the vinylene unit (CF}_3\text{-PPV 2).}
\]
Shim et al. prepared a PPV derivative with a perfluorobiphenyl substituent via the Wessling route (Figure 1.4.6). The absorption maximum occurred at 400 nm and the PL and EL emission at 520 nm. All maxima were blue shifted relative to those of PPV. The IP of the polymer was increased by 0.4 eV relative to PPV. The authors found that the quantum efficiency was higher than that of PPV but the turn-on voltage was also increased.

Figure 1.4.6 Synthesis of a PPV derivative with a perfluorobiphenyl side chain (PPFPV).

Sarker et al. prepared block copolymers with DSB units and non-conjugated flexible linkers, in which the DSB units contained a central fluorinated benzene ring (Figure 1.4.7). The Horner-Wittig reaction was used as the polymerisation reaction.

Three of the reported polymers had additional methoxy groups on the DSB units to aid solubility. These three polymers showed absorption maxima between 362 and 365 nm and PL emission maxima between 487 and 502 nm. A fourth polymer with methyl groups on the DSB unit had blue-shifted absorption and emission maxima (332 and 421 nm, respectively). This was attributed to the fact that the methyl
groups cause the conjugated system to be less planar. The PL quantum efficiencies of all four polymers were low and the authors believe this is due to highly ordered structures based on $\pi-\pi$-interactions between phenyl and perfluorophenyl groups and therefore regard such polymers as unattractive for LEDs.

The absorption, PL and EL maxima, the electron affinities and the ionisation potentials of fluorinated PPV derivatives are compared in Table 1.4.1. The absorption maxima of the fluorinated polymers are either unchanged or show a small blue shift relative to the non-fluorinated equivalents. No general trend is observed for the PL and EL spectra but it is found that not only the electronegativity of the substituent but also the substitution pattern along the polymer affects the outcome.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Figure</th>
<th>$\lambda_{\text{max}}$(abs)</th>
<th>$\lambda_{\text{max}}$(PL)</th>
<th>$\lambda_{\text{max}}$(EL)</th>
<th>EA (HOMO)</th>
<th>IP (LUMO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPV</td>
<td>Figure 1.1.5</td>
<td>450 nm</td>
<td>560 nm</td>
<td>560 nm</td>
<td>2.5 eV</td>
<td>5.2 eV</td>
</tr>
<tr>
<td>CN-PPV</td>
<td>Figure 1.3.2</td>
<td>485 nm</td>
<td>710 nm</td>
<td>-</td>
<td>3.4 eV</td>
<td>5.8 eV</td>
</tr>
<tr>
<td>1F-PPV</td>
<td>Figure 1.4.1</td>
<td>422 nm</td>
<td>560 nm</td>
<td>560 nm</td>
<td>2.7 eV</td>
<td>5.4 eV</td>
</tr>
<tr>
<td>2F-PPV</td>
<td>Figure 1.4.1</td>
<td>420 nm</td>
<td>590 nm</td>
<td>600 nm</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PPV/4F-PPV</td>
<td>Figure 1.4.2</td>
<td>350 nm</td>
<td>550 nm</td>
<td>525 nm/495 nm</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MEH-PPV/4F-PPV</td>
<td>Figure 1.4.3</td>
<td>500 nm</td>
<td>590 nm</td>
<td>590 nm</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CF$_2$-PPV 1</td>
<td>Figure 1.4.4</td>
<td>335 nm*</td>
<td>517 nm</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CF$_2$-PPV 2</td>
<td>Figure 1.4.5</td>
<td>440 nm*</td>
<td>580 nm</td>
<td>-</td>
<td>3.1 eV</td>
<td>5.8 eV</td>
</tr>
<tr>
<td>PF-PPV</td>
<td>Figure 1.4.6</td>
<td>400 nm</td>
<td>520 nm</td>
<td>520 nm</td>
<td>2.9 eV</td>
<td>-</td>
</tr>
<tr>
<td>F-DSB-Block-a</td>
<td>Figure 1.4.7</td>
<td>365 nm</td>
<td>487 nm</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>F-DSB-Block-d</td>
<td>Figure 1.4.7</td>
<td>332 nm</td>
<td>421 nm</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1.4.1 Absorption maxima, the PL maxima and the EL maxima of the polymers described in this section. The asterisks * indicate that these values were not mentioned in the text of the corresponding articles but were taken from diagrams in those articles; a relatively large error ($\pm$ 5 nm) should therefore be kept in mind. The ionisation potential (IP) and the electron affinity (EA) are recorded relative to the vacuum level.

While some reports suggest an improvement in device performance there are also many indications that the presence of fluorinated units or substituents has a negative effect on the emissive properties of the polymer and leads to a decrease in
EL efficiency. Some groups were unable to report any electroluminescence for single layer devices based on the fluorinated polymers due to poor device stability. However, several groups used the polymers to prepare highly efficient double layer LEDs, where the fluoro-polymer aids electron-transport and blocks hole-transport. The electron affinity of fluoro-polymers is always higher than that of their non-fluorinated analogous confirming that such polymers form good electron-transport layers. All structures reported have both hydrogens and fluorines along the polymer backbone. To our knowledge, nobody has so far prepared a fully fluorinated derivative of PPV.

1.5 Aim

The original aim of this work was to study the effect of fluorine on conjugated polymers. To this end various routes to fluorinated systems were investigated. A well characterised block copolymer with alternating fluorinated conjugated units and flexible linker units was synthesised. A copolymer with isolated chromophores bears the potential advantage over a polymer with a fully conjugated backbone in that the flexible linkers provide the solubility and no additional solubilising groups on the polymer backbone are required; in the case of PPV derivatives this means that all four available aromatic positions can be substituted with fluorine atoms. Figure 1.5.1 shows a schematic representation of such a block copolymer.

![Figure 1.5.1 Schematic representation of a block copolymer with fluorinated conjugated units and non-conjugated flexible linkers.](image-url)
The high electronegativity of fluorine was expected to aid electron injection and it was anticipated that a balance of charge carriers should lead to highly efficient electroluminescent polymers. In order to study the effect of fluorine, the non-fluorinated block copolymer was required as well as the fluorinated material.

Furthermore, fluorinated phenylene vinylene oligomers were synthesised in order to study the molecular packing in such molecules.

The use of polymers in LEDs is an area that requires expertise in both chemistry and physics. A network of European scientist in the area of organic semiconductors is currently funded through the EU commission as the LAMINATE (Large Area Molecular-electronics Involving a Novel Approach to Training and Education) programme. The optoelectronic properties of the novel polymers will be studied in cooperation with these partners. The remainder of this thesis reports the synthesis, characterisation and investigation of the materials indicated above.

1.6 References

2 Syntheses of Fluorinated Conjugated Polymers via the McMurry Reaction

2.1 Introduction

This chapter describes the results of an investigation into the potential of McMurry coupling for the synthesis of fluorinated PPVs and related polymers. The reasons for attempting each approach are outlined together with the experimental results and the explanation of why the route was abandoned. Ultimately, the McMurry route was unsuccessful in our hands; nevertheless some interesting chemistry resulted which is reported in this chapter.

In the McMurry reaction aldehydes and ketones are dimerised to yield olefins under reductive conditions with low-valent titanium reagents.\(^1\) The McMurry coupling has been of great use to organic chemists in both inter- and intramolecular reactions allowing the synthesis of sterically crowded olefins, small and large rings as well as a wide range of natural products.\(^2-4\) The accepted mechanism involves an initial electron transfer from titanium to the carbonyl group (Figure 2.1.1).\(^5\) Titanium is oxidised but the exact oxidation states can not be determined. (Changes from (0) to (II) or from (I) to (III) have been suggested.\(^2-4\)) The ketyl radicals bound to a titanium particle then dimerise to the corresponding titanium bound pinacol. Deoxygenation of the bound pinacol occurs due to the large affinity of titanium for oxygen, leading to alkenes.

![Figure 2.1.1 Mechanism of the McMurry reaction.](image-url)
The McMurry reaction is compatible with a range of functional groups, including ethers, amines, saturated alcohols and halides.\textsuperscript{6} The efficiency of the reaction depends on the specific reagents and conditions but yields of 98\% have been reported repeatedly.\textsuperscript{7,8} Such high conversions make the McMurry reaction attractive for polycondensation reactions. Indeed, Feast \textit{et al.} and Schlüter \textit{et al.} used the McMurry reaction to prepare soluble poly(\textit{p}-phenylene vinylene)s.\textsuperscript{9,10} Daik \textit{et al.} have been able to polymerise 4,4'-di(benzoly)biphenyl via the McMurry reaction and obtained poly-(4,4'-diphenylene diphenylvinylene) of high molecular weight and high purity (\textit{Figure 2.1.2}).\textsuperscript{11,12} Also, Daik \textit{et al.} were able to polymerise a fluorinated analogue where \( R = \text{pentafluorophenyl} \). These findings encouraged further investigations into the McMurry reaction, which are described here.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure212.png}
\caption{Synthesis of poly(4,4'-diphenylene diphenylvinylene).}
\end{figure}

It is expected that the McMurry reaction can also be used for the synthesis of copolymers when a mixture of comonomers is used. Given that all monomers have the same reactivity towards low-valent titanium, a statistical distribution of monomers within the polymer-chain can be anticipated.

\subsection*{2.2 Results and Discussion}

\textit{Monomer syntheses}

First, the use of the McMurry reaction as a condensation reaction for fluorinated aromatic ketones was examined. Small model compounds were chosen as analogues for the proposed polymerisation, in order to investigate the efficiency of the reaction and the occurrence of possible side-reactions. It was found that the reaction of pentafluorobenzophenone 1 with low-valent titanium gave the 9-pentafluorophenyl-
10-phenyl-1,2,3,4-tetraphenylpenanthrene 2 as the main product amongst at least eight other by-products. Compound 2 could be isolated in 30% yield and was fully characterised. Bis(pentafluorophenyl)diphenylethene 3 was not found in the product mixture (Figure 2.2.1). However, the second most abundant product identified by GC-MS and $^{19}$F NMR was consistent with replacement of an ortho-fluorine atom by a hydrogen atom in structure 3 (see experimental section 2.4.2). Other products identified by GC-MS were consistent with further replacements of fluorine atoms by hydrogen in structures 2 and 3.

![Figure 2.2.1 McMurry reaction of 2,3,4,5,6-pentafluorobenzophenone. a) TiCl$_3$, LiAlH$_4$, THF](image)

Decafluorobenzophenone, the perfluorinated equivalent of 1, reacted in a similar way with low-valent titanium; again a new carbon-carbon bond was formed between to adjacent rings giving rise to a phenanthrene ring system (reaction not shown). Such phenanthrene ring closures are undesired in polymer forming reactions since there is no control as to where they occur. Therefore, it was concluded that the McMurry reaction was unsuitable for the reductive coupling of fluorinated ketones and the products were not further investigated.

However, using fluorinated aldehydes no side reactions were found; for example pentafluorobenzaldehyde 4 reacts with low-valent titanium to give trans-decafluorostilbene 5 in good yield (89%)(Figure 2.2.2). No cis-isomer and no by-products were detected in the NMR spectra ($^1$H, $^{13}$C, $^{19}$F) of the crude product. This indicates that it is probably the steric crowding in the case of fluorinated ketones that
is responsible for the phenanthrene formation and side-reactions; since no cis-isomer was produced in the case of aldehydes, phenanthrene formation was not possible in this reaction.

![Diagram](image)

*Figure 2.2.2 McMurry reaction of pentafluorobenzaldehyde. a) TiCl₄, Zn, dioxane*

In order to use the coupling of aldehydes for polycondensation reactions a copolymer approach was investigated. The target copolymer consisted of alternating rigid oligo(tetrafluorophenylene vinylene) units and flexible solubilising units. The synthesis required two comonomers: one containing the flexible linker unit and the other one allowing the build up of the oligo(tetrafluorophenylene vinylene) units. Ideally, both monomers should have similar reactivities towards low-valent titanium. The first comonomer was prepared following the route shown in *Figure 2.2.3* and *Figure 2.2.4*.

Using pentafluorobenzaldehyde as the starting material, the aldehyde function was protected as an acetal (*Figure 2.2.3*).

![Diagram](image)

*Figure 2.2.3 Protection of pentafluorobenzaldehyde as an acetal. a) C₂H₅OH, CH(OC₂H₅)₃, H₂SO₄*

Nucleophilic substitution of pentafluorobenzaldehyde diacetal has been reported to occur selectively in the *para*-position.¹³ Two protected aldehydes were connected by nucleophilic substitution with α,ω-diols. Three different α,ω-diols were investigated: sexi(ethylene oxide) 7, neopentyl glycol 8 and 2-ethylhexane-1,3-diol 9. [Compound 7 is termed sexi(ethylene oxide) (SEO) rather than hexa(ethylene oxide) (HEO) since the letter 'H' will be used at a later stage as abbreviation for...
hydrogen.] Each $\alpha,\omega$-diol was deprotonated with $n$-butyllithium. Addition of pentafluorobenzaldehyde diacetal gave compounds 10, 11 and 12 (Figure 2.2.4). Deprotection in aqueous acid gave the flexible linkers 13, 14 and 15, respectively. Each flexible linker consists of a central non-conjugated unit which promotes solubility and two terminal fluorinated aromatic aldehydes.

![Chemical structures](image)

**Figure 2.2.4 Synthesis of flexible linkers. a) BuLi, THF b) THF c) H$_2$O, THF, H$_2$SO$_4$**

The second required comonomer is 2,3,5,6-tetrafluoroterephthalaldehyde 18 (if homopolymerised it would give rise to an insoluble and intractable fluorinated derivative of PPV). Several synthetic approaches, including reduction of the corresponding ester or nitrile, failed.$^{14,15}$ It was possible though to prepare 2,3,5,6-tetrafluoroterephthalaldehyde tetra-acetate 17 by oxidation of 2,3,5,6-tetrafluoroxylene 16 with chromium trioxide in the presence of acetic anhydride (Figure 2.2.5). Compound 17 was hydrolysed to give the desired 2,3,5,6-tetrafluoroterephthalaldehyde 18.
However, the yield for the first step was very low (2.4%) and could not be improved. The overall yield starting from tetrafluoroxylene was only 1.4%. Since only small quantities (70 mg) of compound 18 could be prepared by this method in one batch, this route was unsatisfactory as a starting point for an investigation into new polymers.

The reaction of tetrafluoroxylene 16 with elemental bromine under irradiation with UV-light gave 1,4-bis(dibromomethyl)-2,3,5,6-tetrafluorobenzene 19 in good yield (69%). The reaction conditions were optimised and it was found that several additions of bromine and the use of a large reaction vessel were advantageous for the photolytic cleavage of bromine. Although the reaction conditions were very harsh (excess of bromine, 160 °C, UV-light, 10 h) the C-F bonds stayed intact and no bromine substitution on the aromatic ring was observed by NMR or mass spectroscopy. Hydrolysis of compound 19 with concentrated sulphuric acid gave 2,3,5,6-tetrafluoroterephtalaldehyde 18. The overall yield was improved to 24% and sufficient amounts of 18 (1 g) could be prepared to investigate polymerisations.
Polymer syntheses

Initially, an attempt was made to homopolymerise the monomer 13. However, the product could not be reprecipitated from chloroform into methanol. It was found that the McMurry reaction had produced a cyclic product 20 in 26% yield rather than a polymer (Figure 2.2.7) as shown by mass spectroscopy (m/z = 602) and NMR spectroscopy.

The $^1$H NMR spectrum of 20 shows that the hydrogens in the sexi(ethylene oxide) unit are all shifted towards higher field compared to those in the linear compound 13. Furthermore, the signals for the four central ethylene units are resolved in the case of 20 but they are not resolved in the case of 13. These findings can be explained by the position these methylene units with respect to the aromatic rings and the influence of the ring-current on the shifts.

This cyclisation is favoured by the fact that the McMurry reaction takes place on the surface of titanium particles and the two aldehyde groups are brought into close proximity. An increase in concentration in order to favour inter- over intramolecular reaction was not possible since the reaction mixture was a very viscous slurry of titanium in THF. Cyclisations of aromatic dialdehydes via the McMurry reaction to give stilbenes bridged by oligo(ethylene oxide) units have been reported previously by Fuerstner et al. and Gandour et al.\textsuperscript{4,17}
Using the monomer 13 and 2,3,5,6-tetrafluoroterephthalaldehyde 18 as comonomers (in molar ratio of 4:1), it was possible to prepare a mixture of polymer 21 and the cyclic product 20 (Figure 2.2.8). When a solution of the mixture in chloroform was reprecipitated into methanol the pure polymer was obtained.

![Chemical structure]

Figure 2.2.8 Synthesis of a fluorinated conjugated polymer via the McMurry reaction. a) TiCl₄, Zn, THF

The formation of polymers was due to the fact that in this reaction a range of conjugated units was formed. Stilbene units are formed when two aldehyde endgroups react, whereas if one molecule 18 is incorporated, a distyrylbenzene (DSB) unit is formed and when two molecules 18 are incorporated a distyrylstilbene (DSS) is formed; further incorporation of 18 results in longer conjugated sequences. With units such as DSB and DSS a cyclic product cannot be formed since the sexi(ethylene oxide) unit cannot bridge the larger units. The polymer 21 was characterised by ¹H NMR spectroscopy and Gel Permeation Chromatography (GPC), which indicated a $M_n = 8,300$ and a polydispersity of 3.2 with respect to polystyrene. Due to the formation of the cyclic compound 20 there was little control over the composition of the polymer with respect to relative incorporation of the two monomers; the polymer was expected to contain a higher fraction of 18 than was present in the starting mixture. Furthermore, analysis of the ¹H NMR spectrum of the polymer showed that some aldehydes had reacted incompletely and the polymer contained pinacol defects. For these reasons the synthesis of polymer 21 was not further investigated.

Monomer 12 which contains a shorter flexible linker was used in order to avoid a ring closure. When 12 was homopolymerised the obtained polymer was insoluble in non-chlorinated solvents and only very poorly soluble in chloroform or DCM.
Since the neopentyl glycol unit was insufficient to render the polymer soluble, this reaction was also abandoned.

2-Ethylhexane-1,3-diol 9 is commercially available as a mixture of stereoisomers. The long side chains and the disorder due to the isomeric mixture were expected to give rise to enhanced solubility. Like neopentyl-glycol 8 it is a 1,3-diol and the ring closure of the corresponding flexible linker 15 is not possible. Indeed, 15 and 18 could be copolymerised in the molar ratio x and y using the McMurry reaction.

![Figure 2.2.9 Synthesis of a fluorinated conjugated polymer via the McMurry reaction. a) TiCl₄, Zn, THF](image)

The molar fraction of 18 (y) was varied between 0.1 and 0.3 (Table 2.2.1). The polymers obtained 22a, b and c were soluble in chloroform and were characterised by NMR spectroscopy (¹H, ¹⁹F), GPC and solution-state absorption and emission spectroscopy. The chloroform solution of polymer 22c was slightly cloudy and GPC analysis was not possible. The ¹H NMR spectra of all polymers show that some aldehyde functions have reacted incompletely and all polymers contain pinacol defects.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>molar fraction x</th>
<th>molar fraction y</th>
<th>Mₙ</th>
<th>calculated fraction of stilbene units in the polymer</th>
<th>calculated fraction of DSB units in the polymer</th>
<th>calculated fraction of DSS units in the polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>22a</td>
<td>0.9</td>
<td>0.1</td>
<td>3,500</td>
<td>90.0%</td>
<td>9.0%</td>
<td>0.9%</td>
</tr>
<tr>
<td>22b</td>
<td>0.8</td>
<td>0.2</td>
<td>7,500</td>
<td>80.0%</td>
<td>16.0%</td>
<td>3.2%</td>
</tr>
<tr>
<td>22c</td>
<td>0.7</td>
<td>0.3</td>
<td>--</td>
<td>70.0%</td>
<td>21.0%</td>
<td>6.3%</td>
</tr>
</tbody>
</table>

Table 2.2.1 Composition and molecular weight of polymers 22a, b and c.
The solution state absorption spectra of the polymers 22a, b and c show the typical absorption band for a stilbene unit as the main feature between 290 and 350 nm (Figure 2.2.10). The absorption band of longer conjugated units such as DSB and DSS can be found between 350 and 450 nm.\textsuperscript{18,19}

![Absorption Spectra of Polymers 22a, b, and c](image)

*Figure 2.2.10 Solution state absorption spectra of polymers 22a, b and c.*

The theoretical distribution of stilbene, DSB, DSS and longer units within the polymer chain can be calculated according to the following equation:\textsuperscript{20}

\[
N(n) = P_{aa}^{(n-1)}P_{ab}
\]

N is the probability that a sequence of n units of A (in this case 18) occurs in the copolymer. \(P_{aa}\) and \(P_{ab}\) are the probabilities that a molecule A reacts with another molecule A or with a molecule B (in this case 15), respectively. Assuming that both monomers have the same reactivity these probabilities can be replaced by the molar fractions of the comonomers (x and y). As the fraction of compound 18 in the reaction mixture is increased in polymers 22a, b and c the calculated fraction of DSB and DSS in resulting polymers increases, too, as shown in Table 2.2.1. This increase can also be found in the absorption bands of DSB and DSS as shown in Figure 2.2.11, confirming the proposed structures. A quantitative analysis of the absorption spectrum was not possible since the polymers contain defects and the absorption coefficients are unknown.
Hay and Klavetter have shown that the emission of a copolymer comprising conjugated units of different lengths stems from the longest conjugated units.\textsuperscript{21} It was therefore expected that the emission maximum would be red-shifted as the length of the conjugated units increases from polymer 22a to 22c. Indeed, the emission maximum for polymer 22a is found at 440 nm whereas the maxima for 22b and 22c are found at 450 nm (Figure 2.2.12).

However, it was not possible to prepare polymers with a comonomer 18 feed ratio higher than 30\% because of the solubility problems already observed in the case of polymer 22c. This limited the range of conjugated units, which could be prepared. Furthermore pinacol defects were found in all polymers prepared \textit{via} the McMurry reaction. Therefore, the polymers were found unsuitable for the preparation of electroluminescent devices and not further investigated.

\section*{2.3 Conclusions}

The McMurry reaction was found to be suitable for the coupling of fluorinated aromatic aldehydes but not for fluorinated aromatic ketones. Three comonomers with flexible linkers and fluorinated aromatic aldehyde end-groups were prepared as well as 2,3,5,6-tetrafluoroterephthalaldehyde. A range of polymers with moderate molecular weights ($M_n$ 3,000 – 8,000) were synthesised on the basis of these
monomers. This copolymer approach allowed the variation of the length of conjugated units within those polymers.

However the solubility of the polymers with longer conjugated units was limited. Furthermore, all polymers showed pinacol defects. Therefore, the McMurry reaction was abandoned and different approaches to fluorinated block copolymers were investigated (Chapter 3).

2.4 Experimental

2.4.1 General

Apparatus

Melting points were obtained using an Electrothermal IA9200 series digital melting point apparatus. Elemental analysis data were recorded on an Exeter Analytical Elemental Analyser CE-440. Mass spectra were recorded using either a Micromass AutoSpec mass spectrometer or a Hewlett Packard Series II gas chromatograph with a HP1 GC column, attached to a Fisons Trio 1000 mass spectrometer. Calculated molecular weights are reported in g mol\(^{-1}\). NMR-spectra were recorded using either a Varian Inova (\(^1\)H at 500 MHz and \(^{13}\)C at 125 MHz), a Varian VX400S (\(^1\)H at 399.95 MHz and \(^{13}\)C at 100.58 MHz), a Varian Unity (\(^1\)H at 299.91 MHz and \(^{13}\)C at 75.41 MHz) or a Varian Gemini (\(^1\)H at 200 MHz, \(^{13}\)C at 50.2 MHz and \(^{19}\)F at 188 MHz). Chemical shifts are reported in parts per million with respect to the solvent peak (CDCl\(_3\) \(\delta\) 7.27; TCE-d\(_2\) \(\delta\) 5.99; C\(_6\)D\(_8\) \(\delta\) 7.09, 7.00, 6.98, 2.09). The UV-lamp used was a Blak-Ray longwave UV-lamp (UVP inc., CA, 2 AMPS at 220 V). Molecular weights of polymers were determined using a Viscotec gel permeation chromatograph with refractive index detector using chloroform as eluent and polystyrene standards (3 x PL-swg mixed bed 5 \(\mu\)m columns). Absorption spectra were recorded using a Unicam UV/Vis spectrometer UV2. A FluroMax-2 spectrometer (ISA Instruments) was used for the emission spectra.
Chemicals

Reagents were supplied by Aldrich except pentafluorobenzaldehyde (Apollo), 2-ethylhexane-1,3-diol (Fluka) and lithium chloride (Lancaster). Deuterated solvents were used as supplied (Goss). THF was dried over alumina (EasyPure System).

2.4.2 9-Pentafluorophenyl-10-phenyl-1,2,3,4-tetraphenylpenanthrene (2)

TiCl₃ (1.54 g, 10 mmol) and LiAlH₄ (0.19 g, 5 mmol) were placed in a flask under nitrogen. Dry THF (40 ml) was added at 0 °C. The mixture was refluxed for 1 h and cooled to room temperature. 2,3,4,5,6-Pentafluorobenzophenone (2.55 g, 9.4 mmol) was added. The mixture was refluxed for 20 h and quenched with 2 N hydrochloric acid (20 ml). The THF was removed under reduced pressure. The product did not dissolve in CHCl₃ (10 ml) as expected and 9-pentafluorophenyl-10-phenyl-1,2,3,4-tetraphenylpenanthrene (0.5 g) was collected by filtration. A further fraction was obtained by column chromatography (silica gel /hexane: chloroform 3:1) of the remaining solution. Combined yield of 9-pentafluorophenyl-10-phenyl-1,2,3,4-tetraphenylpenanthrene (0.7 g, 30%) as a white powder, mp 272 °C. Found: C, 63.22%; H, 1.74%; M(MS, Cl) 492 (M⁺). Calculated for C₂₆H₉F₉: C, 63.43%; H, 1.84%; M 492. ¹H NMR (C₇D₈, 200 MHz) δ 7.6–7.4 (m, 9H); ¹³C NMR (C₇D₈, 100 MHz)* δ 144.93*, 143.75*, 142.49*, 141.71*, 138.89*, 138.52, 138.27*, 137.93*, 131.57, 131.40, 129.31, 128.42, 127.87, 127.33, 126.98, 123.85, 117.91, 117.87, 117.37, 117.28, 116.45, 113.31; ¹⁹F NMR (C₇D₈, 188 MHz) δ -134.62 (t, J = 17.5 Hz, 1F), -139.69 (m, 2F), -145.33 (t, J = 17.5 Hz, 1F), -153.06 (t, J = 20.5 Hz, 1F), -155.82 (t, J = 17.5 Hz, 1F), -157.68 (t, J = 17.5 Hz, 1F), -161.59 (m, 2F) (see appendix page 130 and 131).

* The resonances that are marked with an asterix (*) were determined from ¹⁹F decoupled ¹³C NMR spectrum. The remaining resonances were determined from a ¹H decoupled ¹³C NMR spectrum.
1,2-Diphenyl-1-pentafluorophenyl-2-(2,3,4,5-tetrafluorophenyl)ethene

\[
\begin{align*}
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{H} \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F}
\end{align*}
\]

1,2-Diphenyl-1-pentafluorophenyl-2-(2,3,4,5-tetrafluorophenyl)ethane was found as the second most abundant product and characterised by GC-MS and $^{19}$F NMR spectrum. $\text{M} (\text{MS, Cl}) 494 (\text{M}^+)$. $^{19}$F NMR (CDCl$_3$, 188 MHz) $\delta$ -134.23 (ddd, $J = 6$ Hz, 12Hz, 20Hz; 1F, CF ortho to CH), -139.44 (m, 2F, pentafluorophenyl), -139.84 (ddd, $J = 4$ Hz, 12Hz, 25 Hz, 1F, CF ortho to C=C), -152.46 (ddd, $J = 4$ Hz, 20 Hz, 20Hz, 1F, CF meta to C=C), -154.4I (ddd, $J = 6$ Hz, 20 Hz, 25 Hz, 1F, CF meta to CH), -154.65 (m, 1F, pentafluorophenyl), -161.89 (m, 2F, F$_{12}$, pentafluorophenyl) (see appendix page 132 and 133).

### 2.4.3 Decafluorostilbene (5)

\[
\begin{align*}
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F}
\end{align*}
\]

$\text{TiCl}_4$ (1.45 g, 0.85 ml, 7.65 mmol) was added to a suspension of Zn (1.0 g, 15.3 mmol) in dioxane (30 ml) at $-10$ °C under nitrogen. The mixture was refluxed for 1 h and cooled to room temperature. 2,3,4,5,6-Pentafluorobenzaldehyde (1.0 g, 5.1 mmol) was then added and the mixture refluxed for 14 h. The mixture was quenched with 2 N hydrochloric acid (5 ml) and all solvents removed under reduced pressure. The product was re-dissolved in diethyl ether, washed with 2 N hydrochloric acid and water and dried (MgSO$_4$) yielding, after evaporation of the solvent, decafluorostilbene (0.81 g, 89%) as a white solid. As the melting point and the NMR spectra were in good agreement with those reported in the literature$^{22}$ no further analysis was carried out. mp 104 °C (lit.$^{23,24}$ 103-105 °C). $^{1}$H NMR (CDCl$_3$,}
200 MHz) δ 7.33 (s, 2H); $^{19}$F NMR (CDCl$_3$, 188 MHz) δ -142.21 (m, 2F), -153.97 (t, $J = 21$ Hz, 1F), -162.44 (m, 2F).

2.4.4 Pentafluorobenzaldehyde diethylacetal (6)

\[
\begin{align*}
\text{C}_2\text{H}_5\text{O} & \quad \text{F} \\
\text{C}_2\text{H}_5\text{O} & \quad \text{F}
\end{align*}
\]

A mixture of pentafluorobenzaldehyde (20 g, 102 mmol), ethanol (20 ml), ethyl orthoformate (20 ml) and conc. H$_2$SO$_4$ (0.1 ml) were refluxed for 1.5 h. The solvent was removed under reduced pressure and diethyl ether (150 ml) was added. The organic layer was washed with water, aqueous NaHCO$_3$ and water, dried (MgSO$_4$) and the solvent removed under reduced pressure yielding pentafluorobenzaldehyde diethylacetal (27 g, 98%) as a clear liquid. As the NMR spectra were in good agreement with those reported in the literature$^{25}$ no further analysis was carried out. $^1$H NMR (CDCl$_3$, 200 MHz) δ 5.71 (s, 1H, CHO$_2$), 3.4-3.9 (m, 4H, OCH$_2$), 1.26 (t, $J = 7$ Hz, 6H, CH$_3$); $^{13}$C ($^1$H) NMR (CDCl$_3$, 100 MHz) δ 144.86 (d, $J = 250$ Hz, CF), 141.18 (d, $J = 250$ Hz, CF), 137.49 (d, $J = 250$ Hz, CF), 113.21 (C-CHO$_2$), 96.50 (CHO$_2$), 63.71 (OCH$_2$CH$_3$), 14.95 (OCH$_2$CH$_3$); $^{19}$F NMR (CDCl$_3$, 188 MHz) δ -142.91 (m, 2F), -154.48 (t, $J = 20.5$ Hz, 1F), -162.28 (m, 2F).

2.4.5 1,17-Bis(4-diethoxymethyl-2,3,5,6-tetrafluorophenyl oxy)-3,6,9,12,15-pentaoxaheptadecane (10)

\[
\begin{align*}
\text{C}_2\text{H}_5\text{O} & \quad \text{F} \\
\text{C}_2\text{H}_5\text{O} & \quad \text{F}
\end{align*}
\]

Hexa(ethylene glycol) (9.7 g, 34.3 mmol) was dissolved in dry THF (300 ml). n-Butyllithium in hexane (1.6M, 43.7 ml, 70 mmol) was added and the mixture stirred for 30 min under nitrogen. Then 2,3,4,5,6-pentafluorobenzaldehyde diethylacetal (18.5 g, 68.6 mmol) was added. The mixture was refluxed for 14 h. After the addition of water (20 ml) the volatile components were removed under reduced pressure. Diethyl ether (200 ml) was added and the organic phase was washed twice with brine, twice with water and dried (MgSO$_4$). The diethyl ether was removed
under reduced pressure and the product purified by column chromatography (silica gel, hexane: diethyl ether 1:1 followed by pure diethyl ether) yielding 1,17-bis(4-diethoxymethyl-2,3,5,6-tetrafluorophenoxy)-3,6,9,12,15-pentaoxaheptadecane (11.3 g, 42%) as a colourless oil. Found: C, 52.26%; H, 5.95%; M(MS, Cl) 800 (MNH⁺). Calculated for C₃₄H₄₆F₈O₁₁: C, 52.17% H, 5.92%; M 782. ¹H NMR (CDCl₃, 200 MHz) δ 5.67 (s, 2H, acetal CH), 4.35 (t, J = 5 Hz, 4H, ar. COCH₂), 3.62 (m, 28H, OC₂H₄O and OCH₂CH₃), 1.23 (t, J = 7 Hz, 12H); ¹³C {¹H} NMR (CDCl₃, 100 MHz) δ 144.77 (d, J = 260 Hz, ar. CF), 140.91 (d, J = 250 Hz, ar. CF), 137.95 (ar. CO), 111.46 (ar. C-CHO₂), 96.53 (CHO₂) 74.37, 71.05, 70.81, 70.79, 70.76, 70.29 (OC₂H₄O), 63.44 (OCH₂CH₃), 14.92 (OCH₂CH₃); ¹⁹F NMR (CDCl₃, 188 MHz) δ -144.89 (m, 4F, CF ortho to CH₀₂) -157.26 (m, 4F, CF ortho to OC₂H₄) (see appendix page 134).

2.4.6 1,3-Bis(4-diethoxymethyl-2,3,5,6-tetrafluorophenoxy)-2,2-dimethylpropane (11)

2,2-Dimethylpropane-1,3-diol (2.08 g, 20 mmol) was dissolved in dry THF (200 ml). n-Butyllithium in hexane (1.6 M, 25 ml, 40 mmol) was added and the mixture stirred for 30 min under nitrogen. Then 2,3,4,5,6-pentafluorobenzaldehyde diethylacetal (12 g, 44.4 mmol) was added. The mixture was refluxed for 14 h. After the addition water (20 ml) the volatile components were removed under reduced pressure. Diethyl ether (150 ml) was added and the organic phase was washed twice with brine, twice with water and dried (MgSO₄). The diethyl ether was removed under reduced pressure and the product purified by column chromatography (silica gel, hexane: diethyl ether 20:1) yielding 1,3-bis(4-diethoxymethyl-2,3,5,6-tetrafluorophenoxy)-2,2-dimethylpropane (3.38 g, 28%) as a colourless oil. Found: C, 53.41% H, 5.34% M(MS, EI) 604 (M⁺). Calculated for C₂₇H₃₂F₈O₆: C, 53.64% H, 5.34%; M 604. ¹H NMR (CDCl₃, 200 MHz) δ 5.69 (s, 2H, acetal CH), 4.12 (s, 4H, ar. C-O-CH₂), 3.66 (m, 8H, O-CH₂CH₃), 1.25 (t, J = 7 Hz, 12H, O-CH₂CH₃), 1.14 (s, 6H, C(CH₃)₂); ¹³C {¹H} NMR (CDCl₃, 100 MHz) δ 144.87 (d, J = 250 Hz,
2.4.7 1,3-Bis(4-diethoxymethyl-2,3,5,6-tetrafluorophenyloxy)-2-ethylhexane (12)

2-Ethylhexane-1,3-diol (2.92 g, 20 mmol) was dissolved in dry THF (200 ml). n-Butyllithium in hexane (1.6M, 25 ml, 40 mmol) was added and the mixture stirred for 30 min under nitrogen. Then, 2,3,4,5,6-pentafluorobenzaldehyde diethylacetal (11 g, 40.7 mmol) was added. The mixture was refluxed for 14 h. After the addition of water (20 ml) the volatile components were removed under reduced pressure. Diethyl ether (150 ml) was added and the organic phase was washed twice with brine, twice with water and dried (MgSO₄). The diethyl ether was removed under reduced pressure and the product purified by column chromatography (silica gel, hexane: diethyl ether 20:1) yielding 1,3-bis(4-diethoxymethyl-2,3,5,6-tetrafluorophenyloxy)-2-ethylhexane (7.35 g, 57%) as a colourless oil. Found: C, 55.78%; H, 5.96%; M(MS, CI) 646 (M⁺). Calculated for C₂₇H₃₂F₈O₆: C, 55.73%; H, 5.92%; M 646. ¹H NMR (CDCl₃, 200 MHz) δ 5.70 (s, 2H, acetal CH), 4.60 (m, 1H, OCH₂CH₂O), 4.30 (m, 2H, OCH₂CH₂O), 3.67 (m, 8H, O-CH₂CH₃), 2.06 (m, 1H, OCH₂CH₂O), 1.68 (m, 6H, RCH₂CH₃), 1.26 (t, J = 7 Hz, 12H, OCH₂CH₃), 0.98 (m, 6H, RCH₂CH₃); ¹³C ¹H NMR (CDCl₃, 100 MHz) δ 144.95 (d, J = 250 Hz, ar. CF), 141.40 (d, J = 250 Hz, ar. CF), 140.99 (d, J = 250 Hz, ar. CF), 137.69 (ar. CO), 136.78 (ar. CO), 111.32 (ar. CCHO₂), 96.60 (CHO₂), 84.87 (OCH₂CH₂CH₂O) 73.96 (OCH₂CH₂CH₂O), 63.50 (OCH₂CH₃), 43.92, 32.94, 19.52, 19.19, 18.93, 18.26 (aliph. C), 14.98 (OCH₂CH₃), 13.99, 13.92, 12.05, 11.69 (aliph. C); ¹⁹F NMR (CDCl₃, 188 MHz) δ -144.83 (m, 4F, CF ortho to CHO₂), -156.56 (m, 2F, CF ortho to O-CH₂), -157.57 (m, 2F, CF ortho to O-CH₂) (see appendix page 136).
2.4.8 1,17-Bis(4-formyl-2,3,5,6-tetrafluorophenyloxy)-3,6,9,12,15-pentaoxaheptadecane (13)

Bis(4-diethoxymethyl-2,3,5,6-tetrafluorophenyloxy)-3,6,9,12,15-pentaoxaheptadecane (11.3 g, 14.4 mmol) was dissolved in a mixture of THF and water (100 ml/50 ml) and conc. H₂SO₄ (1 ml) was added. The mixture was stirred over night at 55 °C. The THF was removed under reduced pressure and diethyl ether (100 ml) was added. The organic phase was washed with water, aqueous NaHCO₃ and twice with water. It was dried (MgSO₄) and the solvent removed under reduced pressure yielding 1,17-bis(4-formyl-2,3,5,6-tetrafluorophenyloxy)-3,6,9,12,15-pentaoxaheptadecane (8.9 g, 97%) as a colourless oil. Found: C, 48.86%; H, 4.14%; M(MS, Cl) 652 (MNH₄⁺). Calculated for C₂₆H₂₆F₈O₉: C, 49.22%, H, 4.13%, M = 634. 

¹H NMR (CDCl₃, 200 MHz) δ 10.18 (s, 2H, CHO), 4.52 (m, 4H, ar. COCH₂), 3.83 (m, 4H, ar. COCH₂CH₂), 3.59 (m, 16H, OC₂H₄); ¹³C {¹H} NMR (CDCl₃, 100 MHz) δ 182.09 (CHO), 147.52 (d, J = 260 Hz, ar. CF), 143.10 (ar. CO), 140.26 (d, J = 250 Hz, ar. CF), 108.90 (ar. C-CHO), 74.21, 70.80, 70.50, 70.44, 70.03, (OC₂H₄O); ¹⁹F NMR (CDCl₃, 188 MHz) δ -146.75 (m, 4F, C-F ortho to CHO) -157.03 (m, 4F, C-F ortho to OC₂H₄) (see appendix page 137).

2.4.9 1,3-Bis(4-formyl-2,3,5,6-tetrafluorophenyloxy)-2,2-dimethylpropane (14)

1,3-Bis(diocto-4-methyl-2,3,5,6-tetrafluorophenyloxy)-2,2-dimethylpropane (2.8 g, 4.6 mmol) was dissolved in a mixture of THF and water (60 ml/ 30 ml) and conc. H₂SO₄ (0.5 ml) was added. The mixture was stirred over night at 55 °C. The THF was removed under reduced pressure and diethyl ether (80 ml) was added. The organic phase was washed with water, aqueous NaHCO₃ and twice with water. It was dried (MgSO₄) and the solvent removed under reduced pressure yielding 1,3-bis
(4-formyl-2,3,5,6-tetrafluorophenyl)oxy)-2,2-dimethylpropane (2.0 g, 95%) as a colourless oil. Found: C, 50.48%; H, 2.80%; M (MS, El) 456 (M+). Calculated for C\textsubscript{19}H\textsubscript{12}F\textsubscript{8}O\textsubscript{2}: C, 50.01%; H, 2.65%; M 456. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 200 MHz) \(\delta\) 10.22 (s, 2H, CHO), 4.30 (s, 4H, ar. C-O-CH\textsubscript{2}), 1.18 (s, 6H, CH\textsubscript{3}) \textsuperscript{13}C \{\textsuperscript{1}H\} NMR (CDCl\textsubscript{3}, 100 MHz) \(\delta\) 182.02 (CHO), 147.60 (d, \(J = 260\) Hz, ar. CF), 143.06 (ar. CO), 140.20 (d, \(J = 250\) Hz, ar. CF), 109.14 (ar. C-CHO), 79.02 (OCH\textsubscript{2}CCH\textsubscript{3}), 37.38 (OCH\textsubscript{2}CCH\textsubscript{3}), 21.01 (OCH\textsubscript{2}CCH\textsubscript{3}); \textsuperscript{19}F NMR (CDCl\textsubscript{3}, 188 MHz) \(\delta\) -146.30 (m, 4F, CF ortho to CHO) -157.37 (m, 4F, CF ortho to O-C\textsubscript{2}H\textsubscript{4}) (see appendix page 138).

### 2.4.10 1,3-Bis(4-formyl-2,3,5,6-tetrafluorophenyl)oxy)-2-ethylhexane (15)

![Structure](image)

1,3-Bis(4-diethoxymethyl-2,3,5,6-tetrafluorophenyl)oxy)-2-ethylhexane (7.0 g, 10.8 mmol) was dissolved in a mixture of THF and water (200 ml/ 66 ml) and H\textsubscript{2}SO\textsubscript{4} (1.5 ml) was added. The mixture was stirred overnight at 55 °C. The THF was removed under reduced pressure and diethyl ether (200 ml) was added. The organic phase was washed with water, aqueous NaHCO\textsubscript{3} and twice with water. It was dried (MgSO\textsubscript{4}) and the solvent removed under reduced pressure yielding 1,3-bis(4-formyl-2,3,5,6-tetrafluorophenyl)oxy)-2-ethylhexane (4.92 g, 91%) as a colourless oil. Found: C, 53.04%; H, 3.73%; M (MS, El) 498 (M+). Calculated for C\textsubscript{22}H\textsubscript{18}F\textsubscript{8}O\textsubscript{4}: C, 53.02%; H, 3.64%; M 498. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 200 MHz) \(\delta\) 10.23 (s, 2H, CHO), 4.79 (m, 1H, OCH\textsubscript{2}PrCHEtCH\textsubscript{2}O), 4.52 (m, 2H, OCH\textsubscript{2}PrCHEtCH\textsubscript{2}O), 2.06 (m, 1H, OCH\textsubscript{2}PrCHEtCH\textsubscript{2}), 1.68 (m, 6H, RCH\textsubscript{2}CH\textsubscript{3}), 0.98 (m, 6H, RCH\textsubscript{2}CH\textsubscript{3}); \textsuperscript{13}C \{\textsuperscript{1}H\} NMR (CDCl\textsubscript{3}, 100 MHz) \(\delta\) 182.01 (CHO), 147.91 (d, \(J = 260\) Hz, ar. C-F), 143.02, 143.53 (ar. C-O), 140.91 (d, \(J = 250\) Hz, ar. C-F), 140.43 (d, \(J = 250\) Hz, ar. C-F), 109.41 (ar. C-CHO), 109.32 (ar. C-CHO), 85.32 (OCH\textsubscript{2}PrCHEtCH\textsubscript{2}O), 73.09 (OCH\textsubscript{2}PrCHEtCH\textsubscript{2}O), 44.09, 33.45, 33.16, 19.81, 18.92, 18.04, 13.90, 12.00, 11.36 (aliph. C); \textsuperscript{19}F NMR (CDCl\textsubscript{3}, 188 MHz) \(\delta\) -146.26 (m, 4F, CF ortho to CHO), -156.26 (m, 2F, CF ortho to OCR), 157.25 (m, 2F, CF ortho to OCR) (see appendix page 139).
2.4.11 2,3,5,6-Tetrafluoroterephtalaldehyde tetra-acetate (17)

Tetrafluoro-para-xylene (2 g, 11.2 mmol) was dissolved in a stirred mixture of acetic acid (20 ml), acetic anhydride (40 ml) and sulfuric acid (3.3 ml, 6 g) and the mixture was cooled to 5 °C. Chromium trioxide (3.6 g, 36 mmol) was added gradually in order to keep the temperature of the cooled mixture between 5 and 7 °C. After 4.5 h the mixture was poured onto crushed ice (100 g) and left overnight. The product was filtered and washed twice with water. It was then dissolved in diethyl ether (30 ml), again washed twice with water, dried (MgSO₄) and recrystallised from ethanol (6 ml) yielding 2,3,5,6-tetrafluoroterephtalaldehyde tetra-acetate (0.11 g, 2.4%) as a white solid, mp 182 °C. Found: C, 46.66%; H, 3.30%; M(MS, El) 410 (M⁺).
Calculated for C₁₆H₁₄F₄O₈: C, 46.84%; H, 3.44%; M 410.

¹H NMR (CDCl₃, 200 MHz) δ 7.84 (s, 2H, CHO₂), 2.07 (s, 12H, CH₃); ¹³C {¹H} NMR (CDCl₃, 100 MHz) δ 168.23, (CO), 82.96 (CHO₂), 20.53 (CH₃); ¹⁹F NMR (CDCl₃, 188 MHz) δ -141.26 (s, 4F) (see appendix page 140).

2.4.12 2,3,5,6-Tetrafluoroterephtalaldehyde (18)

Starting from 2,3,5,6-tetrafluoroterephtalaldehyde tetra-acetate (17):
2,3,5,6-Tetrafluoroterephtalaldehyde tetra-acetate (0.24 g, 0.59 mmol) was added to a mixture of water (2 ml), ethanol (2 ml) and concentrated sulphuric acid (0.1 ml). The mixture was refluxed for 1.5 h and cooled to room temperature. All solvents were removed under reduced pressure and the mixture extracted with diethyl ether (5 ml), dried (MgSO₄) and the diethyl ether evaporated yielding 2,3,5,6-tetrafluoroterephtalaldehyde (0.07 g, 58%) as a white solid. NMR and mass spectra were identical to those described below.

Starting from 1,4-bis(dibromomethyl)-2,3,5,6-tetrafluorobenzene (19):
1,4-Bis(dibromomethyl)-2,3,5,6-tetrafluorobenzene (7.3 g, 14.7 mmol) was suspended in conc. H$_2$SO$_4$ (20 ml) and heated under vacuum increasing the temperature over 5 h from 100 °C to 140 °C. Further conc. H$_2$SO$_4$ (20 ml) was added and the mixture heated at 140 °C for 3 h. The mixture was cooled to room temperature and poured onto ice (100 g). The aqueous layer was extracted twice with diethyl ether (100 ml), the organic layer subsequently washed twice with water and dried (MgSO$_4$). The solvent was removed under reduced pressure and the product purified by column chromatography (silica gel, diethyl ether: hexane 1:1), yielding 2,3,5,6-tetrafluoroterephthalaldehyde (1.05 g, 35%) as a white solid, mp 131 °C. Found: C, 46.50%; H, 0.98%; M(MS, EI) 206 (M$^+$_). Calculated for C$_8$H$_2$F$_4$O$_2$: C, 46.62%; H, 0.98%; M 206. $^1$H NMR (CDC$_3$, 200 MHz) $\delta$ 10.37 (s, 2H); $^{13}$C ($^1$H) NMR (CDCl$_3$, 100 MHz) $\delta$ 181.79 (CHO), 146.50 (d, $J = 270$ Hz, ar. CF), 118.63 (ar. C-C); $^{19}$F NMR (CDCl$_3$, 188 MHz) $\delta$ -144.05 (s, 4F) (see appendix page 141).

2.4.13 1,4-Bis(dibromomethyl)-2,3,5,6-tetrafluorobenzene (19)

Tetrafluoro-para-xylene (4.0 g, 22.5 mmol) and elemental bromine (5.14 ml, 16.0 g, 100 mmol) were heated to 160 °C under nitrogen in a 250 ml two necked round bottomed flask equipped with a reflux condenser. The reflux condenser was connected to a bubbler followed by a scrubbing tower. The latter was filled with an aqueous solution of NaOH and Na$_2$SO$_3$. The reaction mixture was heated and irradiated with a UV lamp. After 4 h the mixture was cooled and a nitrogen inlet was connected to the flask. Nitrogen was blown through the flask and all HBr and excess bromine removed. More bromine (4.0 ml, 12.44 g, 0.78 mol) was added and the mixture heated and irradiated again for 2.5 h. It was cooled again, HBr and excess bromine were removed, and the procedure repeated three times (once with 4 ml bromine and twice with 1.2 ml bromine). The product was dissolved in CHCl$_3$ and washed with aqueous NaHCO$_3$ solution and twice with water yielding an off-white solid (7.7 g, 69%). The product was used in the next step without further purification. A small fraction (0.3 g) was recrystallised from acetic acid yielding 1,4-
bis(dibromomethyl)-2,3,5,6-tetrafluorobenzene as a white solid, mp 93 °C. Found: C, 19.58%; H, 0.37%; M(MS, EI) 494 (M⁺). C₈H₂F₄Br₄ requires C, 19.46%; H, 0.41%; M 494. ¹H NMR (CDCl₃, 200 MHz) δ 6.83 (s, 2H); ¹³C {¹H} NMR (CDCl₃, 100 MHz) δ 143.05 (d, J = 260 Hz, ar. CF), 121.62 (ar. C), 20.02 (CHBr₂); ¹⁹F NMR (CDCl₃, 188 MHz) δ -138.69 (s, 4F) (see appendix page 142).

2.4.14 5,6,28,29,30,31,32,33-Octafluoro-8,11,14,17,20,23,26-heptaoxa-tricyclo[22.2.2.2⁴.7]tritriaconta-1(30),2,4(33),5,7(32),27(31),25-heptaene (20)

![Chemical Structure](image)

TiCl₄ (0.36 g, 0.21 ml, 1.9 mmol) was added to a suspension of zinc dust (0.25 g, 3.8 mmol) in THF (10 ml) and pyridine (0.15 ml) at 0 °C under nitrogen. The mixture was refluxed for 1 h and then cooled to room temperature. 1,17-Bis (4-formyl-2,3,5,6-tetrafluoro-phenyloxy)-3,6,9,12,15-pentaoxa-heptadecane (0.4 g, 0.63 mmol) was added. The mixture was refluxed for 24 h and then quenched with 2 N hydrochloric acid (10 ml). The mixture was extracted three times with diethyl ether (30 ml). The combined extracts were washed with NaHCO₃ solution, water, dried (MgSO₄) and the solvent removed under reduced pressure. The product was purified by column chromatography (silica gel /diethyl ether) yielding 5,6,28,29,30,31,32,33-octafluoro-8,11,14,17,20,23,26-heptaoxa-tricyclo[22.2.2.2⁴.7]tritriaconta-1(30),2,4(33),5,7(32),27(31),25-heptaene (0.10 g, 26%) as a white solid, mp 81-83 °C. Found: C, 51.66%; H, 4.37%; M(MS, EI) 602 (M⁺). Calculated for C₂₆H₂₆F₉O₇: C, 51.83%; H, 4.35%; M 602. ¹H NMR (CDCl₃, 200 MHz) δ 7.40 (s, 2H, CH=CH), 4.46 (m, 4H, ar. COCH₂), 3.78 (m, COCH₂CH₂), 3.33 (m, 16H, OC₂H₄O); ¹³C {¹H} NMR (CDCl₃, 100 MHz) δ 144.90 (d, J = 250 Hz, ar. CF), 141.91 (d, J = 250 Hz, ar. CF), 137.98 (ar. CO), 120.80 (CH=CH), 110.06 (ar. C-CH=CH) 73.13, 72.23, 70.81, 70.42, 69.78, 69.74 (OC₂H₄O); ¹⁹F NMR (CDCl₃, 188 MHz) δ -145.01 (m, 4F, CF ortho to CH=CH) -157.44 (m, 4F, CF ortho to OC₂H₄) (see appendix page 143).
2.4.15 Polymerisation via the McMurry reaction

An illustrative example of a polymerisation reaction is given below. The choice of the flexible linker (13, 14 or 15) and the fraction (y) of 2,3,5,6-tetrafluoroterephthalaldehyde were varied. TiCl₄ (0.72 g, 0.42 ml, 3.8 mmol) was added to a suspension of zinc dust (0.49 g, 7.6 mmol) in dry THF (20 ml) and pyridine (0.30 ml) at 0 °C under nitrogen. The mixture was refluxed for 1 h and then cooled to room temperature. 1,17-Bis-(4-formyl-2,3,5,6-tetrafluorophenyloxy)-3,6,9,12,15-pentaoxa-heptadecane (0.64 g, 1.0 mmol) and 2,3,5,6 tetrafluoroterephthalaldehyde (0.052 g, 0.25 mmol) were dissolved in dry THF (0.5 ml) and added to the mixture. Within 10 min the solution became so viscous that stirring with a magnetic stirrer ceased. The mixture was refluxed for 14 h and cooled to room temperature. DCM (20 ml) was added followed by 2 N hydrochloric acid (20 ml). The organic layer was washed with aqueous NaHCO₃ and brine, dried (MgSO₄) and the solvent removed under reduced pressure. The product was redissolved in chloroform and precipitated into ethanol. The polymer was characterised by GPC and ¹H NMR spectroscopy since the latter showed pinacol defects in the polymer. ¹H NMR (CDCl₃, 200 MHz) δ 7.39 (trans CH=CH), 6.74 (cis CH=CH), 5.34 (CHOHCHOH), 4.40 (ar. COCH₃), 3.83 (COCH₂CH₂), 3.63(OC₂H₄O); Mₙ = 8,300 g mol⁻¹ Mₚ = 27,000 g mol⁻¹ PDI = 3.23. (see appendix page 144). The results of other polymerisation experiments are recorded in Table 2.2.1 page 9.

2.5 References


3 Synthesis of a Soluble Derivative of PPV and its Fluorinated Equivalent via the Wittig and Horner-Wittig Reactions

3.1 Introduction

The reaction of a phosphorus ylide with an aldehyde or ketone to yield olefins is generally referred to as the Wittig reaction. The phosphorus ylide is usually prepared by treatment of a phosphonium salt with a base.

\[ R-CH_2P(R')_3 + X^- \xrightarrow{\text{base}} \left[ \begin{array}{c} R-CH_2P(R')_3 \rightarrow \xrightarrow{\text{ylide}} R-C=H+P(R')_3 \end{array} \right] \]

*Figure 3.1.1 Synthesis of a phosphorus ylide.*

The generally accepted mechanism of the Wittig reaction involves the formation of an oxaphosphetane that decomposes to give the alkene and phosphine oxide. \(^2\) trans-Alkenes are obtained if the negative charge on the ylide carbon atom is stabilised by conjugation and the presence of electron-withdrawing groups such as COOR or CN. Fluorinated aromatic groups also give rise to trans-alkenes. \(^3\) “Semistabilising” R-groups such as phenyl or allyl often give no great preference for cis- or trans-alkenes. Ylides with R-groups lacking any stabilising effect usually favour cis-alkenes.

\[ R''\text{O} + RCH=PR'R'' \leftrightarrow (R')_3P\text{O} \xrightarrow{\text{R}} RCH=CHR'' + O=PR'_3 \]

*Figure 3.1.2 Mechanism of the Wittig reaction.*

The Horner-Wittig reaction uses phosphonate carbanions instead of ylides. \(^4\) They are stronger nucleophiles since the negative charge is less stabilised than in the case of ylides. Hence phosphonate carbanions react with a wider variety of aldehydes and ketones and under milder conditions. The Horner-Wittig reaction
generally gives rise to trans-alkenes. The mechanism is similar to that of the Wittig reaction. High conversions make both the Wittig and Horner-Wittig reaction attractive for polycondensation reactions. The use of both reactions will be examined for the preparation of fluorinated derivatives of PPV and their hydrogen equivalents.

3.2 Results and Discussion

Synthesis of fluorinated DSB block copolymers

The Wittig reaction has been widely used to prepare block copolymers of alternating DSB units and flexible linkers (see Chapter 1). The two double bonds of the DSB units are created during the polycondensation reaction. In contrast to the McMurry reactions described in Chapter 2, where polymers with conjugated units of varying length were prepared, this approach uses only DSB-units as the conjugated unit. When a flexible linker of a discrete length is used, rather than a mixture of oligomers, the structure of the polymer can be determined unambiguously.

In our first approach to block copolymers with fluorinated DSB units we prepared a comonomer with two terminal phosphonium groups and a central flexible linker unit. The synthesis started from the di-lithium salt of octane-1,8-diol 23 which was reacted with two equivalents of pentafluorotoluene 24 (Figure 3.2.1). The product 25 was brominated with NBS and the bromine subsequently substituted by triphenylphosphine to give the bis-phosphonium salt 27.

A soluble model compound 28 was prepared by reacting 27 with pentafluorobenzaldehyde. The model compound was fully characterised and the NMR spectra ($^1$H, $^{13}$C and $^{19}$F) show that all olefinic bonds have trans-configuration. The reaction of compound 27 with tetrafluoroterephthaldehyde 18 gave a white polymer 29. However, the polymer was only soluble in hot toluene or benzene and therefore not suitable for application in electroluminescent devices where solution
processing is desired. The polymer was characterised by NMR spectroscopy (\(^1\)H, \(^{19}\)F) and not further investigated.

\[
\text{Li}^+\text{O}(\text{CH}_2)_8\text{O}^-\text{Li}^+ + 2\text{H}_2\text{C}-\text{F} \xrightarrow{a} \text{H}_2\text{C}-\text{O}(\text{CH}_2)_8\text{O}-\text{H}_3\text{C}-\text{CH}_3
\]

**Figure 3.2.1** Synthesis a comonomer with two phosphonium end-groups. a) THF b) Br\(_2\), h\(_\nu\), CC/4 c) PPh\(_3\), C\(_7\)H\(_8\)

Since the octane-1,8-diol-spacer did not render the polymer soluble, hexa(ethylene glycol) was used in an analogous reaction sequence as a starting material to give polymers with enhanced solubility (**Figure 3.2.3**). Hexa(ethylene glycol) was deprotonated and reacted with pentafluorotoluene 24 to give compound 55.
30. However, bromination of 30 with NBS was not selective for the methyl-groups but also occurred on the ethylene units of the sexi(ethylene oxide) spacer; the $^1$H NMR spectrum of the product showed a decrease in the intensity for protons in the sexi(ethylene oxide) unit relative to compound 30 while additional signals were found at higher field which were assigned to protons adjacent to both oxygen and bromine in the ethylene oxide unit. Therefore, the route was abandoned.

\[
\begin{align*}
\text{Figure 3.2.3 Synthesis of a flexible linker with a central sexi(ethylene oxide) unit.} \\
a) \text{THF}
\end{align*}
\]

The previous attempts to prepare block copolymers via Wittig reaction used comonomers, which contained a flexible linker and phosphonium end-groups. However, since such attempts were unsuccessful, a new approach starting from a comonomer comprising a flexible linker and aldehyde end-groups was investigated. A comonomer based on sexi(ethylene oxide) with aldehyde end-groups 13 could be prepared in sufficient quantity (11 g) as shown in Chapter 2. The second monomer required for a polymerisation via the Wittig reaction in this route is 2,3,5,6-tetrafluoroxylylen-1,4-bis(triphenylphosphonium bromide) 32 which could be prepared by bromination of tetrafluoroxyylene 16 followed by substitution of bromine with triphenylphoshine (Figure 3.2.4). However, the Wittig reaction of 32 with 13 did not result in a polymer that could be precipitated from chloroform into methanol. Instead, the $^1$H NMR spectrum showed the presence of unreacted aldehyde end-groups, indicating a low conversion, so that this route was also abandoned.

\[
\begin{align*}
\text{Figure 3.2.4 Synthesis of 2,3,5,6-tetrafluoroxylylen-1,4-bis(triphenylphosphonium bromide) and tetramethyl-2,3,5,6-tetrafluoroxylylene bisphosphonate.} \\
a) \text{Br}_2, h\nu \quad b) \quad PPh_3, \text{toluene} \quad c) \quad P(OCH_3)_3
\end{align*}
\]
In a new approach, the Horner-Wittig reaction was employed. Neckers et al. have shown the use of the Horner-Wittig reaction for the preparation of block copolymers (Chapter 1).\(^7\) Tetramethyl-2,3,5,6-tetrafluoroxylylene bisphosphonate 33 can be prepared via the Arbuzov reaction of 1,4-bis(bromomethyl)-2,3,5,6-tetrafluorobenzene 31 with trimethylphosphite (Figure 3.2.4).\(^8\) When the bisphosphonate 33 was reacted with the monomer 13 a soluble fluorinated block copolymer, poly(bis(2,3,5,6-tetrafluoro-p-phenylenevinylene)-2,3,5,6-tetrafluoro-p-phenylene-1,4,7,10,13,16,19-heptaoxanonadecane), (F-DSB-block-SEO) 34 was obtained (Figure 3.2.5).

![Figure 3.2.5 Synthesis of a block copolymer with fluorinated DSB units and sexi(ethylene oxide) linkers. a) THF, NaH](image)

The reaction conditions differed greatly from those normally associated with Horner-Wittig reaction. Instead of stirring overnight at room temperature the reaction had to be kept close to the reflux temperature of THF (50 to 65 °C) for several days. This change in reactivity might be due to the electron-withdrawing effect of fluorine or to the low solubility of the intermediate oligomers in THF. It was found that reflux of the reaction mixture resulted in a side reaction which lead to a black product. Therefore a balance had to be found between increasing the rate of conversion by heating and minimising this side reaction. When the temperature was kept between 50 and 65 °C for 13 days a white polymer could be obtained in sufficient quantity (8 g).

F-DSB-block-SEO is soluble in chloroform and can be reprecipitated into methanol. Free-standing films can be cast from solution. The films are somewhat brittle and bending or stressing the films results in rupture. X-ray photoelectron
spectra and $^1$H NMR spectra showed that the polymer was contaminated with silicon-grease (see also Chapter 4). When the polymer was reprecipitated into hexane the silicone was removed. Cleaned samples were used for further analysis.

The polymer was fractionated by gel chromatography (Bio-Beads S-X1 Beads, chloroform). Two fractions were obtained. Gel Permeation Chromatography (GPC) (Viscoteck, RI detector, we thank RAPRA Technology for this measurement) indicates for the first fraction a $M_n$ of 12,600, a polydispersity of 3.5 and a degree of polymerisation of about 17 with respect to polystyrene. For the second fraction GPC shows a high content of oligomers, a $M_n$ of 7,000, a polydispersity of 4.1 and a degree of polymerisation of about 9. Figure 3.2.6 shows two traces for each fraction. The first fraction (3.5 g) was used for further analysis.

![Molecular Weight Distribution](image)

*Figure 3.2.6 GPC analysis of F-DSB-block-SEO. Two traces for each fraction are shown.*

The ion-content of the sample was analysed by extracting the polymer with boiling water. It was found that filtering the extracts lead to false results due to the ion content of the filter paper. When the extracts were decanted ion chromatography (Dionex, DX 120 Ion chromatograph) indicated the absence of any Na$^+$, K$^+$, Li$^+$ or Mg$^{2+}$ ions and a trace (0.008%) of Ca$^{2+}$ ions.
The $^1$H NMR spectrum of F-DSB-block-SEO shows three resonances due to ethylene protons of the sexi(ethylene oxide) unit between $\delta$ 3.6 and 4.5 (ratio of integrals: 16H: 4H: 4H) (Figure 3.2.7). Next to the solvent peak (chloroform $\delta$ 7.27) a signal typical for an AB quartet is found at $\delta$ 7.38 (4H). The observed coupling constant is 16 Hz characteristic for trans-olefinic protons. Only a trace of a signal for cis-olefinic protons can be observed at $\delta$ 6.75. It is concluded that at least 95% of all double bonds have a trans-configuration.

Figure 3.2.7 $^1$H NMR spectrum of F-DSB-block-SEO. The inset shows the expanded region between $\delta$ 7.1 and 7.7.

The $^{19}$F NMR spectrum shows two signals in the ratio 4:8. The signal at $\delta$ -157.83 is due to the four fluorines in ortho-position to alkoxy groups. The resonances for the remaining eight fluorines coincide at $\delta$ -143.87. The fact that only one set of resonances is observed confirms that all DSB units have a trans-trans-configuration.

Figure 3.2.8 $^{19}$F NMR spectrum of F-DSB-block-SEO.
Figure 3.2.9 shows the FTIR spectrum of F-DSB-block-SEO. The two strongest absorptions are due to the C=C stretching at 1483 cm\(^{-1}\) and the C-H out-of-plane deformation at 972 cm\(^{-1}\). The latter is characteristic for a carbon-carbon double bond with two C-H bonds in the \textit{trans}-position.\(^9\) This very strong absorption confirms the finding from NMR spectroscopy that all or nearly all double bonds have \textit{trans}-configuration. C-H out-of-plane deformations typical for double bonds with \textit{cis}-configuration are generally found between 700 and 850 cm\(^{-1}\).\(^{10}\) It cannot be decided with certainty whether the small signals at 755 cm\(^{-1}\) and 860 cm\(^{-1}\) indicate the presence of a small percentage of \textit{cis}-double bonds or whether they are due to CH\(_2\)-rocking. The absence of a signal at 1700 cm\(^{-1}\) indicates that the polymer is free of aldehyde end-groups.\(^{11}\) The signal at 1650 cm\(^{-1}\) is due to an absorption of fluorinated aromatics (see appendix page 158).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{ftir_spectrum.jpg}
\caption{FTIR-spectrum of F-DSB-block-SEO (film). Since the polymer films were brittle it was not possible to prepare very thin film. The obtained films showed very intense absorption bands.}
\end{figure}

Differential Scanning Calorimetry (DSC) analysis of F-DSB-block-SEO shows three endothermic phase transitions at 78, 98 and 123 °C. These transitions indicate that the polymer contains some ordered structures at room temperature.
Transitions between liquid crystalline phases have been reported for fluorinated DSBs. 1,4-Bis(2,3,4,5-pentafluorostyryl)benzene (Figure 3.2.11 left) shows three endothermic phase transitions though at higher temperature (194, 203 and 208 °C). 1,4-Bis[(2,5-dihexyloxy)styryl]-2,3,5,6-tetrafluorobenzene (Figure 3.2.11 right) shows birefringent behaviour during a heating cycle and textures comparable to those of smectic and discotic mesophases during cooling.

![Figure 3.2.11 1,4-Bis(2,3,4,5-pentafluorostyryl)benzene (left) and 1,4-bis[(2,5-dihexyloxy)styryl]-2,3,5,6-tetrafluorobenzene (right) show liquid crystalline behaviour.](image)

In conclusion the NMR spectra (\(^1\)H, \(^{13}\)C and \(^{19}\)F), FTIR spectra and elemental analysis of F-DSB-block-SEO are consistent with the assigned structure and no indications for defects such as pinacol or aldehyde groups are observed. The optical and electroluminescence properties of the polymer are described in Chapter 4.

**Synthesis of a DSB block copolymer**

Since the effect of fluorine on electroactive polymers was to be studied it was also necessary to prepare the hydrogen equivalent of F-DSB-block-SEO. Karasz et
al. have reported the use of the Wittig reaction to prepare copolymers with DSB units and flexible linkers. In our approach sexi(ethylene oxide) was activated as bis-tosylate 35. The reaction with two equivalents of p-hydroxybenzaldehyde 36 gave the monomer 37 (Figure 3.2.12). p-Xylylen-bis(triphenylphosphonium bromide) 38 was prepared by two-fold substitution of bromine on α,α'-dibromoxylene by triphenylphosphine. Wittig reaction of 37 and 38 gave poly(bis(p-phenylenevinylene)-p-phenylene-1,4,7,10,13,16,19-heptaoxanonadecane) (H-DSB-block-SEO) (Figure 3.2.12) 39.

![Figure 3.2.12 Synthesis of H-DSB-block-SEO. a) DMF, K₂CO₃ b) THF, KO'Bu](image)

Ion chromatography showed no traces of Na, K, Ca, Mg or Li. Two samples of H-DSB-block-SEO were analysed by GPC. Sample 1 was reprecipitated twice, sample 2 three times. Both samples indicated a $M_n$ of 5600 g/mol, a polydispersity of 3.0 and a degree of polymerisation of 10 relative to polystyrene standard (Figure 3.2.13). H-DSB-block-SEO forms robust free-standing films cast from solution. Even though the average molecular weight is lower than in the case of F-DSB-block-SEO the films are stable when bent or stressed. Attempts to prepare the all-trans isomer by refluxing the polymer in toluene with traces of iodine failed and resulted in fragmentation of the polymer. The use of the Horner-Wittig reaction to prepare such an all-trans isomer also failed.
The $^1$H NMR spectrum shows three signals between $\delta$ 3.5 and 4.2 due to ethylene protons in the sexi(ethylene oxide) unit (integral ratio 16H: 4H :4H) (Figure 3.2.14). The resonance at $\delta$ 6.5 is assigned to cis-olefinic protons (also see Figure 3.2.15). The integration of this signal (2H) indicates that on average two out of the four olefinic protons per repeat unit have cis-configuration. The two signals at $\delta$ 6.8 (2H) and 6.9 (2H) can be assigned to aromatic protons in ortho-position to alkoxy-groups. The fact that two resonances appear confirms that there are two different chemical environments, probably due to adjacent cis- or trans-double bonds. The resonance assigned to trans-olefinic protons at $\delta$ 7.0 (2H) overlaps with one of the aromatic signals. The sum of the two integrations is displayed in Figure 3.2.14. The remaining aromatic signals are found between $\delta$ 7.2 and 7.5 (8H).

The expansion of the region $\delta$ 6.4 – 7.1 shows the signals for olefinic protons in more detail (Figure 3.2.15). Two AB quartets with $J_{AB} = 12$ Hz are observed for the cis-vinylenes at $\delta$ 6.5. They are assigned to cis-cis and cis-trans DSB units. Two AB quartets with $J_{AB} = 16$ Hz are observed at $\delta$ 7.0 and assigned to trans-vinylenes in trans-trans and trans-cis DSB units. This findings are consistent with a 50:50 cis:trans distribution of double bonds. Geise et al. have reported similar cis:trans distributions for 4,4' dialkoxy substituted distyrylbenzene prepared by Wittig reaction.9

Figure 3.2.13 GPC analysis of H-DSB-block-SEO. Sample 1 was reprecipitated twice, sample 2 was reprecipitated three times.
Figure 3.2.14 $^1H$ NMR spectrum of H-DSB-block-SEO in TCE-$d_2$.

Figure 3.2.15 $^1H$ NMR spectrum of H-DSB-block-SEO in CDCl$_3$. Expansion of the region between $\delta$ 6.4 and 7.1.

The $^{13}$C NMR spectrum of H-DSB-block-SEO shows the two distinct sets of aromatic carbons (see appendix). This is expected to be due to the presence of cis- and trans-olefinic bonds adjacent to those aromatic rings. The FTIR spectrum of a thin film of H-DSB-block-SEO also shows the typical absorptions for cis- and trans-double bonds; the absorption band at 968 cm$^{-1}$ can be assigned to (C-H) out-of-plane deformation in trans-double bonds. The absorption band at 837 cm$^{-1}$ is characteristic
for cis-double bonds. The small band at 1710 cm\(^{-1}\) indicates the presence of a small amount aldehyde end-groups.\(^{11}\) The DSC of H-DSB-block-SEO shows no exothermic or endothermic phase transitions between -150 °C and 220 °C degrees. The optical and electroluminescence properties of H-DSB-block-SEO are described in Chapter 4.

![Figure 3.2.16 FTIR spectrum of H-DSB-block-SEO (thin film).](image)

### 3.3 Conclusions

Attempts to prepare a block copolymer with fluorinated DSB units and a flexible linker via the Wittig reaction failed. However, a block copolymer with fluorinated DSB units and sexi(ethylene oxide) units could be prepared via the Horner-Wittig reaction. The polymer was fractionated by gel-chromatography. The first fraction shows a degree of polymerisation of 17. The FTIR and NMR spectra of the polymer indicate that all or nearly all the double bonds have trans-configuration.

A second block copolymer with DSB units and sexi(ethylene oxide) linker units, the hydrogen equivalent of the previous polymer, was prepared by the Wittig reaction. A degree of polymerisation of 10 was obtained. FTIR and NMR indicate a
50:50 *cis:*trans distribution of double bonds. Both polymers are soluble in chloroform and free-standing films can be cast from solution.

### 3.4 Experimental

#### 3.4.1 1,8-Di-(4-methyl-2,3,5,6-tetrafluorophenyloxy)octane (25)

Octane-1,8-diol (10.0 g, 68.4 mmol) was dissolved in THF (500 ml). *n*-Butyllithium in hexane (1.6 M, 87 ml, 139 mmol) was added and the mixture was stirred for 10 min. 2,3,4,5,6-Pentafluorotoluene (31.7 g, 174 mmol) was added and the mixture refluxed for 5 days. After the addition of water (80 ml) the THF was evaporated. The mixture was washed three times with diethyl ether (200 ml). The combined extracts were washed with water (200 ml), dried (MgSO₄), concentrated under reduced pressure and purified by column chromatography (silica gel; hexane, diethyl ether 20:1), yielding 1,8-di-(4-methyl-2,3,5,6-tetrafluorophenyloxy)octane (8.8 g, 27 %) as a colourless oil. Found: C, 56.37%; H, 4.80%; M(MS, Cl) 488 (MNH₄⁺).

Calculated for C₂₂H₂₂F₈O₂: C, 56.17%; H, 4.71%; M 470. ¹H NMR (CDCl₃, 200 MHz) δ 4.15 (t, J = 7 Hz, 4H, CH₂O), 2.20 (t, J = 2 Hz, 6H, CH₃), 1.71 (m, 4H, CH₂), 1.40 (m, 8H, CH₂); ¹³C ¹H NMR (CDCl₃, 62.9 MHz) δ 145.21 (d, J = 245 Hz, CF), 140.66 21 (d, J = 245 Hz, CF), 135.50 (CCH₃), 109.15 (CO), 75.12 (CO), 29.72 (CH₂), 29.01 (CH₂), 25.36 (CH₂), 6.84 (CH₃); ¹⁹F NMR (CDCl₃, 188 MHz) δ -145.54 (CF ortho to CCH₃), -158.84 (CF ortho to COR) (see appendix page 145).
3.4.2 1,8-Di-(4-bromomethyl-2,3,5,6-tetrafluorophenylxyloxy)octane (26)

1,8-Di(4-methyl-2,3,5,6-tetrafluorophenylxyloxy)octane (6.3 g, 13.4 mmol) was dissolved in CCl₄ (50 ml). Bromine (4.7 g, 1.5 ml, 29 mmol) was added. The mixture was refluxed and irradiated with UV light for 4.5 h. The CCl₄ was removed by distillation and diethyl ether (100 ml) was added. The mixture was washed with water, dried (MgSO₄), concentrated under reduced pressure and purified by column chromatography (silica gel, hexane: diethyl ether 20:1), yielding 1,8-di-(4-bromomethyl-2,3,5,6-tetrafluorophenylxyloxy)octane as a white powder (3.5 g, 42%) mp 54 °C. Found: C, 41.93%; H, 3.03%; M(MS, EI) 628 (M⁺). Calculated for C₂₃H₂₀Br₂F₈O₂: C, 42.06%; H, 3.21%; M 628. ¹H NMR (CDCl₃, 200 MHz) δ 4.49 (s, 4H, CH₂Br), 4.24 (t, J = 6 Hz, 4H, CH₂O), 1.71 (m, 4H, CH₂), 1.40 (m, 8H, CH₂); ¹³C (¹H) NMR (CDCl₃, 100 MHz) δ 145.14 21 (d, J = 248 Hz, CF), 141.07 21 (d, J = 248 Hz, CF), 138.39 (CCH₂Br), 109.83 (CO), 75.36 (CH₂O), 29.81 (CH₂), 29.04 (CH₂), 25.39 (CH₂), 17.03 (CH₂Br); ¹⁹F NMR (CDCl₃, 188 MHz) δ -144.62 (CF ortho to CH₂Br), -157.13 (CF ortho to OR) (see appendix page 146).

3.4.3 1,8-Bis-(4-triphenylphosphoniummethylen-2,3,5,6-tetrafluorophenylxyloxy)octane dibromide (27)

1,8-Di-(4-bromomethyl-2,3,5,6-tetrafluorophenolxyloxy)octane (0.50 g, 0.80 mmol) was dissolved in toluene (20 ml). Triphenylphosphine (2.07 g, 2.07 mmol) was added, the mixture refluxed under nitrogen for 150 min. The mixture was cooled to room temperature, filtered and the precipitate washed three times with cold toluene yielding 1,8-bis-(4-triphenylphosphoniummethylen-2,3,5,6-tetrafluorophenolxyloxy) octane dibromide (0.76 g, 82%) as a white powder. The product was characterised by ¹H NMR and ¹⁹F NMR spectroscopy and used in the next step without further
purification. $^1$H NMR (CDCl$_3$, 200 MHz) $\delta$ 7.6 - 7.9 (m, 30H, ar. CH$_2$), 5.44 (d, $J = 13.5$ Hz, 4H, CH$_2$P), 4.14 (t, $J = 6$ Hz, 4H, CH$_2$O), 1.66 (m, 2H, CH$_2$), 1.33 (m, 4H, CH$_2$); $^{19}$F NMR (CDCl$_3$, 188 MHz) $\delta$ -138.91 (CF ortho to CH$_2$) -155.87 (CF ortho to OR) (see appendix page 147).

3.4.4 1,8-(Bis-2,3,4,5,6,2',3',4',5',6' nonafluorostilben-4-yloxy)octane

![Diagram of 1,8-(Bis-2,3,4,5,6,2',3',4',5',6' nonafluorostilben-4-yloxy)octane](image)

1,8-Bis-(4-triphenylphosphoniummethylen-2,3,5,6-tetrafluoro-phenyloxy)octanedibromide (440 mg, 0.38 mmol) and LiCl (0.04 g) were dissolved in dry DMF (2 ml). KO'Bu (1 M, 1.2 ml, 1.2 mmol) was added followed by 2,3,4,5,6-pentafluorobenzaldehyde (165 mg, 0.84 mmol). After stirring for 6 h aqueous HCl (5%, 3 ml) was added. All solvents were removed under reduced pressure. The product was redissolved in chloroform, washed twice with water, dried (MgSO$_4$) and purified by column chromatography (silica gel/ hexane : diethyl ether 20 : 1) yielding 1,8-bis-(2,3,4,5,6,2',3',4',5',6'nonafluorostilben-4-yloxy)octane (0.18 g, 58%) as a white powder, m.p. 93 - 94°C. Found: C, 52.38%; H, 2.60%; M(MS, El) 826 (M'). Calculated for C$_{36}$H$_{20}$F$_{18}$O$_2$: C, 52.31%; H 2.44%; M 826. $^1$H NMR (CDCl$_3$, 200 MHz) $\delta$ 7.15 (d, 2H, $J = 17$ Hz, olef. CH), 7.12 (d, 2H, $J = 17$ Hz, olef. CH), 4.12 (t, 4H, $J = 7$ Hz, OCH$_2$), 1.65 (m, 4H, OCH$_2$CH$_2$), 1.27 (m, 8H, CH$_2$); $^{13}$C {$^1$H} NMR (CDCl$_3$, 100 MHz) $\delta$ 146.5-136.5 (CF), 122.38, 119.71 (CHCH), 111.93, 109.57 (ar. CCHCH), 75.32 (OCH$_2$), 29.83, 29.04, 25.40 (CH$_2$); $^{19}$F NMR (CDCl$_3$, 188 MHz) $\delta$ -142.54 (m, 4F, CF ortho to CHCH), -144.00 (m, 4F, CF ortho to CHCH), -154.80 (m, 2F, CF para to CHCH), -157.02 (m, 4F, CF ortho to OR), -162.63 (m, 4F, CF meta to CHCH) (see appendix page 148).
3.4.5 Poly(bis(2,3,5,6-tetrafluoro-p-phenylenevinylene)-2,3,5,6-tetrafluoro-p-phenylene-1,10-dioxodecane) (29)

\[
\begin{align*}
&\text{O-(CH}_2\text{)}_n\text{O-} \\
&\text{F } \quad \text{F } \quad \text{F } \quad \text{F } \\
&\text{F } \quad \text{CH=CH} \quad \text{F } \quad \text{F} \\
&\text{F } \quad \text{CH=CH} \quad \text{F } \quad \text{F} \\
&\text{F } \quad \text{F } \quad \text{F } \quad \text{F} \\
&\text{F } \quad \text{F } \quad \text{F } \quad \text{F} \\
\end{align*}
\]

1,8-Bis-(4-triphenylphosphoniummethylen-2,3,5,6-tetrafluoro-phenyloxy)octandibromide (419 mg, 0.36 mmol) and LiCl (40 mg) were dissolved in DMF (3 ml). KO'Bu (0.75 ml, 0.75 mmol) was added and the mixture stirred at room temperature for 3 h. 2,3,5,6-Tetrafluoroterephtalaldehyde (0.75 mg, 0.36 mmol) was added. After stirring for 18 h the mixture was quenched with aqueous HCl (5%, 3 ml). All solvents were removed under reduced pressure and the residue redissolved in toluene, filtered and dried (MgSO₄). It was suspended in CHCl₃ and precipitated into ethanol yielding poly(bis(2,3,5,6-tetrafluoro-p-phenylenevinylene)-2,3,5,6-tetrafluoro-p-phenylene-1,10-dioxodecane) (106 mg, 46%) as a white solid. The product was analysed by NMR (¹H, ¹⁹F) and not further investigated. ¹H NMR (C₇D₈, 400 MHz) δ 7.36 (d, J = 17 Hz, 2H, CH), 7.28 (d, J = 17 Hz, 2H, CH), 4.04 (m, 4H, OCH₂), 1.64 (m, 4H, CH₂), 1.38 (m, 4H, CH₂), 1.27 (m, 4H, CH₂); ¹⁹F NMR (CDCl₃, 188 MHz) δ -144.26 (m, SF) -158.43 (m, 4F) (see appendix page 149).

3.4.6 1,17- Bis(4-methyl-2,3,5,6-tetrafluorophenylxyloxy)-3,6,9,12,15-pentaoxaheptadecane (30)

Sexi(ethylene oxide) (5.0 g, 17.7 mmol) was dissolved in dry THF (30 ml). n-Butyllithium (1.6 M, 23 ml, 36.8 mmol) was added and the mixture stirred for 1 h. The solvent was removed under reduced pressure and dry DMF (80 ml) was added. 2,3,4,5,6-Pentafluorotoluene (4.6 g, 25 mmol) was added and the reaction refluxed for 16 h. The DMF was removed under reduced pressure and the mixture redissolved in diethyl ether, washed twice with water, dried (MgSO₄) and purified by column chromatography yielding 1,17-bis(4-methyl-2,3,5,6-tetrafluorophenylxyloxy)-3,6,9,12,15-pentaoxaheptadecane (2.3 g, 30%) as a viscous oil. Found: C, 51.61%;
H 5.06%; M(MS, Cl) 607 (MH⁺). Calculated for C₂₆H₃₀F₈O₇:  C, 51.49%; H, 4.99%; M 606. ¹H NMR (CDCl₃, 200 MHz) δ 4.31 (t, J = 5 Hz, 4H, COCH₂), 3.81 (t, J = 5 Hz, COCH₂CH₂), 3.66 (m, 16H, C₂H₄), 2.19 (t, J = 2 Hz, 6H, CH₃); ¹³C {¹H} (CDCl₃, 100 MHz) δ 145.05 (d, J = 250 Hz, ar. CF), 140.90 (d, J = 250 Hz, ar. CF), 135.09 (ar. COC₂H₄), 109.34 (ar. CCH₃), 73.99, 70.62, 70.41, 70.37, 69.98 (C₂H₄), 6.69 (CH₃); ¹⁹F NMR (CDCl₃, 188 MHz) δ -145.45 (m, 4F, CF ortho to CH₃), -158.52 (m, 4F, CF ortho to OC₂H₄) (see appendix page 150).

3.4.7 1,4-Bis(bromomethyl)-2,3,5,6-tetrafluorobenzene (31)

Tetrafluoro-ortho-xylene (10.0 g, 55.1 mmol) and elemental bromine (5.65 ml, 17.6 g, 110 mol) were dissolved in CCl₄ (100 ml) and refluxed for 3h under irradiation with UV-light. CCl₄ was removed by distillation and recovered. Diethyl ether (100 ml) was added to the reaction mixture and the solution was washed with dilute aqueous NaOH, aqueous NaSO₃ and water. The organic extracts were dried (MgSO₄). Evaporation of the solvent and recrystallisation of the product from ethanol (80 ml) gave 1,4-bis(bromomethyl)-2,3,5,6-tetrafluorobenzene (12.0 g, 64%) as white crystals. Elemental analysis, mass and NMR spectra were consistent with those reported in the literature.¹⁵ Found: C, 28.60%; H, 1.15%; M(MS, El) 336 (M⁺). C₈H₄F₄Br₂ requires C, 28.60%; H, 1.20%; M 336. ¹H NMR (CDCl₃, 200 MHz) δ 4.52 (s, 2H); ¹³C {¹H} NMR (CDCl₃, 100 MHz); δ ¹⁹F NMR (CDCl₃, 188 MHz) δ -142.67 (s, 4F).

3.4.8 2,3,4,5-Tetrafluoroxylylene-1,4-bis(triphenylphosphonium bromide)(32)

3.4.7 1,4-Bis(bromomethyl)-2,3,5,6-tetrafluorobenzene (31)
1,4-Bis(bromomethyl)-2,3,5,6-tetrafluorobenzene (0.48 g, 1.43 mmol) and triphenylphosphine (0.82 g, 3.14 mmol) were refluxed in DMF (15 ml) for 22 h. The reaction was cooled to room temperature and dry diethyl ether (30 ml) was added. The white precipitate was recovered by filtration, washed five times with dry diethyl ether (8 ml) and dried (MgSO₄) yielding 2,3,4,5-tetrafluoroxylene-1,4-bis(triphenylphosphonium bromide) (0.85 g, 69%) as a white solid, mp > 300 °C. ¹H NMR (DMSO-d₆, 300 MHz) δ 8.0-7.6 (ms, 30H, ar. CH), 5.30 (d, J = 14 Hz, 4H, CH₂); 3.26 (d, J = 20.4 Hz, 4H, CH₂); ¹³C NMR (DMSO-d₆, 100 MHz) δ 135.57 (ar. CH), 134.09 (ar. CH), 130.17 (ar. CH), 116.60 (d, J = 87 Hz, CH₂); ¹⁹F NMR (DMSO-d₆, 188 MHz) δ -137.26 (s, 4F) (see appendix page 151).

3.4.9 Tetramethyl-2,3,5,6-tetrafluoroxylene bisphosphonate (33)

A mixture of 1,4-bis(bromomethyl)-2,3,5,6-tetrafluorobenzene (6.35 g, 18.9 mmol) and trimethylphosphite (7.0 g, 56.7 g) was heated to 90 °C for 16 h. The mixture was poured into hexane (100 ml) and allowed to solidify at 0 °C. The white solid was recrystallised from ethanol (8 ml) yielding tetramethyl-2,3,5,6-tetrafluoroxylene bisphosphonate (3.35 g, 45%) as a white solid. As the melting point and ¹H NMR spectrum were in good agreement with those reported in the literature⁷ no further analysis was carried out, mp 100 °C (lit. 96 °C), ¹H NMR (CDCl₃, 200 MHz) δ 3.77 (s, 6H, OCH₃), 3.73 (s, 6H, OCH₃), 3.26 (d, J = 20.4 Hz, 4H, CH₂).

3.4.10 F-DSB-block-SEO (34)

Tetramethyl-2,3,5,6-tetrafluoroxylene bisphosphonate (6.46 g, 16.4 mmol) and NaH (3.8 g, 60% in oil, 95 mmol) were dissolved in dry THF (300 ml) under
nitrogen. The mixture was stirred for 30 min. 1,17-Bis (4-formyl-2,3,5,6-tetrafluorophenoyloxy)-3,6,9,12,15-pentaoxa-heptadecane (10.4 g, 16.4 mmol) was dissolved in dry THF (40 ml) under nitrogen and added to the reaction mixture. The reaction temperature was increased from 50 °C to 65 °C over 13 days. The reaction was followed by NMR spectroscopy (\(^1\)H, \(^{19}\)F). The solution was quenched with water (150 ml) and the THF removed under reduced pressure. Chloroform (500 ml) was added and the mixture washed with brine. The chloroform solution was filtered over Celite and concentrated (150 ml). The product was reprecipitated into methanol (450 ml) yielding \(F\)-\(DSB\)-block-\(SEO\) (8.0 g, 62%) as white polymer. The polymer was fractionated by gel-chromatography (Bio-Beads S-X1, BIORAD, chloroform as eluent). Gel Permeation Chromatography (Viscoteck, RI detector, chloroform eluent, 2 x PLgel mixed bed D 30 cm columns, polystyrene standards) fraction 1: \(M_n\) 12500 g/mol; \(M_w\) 44700 g/mol; PDI 3.6; fraction 2: \(M_n\) 7200 g/mol; \(M_w\) 32000 g/mol; PDI 4.4. Found: C, 51.76%; H, 3.63%. Calculated for \(C_{34}H_{28}F_{12}O_7\): C, 52.59%; H 3.36%. \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 7.39 (d, \(J = 17\) Hz, 2H, CH), 7.33 (d, \(J = 17\) Hz, 2H, CH), 4.43 (t, \(J = 4.2\) Hz, 4H, OCH\(_2\)), 3.86 (t, \(J = 4.2\) Hz, 4H, OCH\(_2\)CH\(_2\)), 3.67 (m, 16H, OCH\(_2\)); \(^{13}\)C {\(^1\)H} (CDCl\(_3\), 100 MHz) \(\delta\) 145.20 (d, \(J = 249\) Hz, CF), 144.71 (d, \(J = 249\) Hz, CF), 138.62 (d, \(J = 246\) Hz, CF), 137.41 (ar.CO), 122.51 (CH), 120.79 (CH), 115.46 (ar. CCH), 109.99 (ar. CCH), 74.25 (CH\(_2\)), 70.84(CH\(_2\)), 70.58(CH\(_2\)), 70.13(CH\(_2\)); \(^{19}\)F (CDCl\(_3\), 188 MHz) \(\delta\) -143.80 (m, 8F), -157.83 (m, 4F) (see appendix page 152).

### 3.4.11 Sexi(ethylene oxide) ditosylate (35)

![Sexi(ethylene oxide) ditosylate](image)

Sexi(ethylene oxide) (15.8 g, 56.0 mmol) was dissolved in DCM (300 ml) and pyridine (150 ml) and cooled to 10 °C. Tosyl chloride (55.5 g, 291 mmol) was dissolved in DCM (300 ml) and added dropwise while keeping the reaction temperature between 10 and 15 °C. After the addition was complete the mixture was stirred for 1 h at 10 °C and left to warm overnight. It was poured onto ice (750 g) and acidified with aqueous hydrochloric acid (2 M). The organic layer was washed twice with aqueous hydrochloric acid and five times with water, dried (MgSO\(_4\)) and
the solvent removed under reduced pressure yielding sexi(ethylene oxide) ditosylate (25.4 g, 77%) as a colourless oil. As the \(^1\)H NMR spectrum was in good agreement with the literature\(^{16}\) no further analysis was carried out. \(^1\)H NMR (CDCl\(_3\), 200 MHz) \(\delta\) 7.80 (d, \(J = 8.4\) Hz, 4H, ar. CH), 7.34 (d, \(J = 8.4\) Hz, 4H, ar. CH), 4.17 (t, \(J = 5\) Hz, 4H, OCH\(_2\)), 3.69 (t, \(J = 5\) Hz, 4H, OCH\(_2\)CH\(_2\)), 3.62 (s, 8H, CH\(_2\)), 3.58 (s, 8H, CH\(_2\)), 2.45 (s, 6H, CH\(_3\)).

3.4.12 1,17-Bis (4-formylphenyloxy)-3,6,9,12,15-pentaoxaheptadecane (37)

Sexi(ethylene oxide) ditosylate (25.0 g, 42.3 mmol), \(p\)-hydroxybenzaldehyde (11.0 g, 90.1 mmol) and K\(_2\)CO\(_3\) (17 g, 123 mmol) were dissolved in DMF (70 ml) and heated at 90 °C for 48 h. The product was poured onto ice (100 g) and the solvent removed under reduced pressure. The product was redissolved in CHCl\(_3\), dried (MgSO\(_4\)) and purified by column chromatography (silica gel, hexane: ethyl acetate 1:1 (800 ml), then ethyl acetate) yielding 1,17-bis(4-formylphenyloxy)-3,6,9,12,15-pentaoxa-heptadecane (14.5 g, 70%) as a white solid, m.p. 43 - 45°C. Found: C, 63.49%; H, 7.07%; M(MS, EI) 490 (M\(^+\)). Calculated for C\(_{26}\)H\(_{34}\)O\(_9\): C, 63.66%; H 6.99%; M 490. \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 9.87 (s, 2H, CHO), 7.81 (d, 4H, \(J = 9\) Hz, ar. CH), 7.01 (d, 4H, \(J = 9\) Hz, ar. CH), 4.20 (t, 4H, \(J = 4.5\) Hz, OCH\(_2\)), 3.88 (t, 4H, OCH\(_2\)CH\(_2\)), 3.68 (m, 16H, CH\(_2\)); \(^{13}\)C \(^1\)H NMR (CDCl\(_3\), 63 MHz) \(\delta\) 190.74 (CHO), 163.80 (CO), 131.89 (ar. CH), 130.01 (CCHO), 114.84 (ar. CH), 70.86 (OCH\(_2\)), 70.59, 69.41, 67.17 (CH\(_2\)) (see appendix page 153).

3.4.13 \(\alpha,\alpha'\)‐Dibromoxylene (8.0 g, 30.3 mmol) and triphenylphosphine (17.7 g, 66.7 mmol) were refluxed in DMF (62 ml) for 3 h. The reaction was cooled to room temperature and dry diethyl ether was added (40 ml). The white precipitate was recovered by
filtration, washed three times with dry diethyl ether (20 ml) and dried (MgSO₄), yielding p-xylylenbis(triphenylphosphonium bromide) (0.85 g, 69%) as a white solid. As the melting point and ¹H NMR spectrum were in good agreement with those reported in the literature¹⁷ no further analysis was carried out. mp > 300 °C (lit > 400 °C), ¹H NMR (CDCl₃, 300 MHz) δ 7.5 – 7.8 (m, 30H, ar. CH), 6.91 (s, 4H, ar. CH), 5.38 (d, J = 13 Hz, 4H, CH₂).

3.4.14 H-DSB-block-SEO (39)

![Structural formula]

p-Xylylene-bis(triphenylphosphonium bromide) (7.96 g, 10.1 mmol) and LiCl were dissolved in DMF (60 ml). KO'Bu (1.0 M, 29.6 ml, 29.6 mmol) was added and the mixture stirred for 1 h. 1,17-Bis(4-formylphenyloxy)-3,6,9,12,15-pentaoxaheptadecane (4.95 g, 10.1 mmol) was dissolved in DMF (10 ml) and added to the mixture. After stirring at room temperature for 6 h the mixture was quenched with aqueous HCl (2 M, 20 ml). All solvents were removed under reduced pressure. The product was redissolved in chloroform (200 ml) and washed with water. The chloroform solution was concentrated (10 ml) and the polymer precipitated into methanol (60 ml). The reprecipitation was repeated once more yielding H-DSB-block-SEO (3.8 g, 68%) as a yellow solid. Gel Permeation Chromatography (Viscoteck, RI detector, chloroform eluent, 2 x PLgel mixed bed D 30 cm columns, polystyrene standards) Mₙ 5600 g/mol; Mₘ 16700 g/mol; PDI 3.0. Found: C, 71.69%; H, 7.11%. Calculated for C₃₄H₄₀O₇: C, 72.83%; H 7.19%. ¹H NMR (TCE-d₂, 300 MHz) δ 7.5 – 7.1 (m, 8H, ar. CH), 7.01 (AB q, J = 16 Hz, 1H, CH=CH₂), 6.97 (AB q, J = 16 Hz, 1H, CH=CH₂), 6.90 (m, 2H, ar. CH), 6.77 (m, 2H, ar. CH), 6.49 (AB q, J = 12 Hz, 1H, CH=CH₂), 6.46 (AB q, J = 12 Hz, 1H, CH=CH₂), 4.13 (m, 4H, OCH₂), 3.84 (m, 4H, CH₂), 3.64 (m, 16H, CH₂) ¹³C ¹H NMR (CDCl₃, 100 MHz) δ 158.24, 157.60, 136.37, 135.89, 130.04, 130.00, 129.76, 129.71, 129.56, 129.09, 128.55, 128.42, 127.79, 127.74, 127.66, 126.51, 126.15, 125.99, 114.77, 114.20, 114.15, 70.46, 70.21, 69.40, 67.31, 67.19 (see appendix page 154).
3.5 References

5. McDonald, R. N.; Campbell, T. W. 1960, 82, 4669.
4 Optical and Electroluminescence Properties of a Soluble Derivative of PPV and its Fluorinated Equivalent

This chapter deals with the optical and electroluminescent properties of the two polymers, H-DSB-block-SEO and F-DSB-block-SEO, the syntheses of which were described in Chapter 3. The properties were studied using several techniques: The binding energies of the valence bands (HOMOs) were measured by photoelectron spectroscopy (PES) and cyclic voltammetry. Furthermore, PES was used to study the chemical composition of the near-surface-region of the polymer films. The optical band gaps of the two polymers were determined using UV/Vis absorption spectroscopy. The absorption spectra were recorded in the solid state and in solution. Photoluminescence (PL) spectra and quantum yields were determined for thin films of the polymers. The changes in the absorption and emission spectra and in the electronic energy levels of these materials due to fluorine substitution will be discussed.

A variety of LEDs based on both polymers were prepared; single-layer devices were studied using different low work function metals (Al and Ca) and the effect of additional electron-conducting or hole-conducting layers was examined. The LEDs were characterised by their electroluminescence spectra, their stability and the dependence of current density and luminescence on the applied voltage. The polymer H-DSB-block-SEO was also used as emissive layer in light emitting cells (LECs) and the device characteristics were compared to those of an LED. The surface morphologies of several devices were studied by atomic force microscopy (AFM).

The various techniques used in this study are briefly described in the following sections along with the analysis of the data obtained from the samples under investigation.
4.1 Photoelectron Spectroscopy

Photoelectron spectroscopy (PES) is based on the photoelectric effect. The irradiation of a solid sample with photons of a sufficient energy gives rise to the ejection of inner-shell electrons in the case of X-ray photoelectron spectroscopy (XPS), or valence shell electrons in the case of UV photoelectron spectroscopy (UPS). This photoionisation process can be represented by

\[ M_0 + h\nu \rightarrow M^{++} + e^- \quad (4.1), \]

where \( M_0 \) represents the neutral molecule, \( h\nu \) is the ionising photon, \( M^{++} \) represents the radical cation of the molecule in the excited state and \( e^- \) the photoelectron which carries the kinetic energy. The energy balance for Eq. (4.1) is given by

\[ E_0 + h\nu = E^{++} + E_k \quad (4.2), \]

where \( E_0 \) is the energy of the neutral molecule in the ground state, \( E^{++} \) is the energy of the radical cation and \( E_k \) is the kinetic energy of the electron. If the latter is measured at a fixed frequency \( \nu \) the binding energy of the electron \( E_E \) can be determined as:

\[ E_E = E^{++} - E_0 = h\nu - E_k \quad (4.3) \]

In a simple model the electronic structures of \( M_0 \) and \( M^{++} \) are described as single-electron states which means that the kinetic energy measured can be assigned to individual electronic levels.

*Figure 4.1.1* shows a simple schematic of electrons in core or valence shells. The schematic diagram illustrates that the sum of the energy of the molecule in the ground state and the energy of the photon are equal to the energy of the radical cation of molecule in the excited state plus the kinetic energy of the emitted electron (Eq 4.2).
Figure 4.1.1 An idealised photoelectron spectrum (top) with the corresponding one-electron molecular levels (bottom).

The radiations used for XPS are the Al(Kα) and Mg(Kα) emission lines while a helium resonance lamp is used generally for UPS. The binding energies measured in XPS provide qualitative and quantitative analysis of the chemical composition of the near surface region of the sample; changes in the valence electron density of an atom are reflected in small, but significant shifts of the core level energies and are characteristic for a certain chemical environment of that atom. Consequently, XPS can provide structural information. The technique can be used for studies of the valence band, but the efficiency is approximately one order of magnitude lower than for core photoelectrons.\(^1\) Studies of the valence band are gained more easily by UPS, since the photoionisation cross-section is higher for UV light. The PES measurements presented in this chapter were carried out by Dr. Michel de Jong and Prof. William R. Salaneck at Linköping University, Sweden, and we are grateful for their contribution to this work.

The XPS wide scan of a thin film of F-DSB\,-\,block\,-\,SEO on a gold substrate indicated the presence of a small amount of silicone impurity, probably silicone grease. Tilting the sample and thereby reducing the thickness of the region probed by the incident X-ray beam showed that the silicone was present predominantly on the surface of the sample. After the sample was rinsed with cyclohexane only the
expected signals for C, O and F were observed. All subsequent PES measurements were conducted using this cleaned sample. An XPS wide scan of H-DSB-block-SEO film only showed the presence of C and O, with no silicone contaminant.

The intensity of the binding energy signals of F(1s), O(1s) and C(1s)-electrons in thin films of F-DSB-block-SEO and H-DSB-block-SEO can be used to determine the relative abundance of those elements in the samples. The theoretically expected abundances can be calculated by counting the number of atoms per repeat unit. Table 4.1.1 shows that the observed intensities are consistent with those calculated. The increase of fluorine content might be due to the tendency of fluorinated materials to migrate from the bulk to surface regions.

<table>
<thead>
<tr>
<th>F-DSB-block-SEO</th>
<th>H-DSB-block-SEO</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1s)</td>
<td>O(1s)</td>
</tr>
<tr>
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</tr>
<tr>
<td>calc.</td>
<td>0.64</td>
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<tr>
<td>C(1s)</td>
<td>O(1s)</td>
</tr>
<tr>
<td>measured</td>
<td>0.79</td>
</tr>
<tr>
<td>calc.</td>
<td>0.83</td>
</tr>
</tbody>
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Table 4.1.1 Measured and calculated relative abundance of C, O and F in F-DSB-block-SEO and H-DSB-block-SEO according to the 1s-electron intensities in wide scan XPS spectra.

The XPS narrow scan of the 1s electrons of a specific element gives an indication of the chemical environments of that element; for instance a covalent bond to a highly electronegative atom will decrease the valence electron density around that atom and increase the binding energy for its 1s electrons. Using reference compounds of known structure the observed binding energy can be related to a specific bonding environment. When several chemical environments for one type of atom are present within one molecule, the observed spectrum represents the sum of all signals due to these atoms. The individual binding energies and the relative abundance of the atoms can be determined using Gaussian curves for each individual signal and fitting the sum of those signals to the measured spectrum.

The XPS narrow scan of the C(1s) region of F-DSB-block-SEO shows three different binding energies (Figure 4.1.2, left). The dotted lines correspond to the fitted signals. The peak with the highest binding energy (287.2 eV) corresponds to C bonded to F, the middle peak (286.2 eV) corresponds to C bonded to O and the peak with the lowest binding energy (285.1 eV) corresponds to C bonded to C and H only. In the case of H-DSB-block-SEO only two signals are observed: one for C bonded to O at 285.7 eV and one for C bonded to C and H only at 283.8 eV (Figure 4.1.2
expected signals for C, O and F were observed. All subsequent PES measurements were conducted using this cleaned sample. An XPS wide scan of H-DSB-block-SEO film only showed the presence of C and O, with no silicone contaminant.

The intensity of the binding energy signals of F(1s), O(1s) and C(1s)-electrons in thin films of F-DSB-block-SEO and H-DSB-block-SEO can be used to determine the relative abundance of those elements in the samples. The theoretically expected abundances can be calculated by counting the number of atoms per repeat unit. Table 4.1.1 shows that the observed intensities are consistent with those calculated. The increase of fluorine content might be due to the tendency of fluorinated materials to migrate from the bulk to surface regions.

<table>
<thead>
<tr>
<th></th>
<th>F-DSB-block-SEO</th>
<th>H-DSB-block-SEO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C(1s)</td>
<td>O(1s)</td>
</tr>
<tr>
<td>measured</td>
<td>0.61</td>
<td>0.13</td>
</tr>
<tr>
<td>calc.</td>
<td>0.64</td>
<td>0.13</td>
</tr>
<tr>
<td>measured</td>
<td>0.79</td>
<td>0.21</td>
</tr>
<tr>
<td>calc.</td>
<td>0.83</td>
<td>0.17</td>
</tr>
</tbody>
</table>

*Table 4.1.1 Measured and calculated relative abundance of C, O and F in F-DSB-block-SEO and H-DSB-block-SEO according to the 1s-electron intensities in wide scan XPS spectra.*

The XPS narrow scan of the 1s electrons of a specific element gives an indication of the chemical environments of that element; for instance a covalent bond to a highly electronegative atom will decrease the valence electron density around that atom and increase the binding energy for its 1s electrons. Using reference compounds of known structure the observed binding energy can be related to a specific bonding environment. When several chemical environments for one type of atom are present within one molecule, the observed spectrum represents the sum of all signals due to these atoms. The individual binding energies and the relative abundance of the atoms can be determined using Gaussian curves for each individual signal and fitting the sum of those signals to the measured spectrum.

The XPS narrow scan of the C(1s) region of F-DSB-block-SEO shows three different binding energies (Figure 4.1.2, left). The dotted lines correspond to the fitted signals. The peak with the highest binding energy (287.2 eV) corresponds to C bonded to F, the middle peak (286.2 eV) corresponds to C bonded to O and the peak with the lowest binding energy (285.1 eV) corresponds to C bonded to C and H only. In the case of H-DSB-block-SEO only two signals are observed: one for C bonded to O at 285.7 eV and one for C bonded to C and H only at 283.8 eV (Figure 4.1.2
right). The measured intensities for these signals are consistent with those calculated (Table 4.1.2).

Figure 4.1.2 XPS narrow scan of the C(1s) region of F-DSB-block-SEO (left) and H-DSB-block-SEO (right).

<table>
<thead>
<tr>
<th>C(1s) signal in F-DSB-block-SEO</th>
<th>C(1s) signal in H-DSB-block-SEO</th>
</tr>
</thead>
<tbody>
<tr>
<td>measured</td>
<td>measured</td>
</tr>
<tr>
<td>C-F</td>
<td>0.43</td>
</tr>
<tr>
<td>C-O</td>
<td>0.37</td>
</tr>
<tr>
<td>C-H/C-C</td>
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</tr>
<tr>
<td>calc.</td>
<td>0.35</td>
</tr>
<tr>
<td>calc.</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Table 4.1.2 Measured and calculated relative abundance of C-F, C-O and C-H/C-C carbons in F-DSB-block-SEO and H-DSB-block-SEO according to the 1s-electron intensities in narrow scan XPS spectra.

Figure 4.1.3 shows the UPS spectrum of H-DSB-block-SEO and F-DSB-block-SEO. The electrons close to the valence band edge are found at the right-hand-side of the spectrum (see cartoon Figure 4.1.1). The binding energy of those electrons relative to the vacuum level is the ionisation potential (IP) and can be derived from UPS spectra using the cut-off of secondary electrons at the left-hand-side of the spectrum (not shown in Figure 4.1.3, but see cartoon Figure 4.1.1). The IP for F-DSB-block-SEO is 6.3 ± 0.1 eV and for H-DSB-block-SEO is 5.3 ± 0.1 eV. The π-electron bands observed in both UPS spectra look similar to those observed for PPV. However, the detailed interpretation of the form and position of these bands requires quantum-chemical calculations and was not undertaken during the course of this work.

* The UPS spectrum shows the electrons with the largest kinetic energy on the right-hand-side and those with almost no kinetic energy on the left-hand-side. These two positions are separated by an energy $E_C$. The IP can be calculated as $IP = h\nu - E_C$. 

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Figure 4.1.3 Comparison of the He(II) UPS valence band spectra of H-DSB-block-SEO and F-DSB-block-SEO. The binding energy is measured relative to the Fermi-level of the samples. It should not be confused with $E_E$ (page 77).

The IPs of both polymers were also determined by cyclic voltammetry using ferrocene as the reference (see appendix page 159). According to cyclic voltammetry the IP for F-DSB-block-SEO was at $6.2 \pm 0.1$ eV and for H-DSB-block-SEO at $5.5 \pm 0.1$ eV. These values were consistent with those obtained by UPS measurements. The average values obtained from UPS and the cyclic voltammetry measurements were used in the further discussion (F-DSB-block-SEO: $6.25 \pm 0.15$ eV; H-DSB-block-SEO: $5.4 \pm 0.20$ eV).

The strong increase in the IP of F-DSB-block-SEO relative to H-DSB-block-SEO can be attributed to the effect of the high electron affinity of the fluorine substituents. Kang et al. found an increase of the IP of 0.17 eV when one hydrogen atom per aromatic ring of PPV was substituted by fluorine. In our case four positions on each aromatic ring are substituted by fluorine and an increase of the IP of about 0.85 eV is observed; although F-DSB-block-SEO and H-DSB-block-SEO are copolymers with isolated chromophores and therefore somewhat different to Kang's fully conjugated PPV derivative, a similar increase in IP of about 0.2 eV per fluorine atom is found in both systems. The IPs will be further discussed in the context of the energy levels in LEDs.
4.2 UV/Vis Spectroscopy

Absorption spectra show transitions of electrons from the ground state to an excited state. The observed fine-structure is due to the vibrational structure of the excited state. The solution state UV/Vis spectra of H-DSB-block-SEO and F-DSB-block-SEO were recorded in chloroform. The spectrum of H-DSB-block-SEO shows a maximum at 354 nm for the $\pi,\pi^*$-transition (Figure 4.2.2). This maximum is slightly red-shifted with respect to the parent compound DSB ($\lambda_{\text{max}} = 350$ nm). A red shift is expected due to the effect of the two alkoxy-groups in the 4 and 4' positions, which extend the conjugation and therefore lower the band gap. A more pronounced red shift is observed in the case of 4,4'-diethoxy-distryrylbenzene ($\lambda_{\text{max}} = 368$ nm); like H-DSB-block-SEO this molecule contains ca. 50% of double bonds in the cis-configuration and ca. 50% in the trans-configuration. The difference in the absorption maximum for these two compounds with identical chromophores might be explained by the fact that the absorption shows a vibronic fine-structure which is not well resolved. Different solvent conditions might lead to a better resolution and a different vibronic peak might be the maximum.

The vibronic fine-structure is more resolved in the case of F-DSB-block-SEO, which shows two maxima at 340 nm and 354 nm (Figure 4.2.2). Although the second maximum coincides with the maximum of H-DSB-block-SEO the spectrum is overall about 10 nm blue shifted relative to H-DSB-block-SEO.

Bazan et al. have studied the effect of fluorine substitution on DSB derivatives and found that the absorption maxima do not change more than a few nm (less than 10 nm) when between 2 and 12 fluorines are introduced on the aromatic rings. However, their study does not include a DSB molecule with all 14 aromatic positions substituted by fluorine. This DSB derivative was synthesised during the course of this study and will be discussed in more detail in Chapter 5. In the
polymer F-DSB-block-SEO the DSB unit carries 12 fluorine atoms and a shift of 10 nm is observed.

![Absorption spectra of F-DSB-block-SEO and H-DSB-block-SEO](image)

**Figure 4.2.2 Absorption spectra of F-DSB-block-SEO and H-DSB-block-SEO in chloroform solution.**

The onset of the absorption spectrum is a good measure of the HOMO-LUMO gap since it shows the minimum energy required to transfer an electron from the ground state to the excited state. The onset of absorption in the case of H-DSB-block-SEO is at 410 nm indicating a HOMO-LUMO gap of 3.0 eV. For F-DSB-block-SEO the onset is at 400 nm corresponding to a HOMO LUMO gap of 3.1 eV (Table 4.2.3).

The extinction coefficients of the DSB units within F-DSB-block-SEO and H-DSB-block-SEO are 4.0 and 3.6 x 10^4 1 cm⁻¹ mol⁻¹, respectively. Such values are typical for DSB units; for the case of 4,4'-dimethoxy-distrylbenzene extinction coefficients of 2.3 and 6.8 x 10^4 1 cm⁻¹ mol⁻¹ have been reported.5,7

<table>
<thead>
<tr>
<th>Polymer</th>
<th>λ_{max} (solution)</th>
<th>ε (solution) /10^4 cm⁻¹ mol⁻¹</th>
<th>onset (solution)</th>
<th>λ_{max} (solid state)</th>
<th>onset (solid state)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-DSB-block-SEO</td>
<td>354 nm (3.5 eV)</td>
<td>3.6</td>
<td>410 nm (3.0 eV)</td>
<td>334 nm (3.7 eV)</td>
<td>415 nm (3.0 eV)</td>
</tr>
<tr>
<td>F-DSB-block-SEO</td>
<td>354 nm (3.5 eV)</td>
<td>4.0</td>
<td>400 nm (3.1 eV)</td>
<td>301 nm (4.1 eV)</td>
<td>415 nm (3.0 eV)</td>
</tr>
</tbody>
</table>

*Table 4.2.3 Solution state and solid state absorption characteristics of H-DSB-block-SEO and F-DSB-block-SEO*
The solid state absorption spectra of both polymers were investigated since the polymers were used as thin films in LEDs. The absorption spectra of both polymers were blue shifted relative to their solution state spectra (Figure 4.2.3). This shift is particularly strong in the case of F-DSB-block-SEO. The first absorption maximum in the solid state is at 301 nm compared with the maximum at 354 nm in the solution state spectrum. This may be an indication of a strong aggregation in the solid state. The shape of the curve is typical for an H-aggregate. The main absorption in a H-aggregate is blue-shifted relative to the isolated chromophore. A second absorption is red-shifted but the transition is forbidden and appears only as a weak shoulder in the spectrum. Kilbinger et al. have reported strong blue shifts for aggregates of oligothiophene-PEO-block copolymers relative to molecularly dissolved molecules. Similar results were found by Song et al. for stilbene-aggregates and Neckers et al. for block copolymers with partially fluorinated DSB units.

The solid state absorption maximum for H-DSB-block-SEO is at 334 nm. The difference in absorption maximum in the solid state (334 nm) and the solution state (354 nm) for H-DSB-block-SEO is less pronounced than in the case of F-DSB-block-SEO indicating that the former might show less or less strong aggregation. Benfaremo et al. have prepared a similar block copolymer with all-trans DSB units and long PEO spacer units (see Chapter 1, Figure 1.3.5). The solid state absorption maximum for this polymer (330 nm) is similar to that of H-DSB-block-SEO (334 nm); this shows that the different configurations of the double bonds (all-trans relative to 50% cis and trans) has little effect on the solid state absorption spectra.

The onset of absorption in the solid state is at 415 nm for F-DSB-block-SEO and H-DSB-block-SEO. Therefore, the HOMO-LUMO gap for both polymers in the solid state is 3.0 eV. It can be concluded that the replacement of hydrogens by fluorines in this type of block copolymer not only changes the IP (potential of the HOMO relative to the vacuum level) but also to the same extent the electron affinity (EA, potential of the LUMO relative to the vacuum level). The electron affinities of the polymers can now be calculated; for H-DSB-block-SEO the EA is 2.4 ± 0.2 eV and for F-DSB-block-SEO the EA affinity is at 3.25 ± 0.15 eV. The energy levels of the HOMO and the LUMO will be further discussed in the context of LEDs.
4.3 Photoluminescence

All photoluminescence (PL) and electroluminescence (EL) measurements described in this chapter were conducted by the author in collaboration with Dr. Franco Cacialli at the Cavendish Laboratories in Cambridge. We are very grateful for his support of this work.

Photoluminescence spectra are emission spectra of samples, which have been excited by photons. The observed fine-structure is due the vibrational structure of the ground state. Luminescence in conjugated polymers is believed to be the result of the radiative decay of singlet excited states. In the case of solid state photoluminescence the angular distribution of the emitted light is not uniform. In
order to obtain an average of the emission over all angles a hollow sphere (integrating sphere) is used which is coated on the inside with a reflecting material. A glass disk covered with the polymer film is placed in the centre of the integrating sphere. A laser beam is fired at the sample and the emission detected by a photodiode at a right angle relative to the incident laser beam. In our case a He-Cd laser with an emission wavelength of 325 nm was used.

![Figure 4.3.2 Schematic representation of the photoluminescence experiment.](image)

The PL efficiency is the ratio of the emitted photons to the absorbed photons. To measure the PL efficiency three different experiments are used. In the first experiment the sphere is empty and the laser beam is simply reflected at the wall of the sphere. In the second experiment the sample is placed in the sphere and the laser beam is aimed at the walls of the sphere. In a third experiment the laser is aimed at the sample. The loss in the intensity from the second experiment ($L_b$) to the third experiment ($L_c$) can be used to determine the absorption coefficient of the sample. The absorption coefficient ($A$) is the ratio of the photons that hit the sample to those absorbed and is given by:

$$A = (1 - L_c/L_b)$$

The intensity of the emission spectrum is measured in experiments two ($P_b$) and three ($P_c$). The photoluminescence efficiency $\eta$ can then be calculated as

$$\eta = [P_c - (1 - A) P_b] / L_0 A,$$

where $L_0$ is the light intensity measured in the first experiment. A full derivation of this equation is given in the appendix (see page 129).
The photoluminescence efficiency of H-DSB-block-SEO is 34%, while the PL efficiency of F-DSB-block-SEO is 17%. These results are comparable to the PL efficiency of PPV, which is generally quoted as 27%,\textsuperscript{14} but efficiencies as high as 80% have also been claimed.\textsuperscript{15}

The solid state photoluminescence spectrum of H-DSB-block-SEO shows fine-structure with two maxima at 530 nm (2.34 eV) and 494 nm (2.50 eV) (Figure 4.3.3). The arrows on the spectra point towards the corresponding y-axes. The emission spectrum of the block copolymer with all-trans DSB units and PEO spacers prepared by Benfaremo et al. is reported to show two maxima at about 455 and 490 nm.\textsuperscript{11} The similar separation of these maxima indicates that the ground states of both polymers have similar vibrational structures. The fact that the polymer with all-trans double bonds is blue shifted with respect to H-DSB-block-SEO, which contains a mixture of cis- and trans-double bonds, is surprising since steric hindrance and a decrease in conjugation and therefore a bigger optical band gap might be expected in the case of cis-double bonds. However, it is also possible that the entire emission of H-DSB-block-SEO arises from trans-trans-DSB units since the energy in the excited states of cis-cis and cis-trans-DSB units can be transferred to the trans-trans-DSB units, which are expected to have the smallest optical band gap. The reason for the blue-shift of the emission in the case of the polymers prepared by Benfaremo et al. remains unclear in particular since the absorption of this polymer is similar to that of H-DSB-block-SEO. These systems are not identical, though; in the Benfaremo-system the all trans DSB units constitute 24 wt.% of the total mass whereas in our system the trans-trans, trans-cis and cis-cis DSB units constitute 50 wt.%. The consequences of these differences merit further examination but this was not possible with the constraints of this study.

The Stokes’ shift, which is the difference between the absorption maximum and the emission maximum, is 162 nm (Figure 4.3.3). For PPV the Stokes’ shift is 110 nm. Stokes’ shifts indicate differences between the excited state reached immediately after absorption and the excited state from which the emission occurs. These differences can be due to vibrational, electronic or geometric changes.\textsuperscript{5}
The emission spectrum of F-DSB-block-SEO shows no fine structure and is in the same region as the emission of H-DSB-block-SEO (Figure 4.3.4). The maximum is at 502 nm (2.47 eV). Due to the strong blue-shift of the solid state absorption maximum an even larger Stokes' shift (201 nm) is observed when the absorption and the emission spectra are compared.

There is some disagreement in the literature about the effect of the cis-trans vinylene ratio in poly(arylene vinylene)s on the PL and EL efficiencies of devices. Feast et al. have prepared a range of poly(4,4'-diphenylene diphenylvinylene)s and related structures with varying cis and trans contents and shown that a maximum for the photoluminescence efficiency is reached at a cis:trans ratio of 1.16-18 On the other hand Karasz et al. have reported that in the case of block copolymers optimum efficiencies are obtained when more than 90% of double bond configurations are trans.19 However, they do not report any absolute values for their polymers. The results presented in this work show that polymers containing a mixture of cis and
trans double bonds can have high solid state PL efficiencies. There is also work on PPV obtained via the precursor route which shows that increasing the cis-vinylene content parallels increasing luminescence efficiency.\textsuperscript{20}

Cornil, Heeger and Bredas have carried out quantum chemical calculations on dimers and trimers of stilbene as model compounds for PPV.\textsuperscript{21} They found that in aggregates with high symmetry the absorption is blue shifted and luminescence is quenched. This blue shift in absorption along with the reduction in photoluminescence quantum efficiency is in agreement with the findings of the DSC analysis for F-DSB-block-SEO, which shows ordered structures. Cornil \textit{et al.} also found that aggregates with lower symmetry and therefore less ordered structures did not show quenching of luminescence. The authors go on to suggest that high PL efficiencies can be expected for polymers with a supramolecular architecture that promotes different relative orientations of adjacent chains. Such disorder is certainly promoted in a polymer comprising a mixture of cis and \textit{trans} vinylene units since the alignment of polymer chains is hindered by the different orientations of cis and \textit{trans} double bonds.

It is not possible to make an unambiguous generalisation about the relationship between the cis and \textit{trans} content of poly(arylene vinylene)s and PL efficiency. However, the wide spread view that all-\textit{trans} configurations are generally beneficial is certainly questionable and it is clear that the outcome is related to the details of structure and organisation.

A blend of H-DSB-block-SEO and F-DSB-block-SEO (50 wt.\%, 50 wt.\%) prepared from solutions of both polymers shows a drop in solid state PL efficiency to 10\%. This decrease might be due to a quenching process based on $\pi,\pi$-stacking of aromatic rings. $\pi,\pi$-stacking is a typical behaviour in mixtures of aromatics and perfluoroaromatics\textsuperscript{22} and will be discussed in more detail in Chapter 5. In the case of photoluminescence, the stacking might lead to regions of high order where the excited state is quenched by non-radiative processes.
4.4 Light emitting diodes

Single-layer devices based on H-DSB-block-SEO

The principles of a polymer LED were described in Chapter 1. Indium-tin-oxide (ITO) is the most prevalent material used as the anode because of its high work function (4.5-5.1 eV) and its transparency in the visible region of light. Commercially available ITO-glass-substrates were treated first with an oxygen plasma, in order to increase the work function and surface energy of ITO. After spin-coating with the emissive polymer, thin calcium or aluminium layers were deposited at a pressure below $10^{-7}$ mbar (see Experimental).

![Figure 4.4.1 Schematic diagram of a light emitting diode.](image)

First, single-layer devices with H-DSB-block-SEO as the emissive layer and calcium or aluminium as cathodes were prepared. These devices were then characterised by measuring the current density and luminescence relative to the voltage applied to the device. These so called current density/voltage/luminescence (IVL) curves show several characteristics of the device. The turn-on voltage is the minimum voltage required for electroluminescence. All IVL curves presented in this work show the luminescence on a logarithmic scale on the right hand axis of the graph. Due to the logarithmic scale the luminescence drops sharply to zero at the turn-on voltage, so that the turn-on voltage can be determined easily. The current density is shown on the left hand side of the IVL curves. Figure 4.4.2 shows the IVL curves for the devices ITO/H-DSB-block-SEO/Ca and ITO/H-DSB-block-SEO/Al. For both devices current and luminescence increase steadily with increasing voltage. When Ca was used as the cathode the turn-on voltage was 6.5 V and when Al was used the turn-on voltage was 7.0 V. The devices were stable and
did not degrade over a period of ten minutes while a series of measurements was conducted. Maximum luminescences over 1000 cd/m² were observed at 24 V for a device with a Ca-cathode and luminescences over 2000 cd/m² were observed at 19 V in the case of an Al-cathode. The device structure with the Al-cathode was still capable of electroluminescence after storing in air for seven months.

![IVL curves for the devices](image)

*Figure 4.4.2 IVL curves for the devices a) ITO/H-DSB-block-SEO/Ca (left) and b) ITO/H-DSB-block-SEO/Al (right).*

The average luminescence of a television screen is 100 cd/m² showing that the devices are very bright. Although the devices cannot be used over a prolonged period at 19 V, since degradation occurs at such high current densities, the devices were stable at lower voltages. These findings are particularly noteworthy with respect to polymers prepared by Benfaremo et al. and Li et al. These authors have prepared similar polymers but were unable to use them in electroluminescent devices due to their poor emission and stability characteristics. *Figure 4.4.3* shows the structures of the polymers prepared by Benfaremo et al. (left) and Li et al. (right). Possible reasons for the improved properties of H-DSB-block-SEO compared to these polymers include high purity, few defects and careful processing.

![Polymers prepared by Benfaremo et al.](image)

*Figure 4.4.3 Polymers prepared by Benfaremo et al. (left) and Li et al. (right).*

The maximum luminescence efficiency is about 0.5 cd/A for both devices. This corresponds to an internal quantum efficiency of 1.1%. Quantum efficiencies of up to 0.1% have been reported for PPV itself and up to 0.8% for block copolymers. The high quantum efficiency of devices based on H-DSB-block-SEO confirms the excellent properties of the polymer as an emitter in LEDs.
The ionisation potential (IP) of H-DSB-block-SEO is $5.4 \pm 0.2$ eV and the electron affinity is $2.4 \text{ eV} \pm 0.2$ eV. The work function of Ca is $2.9$ eV and the work function of Al is $4.3$ eV. Figure 4.4.4 shows the energy levels of the polymer and the work functions of the electrodes. Without any barriers at either electrode the turn-on voltage should have a value close to the optical band gap i.e. $3.0$ eV in the case of H-DSB-block-SEO. A small barrier is expected for the injection of electrons from Ca since its work function ($2.9$ eV) is close to the LUMO of H-DSB-block-SEO ($2.4$ eV). A larger barrier is expected for Al because of its higher work function ($4.3$ eV). Indeed, the turn-on voltage was slightly lower when Ca ($6.5$ V) was used instead of Al ($7.0$ V). However, due to the large difference between the two work functions a bigger difference in turn-on voltage and efficiency was originally expected.

![Figure 4.4.4 Electron energy level diagram of H-DSB-block-SEO and work functions of ITO, Ca and Al.](image)

The EL spectra for the two single-layer devices are very similar (Figure 4.4.5). They show a fine-structure with two maxima at $2.37$ eV and $2.51$ eV, similar to those observed in the PL spectrum ($2.34$ eV and $2.50$ eV). This confirms that the emission in photoluminescence and electroluminescence are based on the same excited states.

![Figure 4.4.5 EL spectra for the devices a) ITO/H-DSB-block-SEO/Ca (left) and b) ITO/H-DSB-block-SEO/Al (right).](image)
Double-layer devices based on H-DSB-block-SEO and PEDOT:PSS

Poly(dioxyethylene thienylene) (PEDOT) doped with polystyrenesulfonic acid (PSS) is widely used as the hole-injection layer. It has a high work function and thereby provides low barriers for hole-injection to the polymer. It is likely that some diffusion of the dopant PSS into the emissive polymer layer occurs during the processing which helps charge injection from the PEDOT into the emissive polymer. However, the diffusion is restricted to the interface because of the polymeric nature of the dopant.

Figure 4.4.6 PEDOT and the dopant PSS provide a stable hole-injection layer.

An aqueous PEDOT:PSS solution was spun-cast onto ITO substrates and dried. H-DSB-block-SEO was spun-cast on top of this layer and the devices were completed by evaporation of Ca or Al cathodes. Figure 4.4.7 shows the IVL curves for the double-layer devices ITO/PEDOT:PSS/H-DSB-block-SEO/Ca and ITO/PEDOT:PSS/H-DSB-block-SEO/Al. The onset of luminescence for both devices is 8.5 V. This increase compared to the single-layer devices is probably due to the increased thickness; the double-layer devices consist of a 100 nm-thick emissive layer plus a 90 nm-thick hole-conducting layer. The maximum efficiencies are 0.44 cd/A for the device with a Ca electrode and 0.39 cd/A for a device with an Al electrode, corresponding to internal quantum efficiencies of 1.1% and 1.0%, respectively. Both devices were stable over the period of measurements.

Hole-injection is facile from ITO to PPV and a similar situation can be expected for H-DSB-block-SEO because of the similarity in the energy levels. Since hole-injection is not the limiting factor for the efficiency of the device, the introduction of a hole-conducting layer does not improve the device characteristics, which is readily appreciated with the wisdom of hindsight.
Devices based on F-DSB-block-SEO

Single-layer devices with F-DSB-block-SEO as the emissive layer were prepared in the same way as those based on H-DSB-block-SEO. Calcium or aluminium was used as the cathode. In general, the devices based on F-DSB-block-SEO were disappointing with respect to their electroluminescence properties; the devices were unstable and the electroluminescence faded away within a few seconds after current was passed through the device; consequently, no luminescence vs. voltage curves could be recorded. The current density vs. voltage curves show that very little current passes through the devices; while a current of 500 - 700 mA/cm$^2$ at 19 V is observed in devices based on H-DSB-block-SEO the current is only between 3 and 5 mA/cm$^2$ for devices based on the fluorinated equivalent. The injection or transport of at least one charge carrier must therefore be hindered.
The EL spectrum for the device ITO/F-DSB-block-SEO/Al could be obtained, when several pixels were switched on successively and the individual emissions were summed. *Figure 4.4.9* shows EL spectrum with a maximum emission at 2.44 eV, similar to the PL maximum at 2.47 eV. No fine structure is observed. The similarity between the PL spectrum and the EL spectrum confirms that the emission originates from the same excited states.

![EL spectrum graph](image)

*Figure 4.4.9* PL spectrum of the device ITO/F-DSB-block-SEO/Al.

Double-layer devices with PEDOT:PSS as the hole conducting layer were prepared. For these devices a much higher current was recorded, particularly when Ca was used as the cathode (*Figure 4.4.10*). However, the additional hole-conducting layer did not improve the electroluminescence properties. The increase in current indicates that there is a large barrier for hole-injection from ITO into F-DSB-block-SEO. This barrier can be bridged by a hole-conducting layer such as PEDOT:PSS.

![Current vs. voltage graphs](image)

*Figure 4.4.10* Current vs. voltage curves for the devices a) ITO/PEDOT:PSS/F-DSB-block-SEO/Ca (left) and b) ITO/PEDOT:PSS/F-DSB-block-SEO/Al (right).
The electron energy level diagram is shown in Figure 4.4.11. The IP of F-DSB-block-SEO is 6.25 eV and the EA is 3.25 eV. The large gap between the work function of ITO and the HOMO of F-DSB-block-SEO explains the hole-injection difficulty.

![Electron energy level diagram of F-DSB-block-SEO and work functions of ITO, Ca and Al.](image)

In order to examine the electron-conducting properties of F-DSB-block-SEO, a double-layer device was prepared with PPV as the emissive layer and F-DSB-block-SEO as the electron-conducting layer (ITO/PPV/F-DSB-block-SEO/Al). Its properties were compared to those of a single-layer device based on PPV (ITO/PPV/Al). The spectra of both devices were identical showing that indeed PPV was the emissive layer in both devices. The EL efficiency of both devices was also the same. This shows that F-DSB-block-SEO is a good electron-carrier and the increase in thickness of the device is compensated for by the beneficial effect of an additional electron-injection layer.

It can be concluded that fluorine has a strong effect on the energy levels of the block copolymer. The electron affinity of the polymers is increased and the polymer becomes a good electron-conducting material. However, the emissive properties of the polymer are poor; the PL efficiency is half that of H-DSB-block-SEO and the EL properties are very poor. Similar findings have been previously reported for fluorinated conjugated polymers (see Chapter 1). It appears that the substitution of hydrogen by fluorine not only changes the position of the energy levels but also
gives rise to new non-radiative processes, which are not present in the pure hydrocarbons.

Several further attempts were made to improve the properties of devices based on F-DSB-block-SEO. Blends of H-DSB-block-SEO and F-DSB-block-SEO were prepared in order to examine whether the good emissive properties of the former and the electron-conducting properties of the latter could be combined. Solutions of both polymers with equal concentrations were mixed and devices prepared in the usual manner using Al as the cathode. A very high current density (over 600 mA/cm²) was observed for such devices at low voltages (3 V) but no electroluminescence was recorded. Rather than helping electron-injection, the blend provides an additional route for charge transport that is not found in either of the pure polymers. A possible explanation for this high current density could be the previously mentioned arene/perfluoroarene interactions, which could lead to alternating stacks of both chromophores. Such stacks would give rise to a quick charge transport across the polymer layer and not allow time for charge recombination.

A blend 95 wt.% of H-DSB-block-SEO and 5 wt.% of F-DSB-block-SEO (blend 2) was prepared in order to examine the properties of the fluoro-polymer as a dopant to aid electron-injection. The IVL curve of this polymer blend is shown in Figure 4.4.12. The onset of luminescence is at 8.0 V. The device is stable and luminescence efficiency is 0.17 cd/A. However, the device properties are not improved compared to single-layer devices based on pure H-DSB-block-SEO.

![Figure 4.4.12 Current vs. voltage curves for the devices ITO/blend2/Al. Blend 2 consists of H-DSB-block-SEO(95 wt.%) and F-DSB-block-SEO(5%).](image)

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The use of an additional hole-conducting polymer, poly(9,9-diocetylfluorene-co-bis-N,N’-(4-butyphenyl)-bis-N,N’-phenyl-1,4-phenylenediamine (PFB) was examined (Figure 4.4.13). The ionisation potential of PFB is at 5.1 eV and it is often used in double-layer devices as hole-transporting layer. However, a double-layer device of the form ITO/PFB/F-DSB-block-SEO/Ca could not be prepared since PFB is soluble in chloroform which is the only appropriate solvent for F-DSB-block-SEO. The solvent of the polymer forming the second layer has to be a non-solvent for the first layer to achieve a layered structure in the device. Therefore a single-layer device based on a blend of 60 wt.% F-DSB-block-SEO and 40 wt.% PFB was prepared using Ca as the cathode. However, the device showed very little luminescence (3 cd/m²) and a high turn-on voltage (16 V) (Figure 4.4.14 left).

![Figure 4.4.13 PFB, a hole-conducting polymer.](image)

A device based on a blend of PFB (40 wt.%) and H-DSB-block-SEO (60 wt.%) and Ca as cathode was prepared. The IVL curve is shown in Figure 4.4.14 (right). The current density vs. voltage curve peaks at 5 V possibly due to a short-circuit. The onset of luminescence is at 8.5 V and a maximum luminescence of 100 cd/m² is obtained at 20 V. However, the device based on the blend has no improved properties compared with the device based on pure H-DSB-block-SEO and blends were therefore not further investigated as emissive layers in LEDs.

![Figure 4.4.14 IVL curves for single-layer devices based on a) blend of F-DSB-block-SEO(60 wt.%) and PFB(40 wt.%) (left) and b) blend of H-DSB-block-SEO(60 wt.%) and PFB(40 wt.%) (right).](image)
4.5 Light-emitting cells

In a light-emitting cell (LEC) an electroluminescent polymer mixed with a polymer electrolyte is sandwiched between two electrodes. LECs were first described by Pei et al. who used PPV as the electroluminescent polymer and a complex of poly(ethylene oxide) (PEO) and lithium trifluoromethanesulfonate (LiTf) as electrolyte. When a voltage is applied, PPV near the anode is oxidised and PPV near the cathode is reduced. In contrast to LEDs, counter-ions from the electrolyte can move to compensate the charges created on the polymer chains. PPV is now p-doped at the anode and n-doped at the cathode. Due to the balance of charges and the relatively good electronic conductivity of PPV, the PPV/electrode interfaces are low-resistance contacts.

The current passing through the LEC consists of an ionic contribution and an electronic contribution. At an applied voltage an electrochemical equilibrium is established and the ionic current goes to zero. If the applied voltage is higher than the optical band gap of the polymer, holes in the HOMO move towards the cathode and the electrons in the LUMO move towards the anode. These p- and n-type carriers meet in a so-called p-n-junction to form an excited state, which can radiatively decay to the ground state (Figure 4.5.1). Such p-n-junctions are reversible. If the former cathode becomes the anode and the former anode the new cathode, a new equilibrium is established and the LEC can be used in reverse bias. The luminescence vs. voltage curve is therefore symmetric about zero bias. Due to the low resistant contacts the threshold voltages for electroluminescence in LECs are very close to the optical band gap of the luminescent polymer.

\[\text{Figure 4.5.1 Schematic diagram of the EL process in a LEC. a) doping of the semiconducting polymer as p-type or n-type. b) charge migration and radiative decay in the p-n junction.}\]
The use of a blend of PPV and PEO in LECs can result in phase separation.\textsuperscript{30} This can be overcome by incorporating oligo(ethylene oxide) units and oligo(phenylene vinylene) units into one polymer. Indeed, Huang \textit{et al.} have prepared a conjugated polymer with a PPV backbone and two tri(ethylene oxide) side chains per aromatic ring (Figure 4.5.2).\textsuperscript{30} The authors were able to demonstrate a low threshold voltage of 2.5 V and a luminescence vs. voltage curve symmetric about zero bias.

![Figure 4.5.2 PPV derivative with tri(ethylene oxide) side chains.](image)

H-DSB-\textit{block}-SEO contains oligo(ethylene oxide) units as well as DSB units within its backbone and is therefore a good candidate to be used in LECs. H-DSB-\textit{block}-SEO was complexed with lithium trifluoromethylsulfonate (LiTf) in a chloroform/methanol mixture and spin-coated onto ITO substrates. The Al anode was deposited by thermal evaporation. Under forward bias ITO was the anode and Al the cathode. An IVL curve conducted in forward bias is shown in Figure 4.5.3. The threshold for luminescence was at 3.8 V. This is still significantly higher than the optical band gap of 3.0 V but demonstrates a great improvement compared with the threshold of an LED based on H-DSB-\textit{block}-SEO (6.5 V or 7.0 V). The luminescence increased sharply with increasing voltage; at 4.5 V a luminescence of 190 cd/m\textsuperscript{2} was observed. However, the current density was high and at 4.5 V 2000 mA/cm\textsuperscript{2} passed through the device. The prepared LEC devices were not as stable as the corresponding LEDs.

![Figure 4.5.3 IVL curve of the LEC ITO/H-DSB-\textit{block}-SEO(LiTf)/Al.](image)
The device could also be used in reverse bias. Current and luminescence were recorded starting at -6.0 V and increasing the voltage to 4.5 V. The luminescence-voltage curve is approximately symmetrical about zero bias (slightly displaced towards reverse bias) with luminescence observed between -6.5 V and -4.0 V as well as between 3.8 V and 5.0 V. The current-voltage curve is antisymmetric about the origin similar to those reported by Pei, et al.29

![IVL curve of LEC based on a H-DSB-block-SEO(LiTf) complex in reverse and forward bias.](image)

Figure 4.5.4 IVL curve of LEC based on a H-DSB-block-SEO(LiTf) complex in reverse and forward bias.

It was also possible to show that while the electrochemical equilibrium is established, the current density decreases over time at a constant voltage while the luminescence increases. Figure 4.5.5 shows the decrease of the current density from 3.6 to 2.9 A/cm² and the increase of luminescence from 0 to 2.5 cd/m² over a period of 110 s at a constant voltage of 4 V. The two peaks in luminescence and current after 80 s and 95 s are probably due to local short circuits, which result in a sharp increase in current and luminescence.

![IVL curve of an LEC based on a H-DSB-block-SEO/LiTf complex.](image)

Figure 4.5.5 IVL curve of an LEC based on a H-DSB-block-SEO/LiTf complex.
4.6 Atomic force microscopy

Atomic force microscopy (AFM) was used to analyse the surface morphology of the LED samples. Commercial atomic force microscopes consist of a piezoelectric scanner, a cantilever, an optical head and a base. The piezoelectric scanner controls the motion of the sample. The cantilever has a sharp tip and a soft spring. The sample is moved under the tip and features on the sample cause the cantilever to deflect. An optical system is used to determine the position of the tip relative to the sample; the beam of a laser is reflected off the back of the cantilever and detected by a photodiode. The differential signal of the photodiode provides a sensitive measure of the cantilever's deflection.

AFM studies of the thin polymer films of H-DSB-block-SEO and F-DSB-block-SEO as used in the corresponding single-layer devices showed a flat surface; no morphology is expected for a homogeneous polymer. In the case of blends of F-DSB-block-SEO and PFB the AFM studies revealed that phase segregation had occurred (Figure 4.6.1). Phase segregation can be beneficial in LEDs when it is controlled in a way which results in the electron-conducting polymer being in contact with the cathode and the hole-conducting polymer being in contact with the anode so that the current cannot pass through just one of the polymers. However, little control is gained in the case of blends of F-DSB-block-SEO and PFB. The aim of aiding hole-injection into the polymer and therefore improving the device properties was not achieved.

![AFM study of a blend of F-DSB-block-SEO (60 wt.%) and PFB (40 wt.%).](image)

Figure 4.6.1 AFM study of a blend of F-DSB-block-SEO (60 wt.%) and PFB (40 wt.%).
In the case of LECs the AFM studies revealed demixing of H-DSB-block-SEO and LiTf (Figure 4.6.2). Holes with a diameter between 0.1 and 0.5 μm are found in the polymer layer and are probably due to the fact that LiTf particles deposit on the ITO substrate and prevent the polymer from covering these spots. The LiTf content of 10 wt.% corresponds to 2.5 sexi(ethylene oxide) units per LiTf ion pair. This ratio is probably too high to allow all LiTf ions to be fully complexed and demixing occurs. Further investigations should therefore include the reduction of the LiTf content.

![AFM study of a 100 nm thick film of H-DSB-block-SEO-LiTf complex](image)

**Figure 4.6.2 AFM study of a 100 nm thick film of H-DSB-block-SEO-LiTf complex**

### 4.7 Conclusions

The energy levels of the HOMO and LUMO of H-DSB-block-SEO and F-DSB-block-SEO were determined by cyclic voltammetry, UPS and UV-absorption spectra. The IP and EA of H-DSB-block-SEO are 5.4 eV and 2.4 eV, respectively, and the IP and EA of F-DSB-block-SEO are 6.25 eV and 3.25 eV, respectively. The substitution of aromatic hydrogens by fluorines in the block copolymer did not change the size of the optical band gap (3.0 eV). However, this substitution increased the electron affinity and the ionisation potential by 0.85 eV.

The shape of the solid-state absorption spectrum of F-DSB-block-SEO indicates the presence of H-aggregates. The maximum of this spectrum is also strongly blue-shifted relative to the solution-state spectrum. Large Stokes' shifts between the solid state absorption and emission maxima are observed for both polymers.

H-DSB-block-SEO showed a high photoluminescence quantum efficiency (34%) and single-layer LEDs with aluminium as cathode exhibited luminescences
over 2000 cd/m². The luminescence efficiency was as high as 0.5 cd/A, corresponding to an internal quantum efficiency of 1.1%. The onset of luminescence was at 6.5 V. The polymer emitted in the yellow-green region of the visible spectrum. LEDs using calcium as the cathode showed very similar properties. A light emitting cell based on H-DSB-block-SEO complexed with lithium triflate showed a reduced threshold for luminescence (3.8 V).

A large barrier was found for the hole-injection from ITO to F-DSB-block-SEO. Although the hole-injection could be improved by adding a PEDOT:PSS layer, the fluoro-polymer generally showed very poor characteristics as an emissive layer in LEDs. However, the polymer proved to be a good electron-carrier due to its high electron affinity.

### 4.8 Experimental

#### Photoelectron Spectroscopy

In the case of XPS the photoelectrons were generated with Al (Ka) irradiation (1486 eV) and detected using a Scienta ESCA 200 hemispherical analyser (Gammadata-Scienta, Sweden). For UPS a He discharge lamp and monochromator (He II radiation, 40.8 eV) were used. The spectrometer for UPS was designed and constructed in Linköping, Sweden.

#### UV/Vis Spectroscopy

Solution state UV/Vis spectra of H-DSB-block-SEO and F-DSB-block-SEO were recorded in chloroform using a Unicam UV/Vis spectrometer UV2. Spectrosil substrates were used for solid state absorption experiments. Thin films of the polymer were prepared on these substrates by spin-coating (60 s, 2000 rpm) from a chloroform solution (approximately 2 wt.%, filtered through a Millipore membrane with a pore size of 1 μm). The solid state spectra were recorded using a Lambda 9 Perkin-Elmer double beam spectrometer.

#### Photoluminescence Spectroscopy

Samples were prepared on Spectrosil substrates as described under UV-Vis spectroscopy. The PL efficiency were determined in an integrating sphere, purged with nitrogen to avoid photo-oxidation using a He-Cd laser (325 nm).
**Light emitting diodes**

Thin films of polymer were prepared by spin-coating (60 s, 2000 rpm) from chloroform solution (approximately 2 wt.%, filtered through a Millipore membrane with a pore size of 1 μm). Film thicknesses were determined with a Dektak IIa stylus profiler and concentrations adjusted so that 90-100 nm thick films were obtained. Commercially available ITO-coated glass substrates (Asahi) were used for the fabrication of LEDs. The ITO was patterned so that the metal electrodes on top of the polymer films could be contacted on the edge of the substrate without shorting (*Figure 4.8.1*). The ITO substrates were cleaned in an ultrasonic bath with acetone and 2-propanol, each for 15 min and then treated for 10 min with oxygen plasma at approximately 300 W. For double-layer LEDs with PEDOT:PSS (Bayer AG), the commercially available PEDOT:PSS was spun-cast from an aqueous suspension. It was dried and cross-linked by thermal treatment for 1 h at 100 °C under nitrogen.\(^{31}\) A thin calcium or aluminium layer was subsequently deposited over the substrate through a shadow mask at a pressure below 10\(^{-7}\) mbar. The pixel size was determined by the overlap of the ITO and the cathode patterns yielding an area of about 2 x 10\(^{-2}\) cm\(^2\). The calcium layer was covered with an aluminium layer in the same way in order to protect the anode from oxidation and improve the mechanical integrity of the device for the measurements. All processing of LEDs was carried out in a glove box under a nitrogen atmosphere with less than 20 ppm residual water vapour and 5 ppm oxygen.

Measurements were carried out in a sample holder specially designed to allow the transfer of the sample from the glove box to the measuring station without exposure to air. The luminous output was measured with a calibrated silicon photodiode, and the EL efficiency calculated by taking into account the refraction and reflection at the interfaces. Spectral characterisation was performed by means of an Oriel CCD-matrix spectrograph, with a spectral resolution better than 5 nm.
**Atomic force microscopy**

AFM investigations were carried out with a Nanoscope IIIa Dimension 3100 (Digital Instruments Inc., Santa Barbara).

### 4.9 References


5 Molecular Organisation in Fluorinated Oligo(phenylene vinylene)s

5.1 Introduction

This chapter deals with the molecular organisation of two fluorinated oligo(phenylene vinylene)s. The understanding of the molecular organisation in small molecules provides useful information about these specific compounds as well as guidelines, which may be relevant to related structures such as polymers. The structures of aggregates of organic materials have profound effects on their optical properties; this has been shown in the case of sexithiophene, for instance, where different morphologies give rise to different fluorescence spectra.\(^1\)

Oligo(phenylene vinylenes)s have been studied as model compounds for PPV. Hadziioannou \textit{et al.} have prepared 1,4-bis(p-styrylstyryl)benzene, studied the crystal structure and measured optoelectronic properties (\textit{Figure 5.1.1}).\(^2\) Like PPV this model compound crystallises in a herringbone structure. The absorption maximum and the absorption edge of the model compound are 0.2 eV blue-shifted relative to PPV indicating that the effective conjugation length of PPV exceeds that of the model. The authors were able to prepare LEDs based on the model compound but the turn-on voltage for such devices was high (18 V).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{5.1.png}
\caption{1,4-Bis(p-styrylstyryl)benzene, a model compound for PPV.}
\end{figure}

Fluorinated aromatics show strong interaction with non-fluorinated aromatics. This was first discovered by Patrick and Prosser in 1960,\(^3\) who demonstrated that benzene (mp 5.5 °C) and hexafluorobenzene (mp 4 °C) form a stable 1:1 complex (mp 24 °C), consisting of a face-to-face stack of alternating benzene and hexafluorobenzene molecules. The origin of this stable arrangement is thought to lie in the quadrupolar interaction between the two molecules;\(^4\) both molecules have large molecular quadrupole moments but of opposite sign. \textit{Figure 5.1.2} shows
schematic representations of the quadrupole moments of benzene (a) and hexafluorobenzene (b). While benzene has a high electron density in the centre and a low electron density on the outside, the situation is exactly opposite in the case of hexafluorobenzene. The face-to-face stacking of alternating benzene and hexafluorobenzene rings in a 1:1 mixture of the two compounds is shown in Figure 5.1.2 (d). Recent work suggests that van der Walls interactions also play an important role in this interaction. Benzene and hexafluorobenzene on their own crystallise in a herringbone structure, where one molecule is orientated perpendicular to its neighbour, shown for benzene in Figure 5.1.2 c.

Grubbs et al. have studied the aggregation of fluorinated stilbenes and DSBs. They found that 2,3,4,5,6-pentafluorostilbene (PFS) crystallises in stacks with an alternating orientation of the molecules. Figure 5.1.3 (left) shows two molecules in such a stack. Each phenyl ring is sandwiched between two pentafluorophenyl rings and vice versa. Photodimerisation occurs when the crystals are irradiated with UV light. The authors obtained X-ray crystal structures for PFS and the cyclobutane adduct. The PFS molecules are paired in the stack in the sense that one molecule is slightly closer to its neighbour above than the one below. The distances between the double bonds are 3.700 Å and 3.707 Å. The authors suggest that this pairing leads to 100% conversion in the [2+2] photodimerisation. In general, solid-state photodimerisations give less than 100% yield because some olefins are isolated between cyclobutane molecules in the crystal matrix.
Grubbs et al. also investigated the molecular packing of 1,4-distyryl-2,3,5,6-tetrafluorobenzene (Figure 5.1.4). The molecule crystallises in stacks in which each tetrafluorobenzene ring is sandwiched between two phenyl rings. However, the phenyl rings can only \( \pi \)-stack on one side since the molecule contains two phenyl rings for each fluorinated benzene ring. The photodimerisation leads to a polymer since each molecule contributes to the formation of two cyclobutane rings. The authors obtained a X-ray crystal structure of 1,4-distyryl-2,3,5,6-tetrafluorobenzene. The presence of a polymer was demonstrated by GPC and NMR spectroscopy.
5.2 J aggregates

This project was carried out in collaboration with Prof. Carlo Taliani at the Institute of Molecular Spectroscopy in Bologna. As part of the EU LAMINATE Network we became interested in using the directing effect of phenyl-pentafluorophenyl interactions to prepare J aggregates of large aromatic chromophores suitable for optoelectronic applications. J aggregates are characterised by a narrow and intense absorption band that shows a bathochromic shift relative to the single isolated molecule. They were first described by Jelly who observed a strong absorption for the case of cyanine dyes. A possible arrangement for J aggregates is the simple 'brickwall' motif, in which each brick or molecule is situated over the gap between the bricks in the row below (Figure 5.2.1).

The red shift in absorption can be understood using a simple model. The underlying principles are explained for the case of stilbene, a simple conjugated rod-like molecule. The absorption of a photon by an isolated stilbene molecule is shown on the left-hand side of Figure 5.2.2. The ground state of stilbene has no dipole moment. The absorption of a photon requires a change in the dipole moment of the molecule and the excited state can be represented by a structure, which has a negative charge on one side and a positive charge on the other side of the molecule. In Figure 5.2.2 this excited state is also represented by a simple rod with a positive and a negative sign on opposite sides. The absorption in the case of a J aggregate is shown on the right-hand side of Figure 5.2.2. For the case of two molecules in a 'brickwall' motif two excited states are possible. In one case the dipole moments point in the same direction resulting in an attractive interaction between the negative charge on one molecule with the positive charge on the other. Due to this attractive interaction the excited state is lower in energy than the excited state of the isolated molecule. If the dipole moments of the two molecules point in opposite directions the excited state is higher in energy since two equal charges are in proximity. Furthermore, the net dipole moment of these two excited states is zero so that the transition to this state is in fact forbidden.
This simple model shows why J aggregation leads to a red shift in absorption. This so-called excitonic coupling leads to narrow and intense absorption and fluorescence bands.

Figure 5.2.2 Energy diagrams for the absorption in isolated stilbene molecules (left) and stilbene molecules in J aggregates (right).

5.3 Results and discussion

4,4'-Bis(2,3,4,5,6-pentafluorostyryl)stilbene

Our first target molecule was an oligo(phenylene vinylene) which forms a J aggregate on the basis of phenyl-perfluorophenyl-interactions. An oligo(phenylene vinylene) containing four benzene rings was chosen in which the two terminal benzene rings were fully fluorinated. The synthesis started from p-tolylaldehyde 40 which was coupled in a McMurry reaction to give trans-4,4'-dimethylstilbene 41 (Figure 5.3.1). The two methyl groups were mono-brominated with NBS yielding 4,4'-bis(bromomethyl)stilbene 42. Substitution of the bromine with triphenylphosphine gave the bis(phosphonium salt) 43. A Wittig reaction with two equivalents of pentafluorobenzaldehyde gave 4,4'-bis(2,3,4,5,6-pentafluorostyryl) stilbene 44. Compound 44 is a yellow solid and was prepared on a scale of 2.2 g.
Figure 5.3.1 Synthesis of bis(2,3,4,5,6-pentafluorostyryl)stilbene.

The $^1$H NMR spectrum of 44 shows three resonances for olefinic protons in a 1:1:1 intensity ratio; a singlet at $\delta$ 7.17 and an AB quartet with $\delta_A$ 7.00, $\delta_B$ 7.43 and a coupling constant of 16.5 Hz typical for a trans-vinylene configuration. The singlet signal for aromatic protons is observed at $\delta$ 7.57.

Figure 5.3.2 $^1$H NMR spectrum of bis(2,3,4,5,6-pentafluorostyryl)stilbene.

Crystals of 44 suitable for X-ray structure analysis were obtained both by sublimation in a thermal gradient oven and from a solution in trans-stilbene. The latter technique was described by Hadziioannou et al. to prepare crystals of 1,4-bis(p-styrylstyryl)benzene (Figure 5.1.1); in this method trans-stilbene (mp 125 °C) is used as a high boiling solvent. The crystallisation occurs between 270 and 170 °C.
and the trans-stilbene is removed at 170 °C by filtration. Both techniques lead to identical crystals indicating one predominant form of aggregation. The crystal structure shows that all double bonds have a trans-configuration, confirming the $^1$H NMR analysis (Figure 5.3.3). The centre of each molecule is an inversion centre so that only half the molecule is crystallographically unique. The planes of the fluorinated and the non-fluorinated rings are twisted very slightly relative to each other (2.2°) and the two central rings are twisted with an angle of 3°. This almost planar arrangement allows strong π-π interactions.

![Figure 5.3.3 Crystal structure of 44 – top view.](image)

The molecules aggregate in a simple ‘brickwall’ motif in which each molecule overlaps with two halves of neighbouring molecules in the row below and above it. Thereby, each central aromatic ring is sandwiched between two terminal fluorinated aromatic rings of neighbouring molecules and vice versa. The distance between the mean planes of all the atoms in the molecules is 3.41 Å. However, the situation is further complicated by the fact that there is some lateral slippage between the aromatic rings which results in successive rows of the ‘brickwall’ being slightly offset with respect to each other; analogous structures have been reported and described as ‘molecular staircases’. This slippage is not equally distributed between all aromatic rings but the molecules are paired in the sense that one ring overlaps more with its fluorinated counterpart above than the one below or vice versa. As a consequence of this the two olefinic carbons of the central molecule in Figure 5.3.3 and Figure 5.3.4 are closer to their counterparts below (3.659 Å) than to the one above (3.869 Å).
The unit cell of 44 is shown in Figure 5.3.5. Each unit cell contains one molecule (Z=1).

In addition to the face-to-face $\pi$-stacking the molecular packing is associated with intermolecular C-F···H-C interactions. Four such interactions are observed on each ring resulting in 16 per molecule. The H···F distances determined in this X-ray study are 2.390, 2.467, 2.480 and 2.595 Å, derived using the neutron normalised C-H distance of 1.083 Å. The corresponding C-H···F angles are 159.4°, 157.4°, 132.1° and 122.9°. The distance between the terminal fluorine atoms in the 4-positions of edge-to-edge neighbours is short (2.676 Å).

The packing of compound 44 is similar to that of 2,3,4,5,6-pentafluorostilbene (PFS) (see section 5.1). The densities of both compounds are very similar (1.635 g cm$^{-3}$ for 44, 1.641 g cm$^{-3}$ for PFS). Molecules of PFS in the crystal are also paired but the pairing is less obvious than in the case of compound 44. Because of these similarities we expected photochemically induced [2+2] reactions for the double bonds in the crystal. UV irradiation of a thin film of 44 resulted in a colour change from yellow to almost colourless consistent with the loss of conjugation. $^1$H NMR
spectroscopy of the product shows a new signal at δ 4.88 for cyclobutane hydrogens and the $^{19}$F NMR spectrum shows three new resonances at δ -142.11, -156.11 and -162.98 with concomitant reduction in the intensity of the initial signals at δ -143.81, -157.47 and -163.75. These findings indicate that a photochemically induced [2+2] reaction occurs in the solid state of compound 44. Figure 5.3.6 shows the photochemical [2+2] reaction of two molecules of 44. In a crystal with many millions of unit cells this reaction would lead to polymers similar to the case of 1,4-distyryl-2,3,5,6-tetrafluorobenzene.

![Figure 5.3.6 Photochemically induced [2+2] reaction in the solid state of 44.](image)

The electronic and optical properties of compound 44 are currently under investigation in the Institute of Molecular Spectroscopy in Bologna.

1,4-Bis(2,3,4,5,6-pentafluorostyryl)-2,3,5,6-tetrafluorobenzene

Our second target molecule was a DSB derivative in which all aromatic positions are substituted with fluorine. Fluorinated DSBs have been studied as model compounds for fluorinated conjugated polymers. Bazan et al. have prepared a series of DSB derivatives via the Wittig and Heck reactions. 1,4-Bis(pentafluorostyryl)-2,5-difluorobenzene was the DSB derivative containing the most fluorine atoms prepared in this study (Figure 5.3.7).
Figure 5.3.7 Synthesis of 1,4-bis(pentafluorostyryl)-2,5-difluorobenzene via the Heck reaction.

Oligo(p-tetrafluorophenylene vinylene)s have been prepared previously by Brooke et al. in a reaction of pentafluorostryryl lithium with hexafluorobenzene (Figure 5.3.8). A series of oligomers was prepared in this reaction (n = 1-6). 1,4-Bis(2,3,4,5,6-pentafluorostyryl)-2,3,5,6-tetrafluorobenzene (n = 2) was one of the products and was characterised by NMR and mass spectroscopy. However, because of the low yield (12 mg) this route was not attractive for a further investigation into this DSB derivative.

Figure 5.3.8 Synthesis of oligo(p-tetrafluorophenylene vinylene)s.

The Wittig reaction of 2,3,5,6-tetrafluoroxylencylen-1,4-bis(triphenylphosphonium bromide) 32 with pentafluorobenzaldehyde 4 was examined as a more selective route to 1,4-bis(2,3,4,5,6-pentafluorostyryl)-2,3,5,6-tetrafluorobenzene 45. However, the reaction was unsuccessful and no DSB derivative was obtained.

Figure 5.3.9 Attempted Wittig reaction of compound 4 and 32.

The synthesis of tetrafluoroterephtalaldehyde 18 (as described in chapter 2) opened an alternative route to compound 45 (Figure 5.3.10). While the previous reaction required the formation of two ylides on the central benzene ring, in this approach the ylides are formed on the terminal rings. 2,3,4,5,6-(pentafluorobenzyl)triphenylphosphonium bromide 46 could be prepared by the reaction of pentafluorobenzylbromide and triphenylphosphine. The Wittig reaction
between 46 and 18 gave 1,4-bis(2,3,4,5,6-pentafluorostyryl)-2,3,5,6-tetrafluorobenzene 45 in acceptable yield (57%).

\[
\begin{align*}
&\begin{array}{c}
\begin{array}{c}
\text{Figure 5.3.10 Synthesis of 1,4-bis(2,3,4,5,6-pentafluorostyryl)-2,3,5,6-tetrafluorobenzene.}
\end{array}
\end{array}
\end{align*}
\]

The NMR spectra (\(^1\)H, \(^{19}\)F) of compound 45 show that all double bounds have trans-configuration. The UV absorption spectrum of 45 in chloroform shows a maximum at 342 nm. This is slightly blue shifted with respect to the absorption maximum of DSB itself (350 nm). Such a small shift is in good agreement with results reported by Bazan et al.\(^9\) These authors found that the absorption maxima of DSB derivatives with a varying number of fluorine substituents all show very similar absorption maxima with shifts smaller than 10 nm.

Attempts were made to prepare 1:1 cocrystals of compound 45 and DSB. Yellow crystals could be obtained from an equimolar solution of the two compounds, but the crystals were unsuitable for X-ray structure analysis and only a few oval shaped reflections were observed.

However, the solubilities of compound 45 and DSB show that aggregation is occurring. The solubilities of 45 and DSB in toluene are 6.8 x 10\(^{-3}\) mol l\(^{-1}\) and 3.2 x 10\(^{-3}\) mol l\(^{-1}\), respectively. When both are mixed in a molar ratio of 1:1 the solubility decreases to 0.28 x 10\(^{-3}\) mol l\(^{-1}\) (with respect to each component).

A possible structure for the stacking of the two compounds is shown in Figure 5.3.11 in which DSB and the fluorinated derivative alternate. No charge transfer band was observed.
5.4 Conclusions

A self-assembling J aggregate based on aryl-fluoroaryl interactions was synthesised. The molecule contains two terminal fluorinated benzene rings and two central non-fluorinated benzene rings, all connected by vinylene bridges. The X-ray crystal structure shows the packing of the molecules in a 'brickwall' motif and 16 H···F interactions per molecule. A photochemically induced [2+2] reaction in the solid state was demonstrated.

An efficient synthetic route to the fluorinated DSB derivative 1,4-bis(2,3,4,5,6-pentafluorostyryl)-2,3,5,6-tetrafluorobenzene has been demonstrated. An equimolar mixture of this fluorinated derivative and DSB itself shows evidence for aggregation.

5.5 Experimental

5.5.1 4,4'-Dimethylstilbene (41)

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{ vinylene } \\
& \quad \text{ vinylene } \\
& \quad \text{CH}_3
\end{align*}
\]

TiCl₄ (16.6 g, 9.6 ml, 87.4 mmol) was added to a suspension of Zn (11.4 g, 175 mmol) in THF (400 ml) at 0 °C under nitrogen. The mixture was refluxed for 1 h and cooled to room temperature. \(p\)-Tolualdehyde (7.1 g, 59 mmol) was then added and the mixture refluxed for 14 h. The mixture was quenched by addition of aqueous hydrochloric acid (40 ml, 2 N) and the THF was removed under reduced pressure. The product was redissolved in diethyl ether (300 ml), washed three times with water (200 ml) and dried (MgSO₄) yielding, after evaporation of the solvent, 4,4'-dimethylstilbene (5.9 g, 96%) as a white solid. As the melting point and the \(^1\)H NMR spectrum were in good agreement with those reported in the literature\(^{11}\) no further analysis was carried out, mp 181 °C (lit.\(^{11,12}\) 180-182 °C). \(^1\)H NMR (CDCl₃,
200 MHz) δ 7.42 (m, 4H, ar. C-H), 7.18 (m, 4H, ar. C-H), 7.07 (s, 2H, CH=CH), 2.39 (s, 6H, CH₃).

5.5.2 4,4'-Bis(bromomethyl)stilbene (42)

\[
\text{Br} \quad \text{Br}
\]

4,4'-Dimethylstilbene (6.0g, 28.8 mmol) and N-bromosuccinimide (15.0 g, 84 mmol) were dissolved in chloroform (600 ml). AIBN (0.06 g, 0.36 mmol) was added and the mixture refluxed. Two further additions of AIBN (0.06 g, 0.36 mmol) were made after 2 h and 4 h, respectively. After a total of 8 h of reflux the mixture was washed five times with water (200 ml) and dried (MgSO₄). The solution was concentrated to 90 ml, warmed to 65 °C and then cooled slowly to room temperature to allow crystallisation. The white crystals were recovered by filtration and the product was recrystallised once more from a hexane/toluene mixture (1:1) yielding 4,4'-bis(bromomethyl)stilbene (3.1 g, 30%) as white crystals. As the melting point and the ¹H NMR spectrum were in agreement with those reported in the literature, no further analysis was carried out. mp 187 °C (lit. 14,15 188-193 °C). ¹H NMR (CDCl₃, 200 MHz) δ 7.50 (m, 4H, ar. C-H), 7.39 (m, 4H, ar. C-H), 7.11 (s, 2H, CH=CH), 4.53 (s, 4H, CH₂Br).

5.5.3 4,4'-bis(methyltriphenylphosphonium bromide)stilbene (43)

\[
\text{Ph₃P}^\text{+} \quad \text{Br}^- \quad \text{Br}^- \quad \text{Ph₃P}^\text{+}
\]

4,4'-Bis(bromomethyl)stilbene (3.1 g, 8.47 mmol) and triphenylphosphine (5.04 g, 19.2 mmol) were dissolved in DMF (35 ml) and the resulting mixture was refluxed for 4 h. The mixture was cooled to room temperature. The white precipitate was collected by filtration and washed with toluene (50 ml) and diethyl ether (50 ml) yielding 4,4'-bis(methyltriphenylphosphonium bromide)stilbene (6.64g, 88%) as a white solid. The product was used in the next step without further purification.
5.5.4 4,4'-bis(2,3,4,5,6-pentafluorostyryl)stilbene (44)

A mixture of LiCl (0.9 g) and 4,4'-bis(methyltriphenylphosphonium bromide)stilbene (6.6 g, 7.41 mmol) was dissolved in DMF (57 ml). KOtBu (14.8 ml, 14.8 mmol) was added and the mixture stirred for 2 h. Pentafluorobenzaldehyde (3.5 g, 17.8 mmol) was added and the mixture stirred at room temperature for 6 h. The reaction was quenched by addition of water (10 ml) and a yellow powder collected by filtration. The product was washed with diethyl ether (20 ml) and dried under vacuum yielding 4,4'-bis(2,3,4,5,6-pentafluorostyryl)stilbene (2.24 g, 54%) as a yellow solid. Found C: 63.68%; H, 2.46%; M(MS, EI) 564 (M⁺). Calculated for C₃₀H₁₄F₁₀: C, 63.84% H, 2.50%; M 564. ¹H NMR (TCE-d₂, 300 MHz) δ 7.57 (s, 8H, ar. C-H), 7.43 (d, J = 16.5 Hz, 2H, CH=CH), 7.17 (s, 2H, CH=CH), 7.00 (d, J = 16.5 Hz, 2H, CH=CH); ¹⁹F NMR (C₇D₈, 188 MHz) δ -163.75 (m, 4F), -157.47 (t, J = 21 Hz, 2F), -143.81 (m, 4F) (see appendix page 155).

Crystal-preparation from solution in stilbene

A U-shaped glass tub was prepared with a pore-3-sinter in the middle (Figure 5.5.1). 4,4'-bis(2,3,4,5,6-pentafluorostyryl)stilbene (80 mg) was thoroughly mixed with stilbene (800 mg) and placed in one side of the glass-tube. The glass-tube was placed in a high temperature oil-bath and heated to 260 °C for 10 min. The oil-bath was then cooled at a rate of 0.5 °C per minute to 170 °C and kept at 170 °C for 10 h. A small pressure of nitrogen gas was applied to the side of the glass-tube containing the mixture so that the melt was forced through the filter. The remaining crystals of 4,4'-bis(2,3,4,5,6-pentafluorostyryl)stilbene were washed out of the tube with diethyl ether and washed three times with diethyl ether. These crystals were suitable for X-ray crystal structure analysis.
**Crystal-preparation by sublimation**

4,4'-bis(2,3,4,5,6-pentafluorostyryl)stilbene (300 mg) was placed in a Carius-tube and evacuated overnight. The tube was sealed and placed in a thermal gradient oven with a maximum temperature between 180 – 210 °C. After 7 days the tube was cooled to room temperature and opened carefully. Small crystals of 4,4'-bis(2,3,4,5,6-pentafluorostyryl)stilbene were obtained. The crystals were suitable for X-ray crystal structure analysis.

**Crystallographic data for 4,4'-bis(2,3,4,5,6-pentafluorostyryl)stilbene**

$M_r = 564$, space group $P1$, $a = 6.0624$, $b = 7.4468$, $c = 13.0565$, $\beta = 82.972$, $\gamma = 85.693^\circ$, $U = 572.378 \text{ Å}^3$, $T = 100 \text{ K}$, $Z = 1$, $\mu$ (Mo-Kα) = 0.152 mm$^{-1}$, 2604 reflections measured, 2604 unique ($R_{int} = 0.0797$) which were used in all calculations and 1486 greater than $2\sigma(I)$ The final $R(F)$ was 0.0853 ($I>2\sigma(I)$ data) and the $wR(F^2)$ was 0.1885 (all data). The relatively large $R$ factor is due to the small crystals available, 0.20 x 0.10 x 0.05 mm$^3$. See http://www.rsc.org/suppdatalcc/lb100002k/ for crystallographic files in .cif formats.

**[2+2] reaction of 4,4'-bis(2,3,4,5,6-pentafluorostyryl)stilbene**

A thin film of 4,4'-bis(2,3,4,5,6-pentafluorostyryl)stilbene in a quartz-tube was irradiated with a UV-lamp. The colour changed from yellow to white. $^{19}$F NMR (C$_7$D$_8$, 188 MHz) $\delta$ -142.11, -143.81, -156.11, -157.47, -162.98, -163.75 (see appendix page 156).

**5.5.5 1,4-Distyrlybenzene**

\[ \text{p-Xylylene-bis(triphenylphosphonium bromide) (21.0g, 26.6 mmol) and benzaldehyde (6.2 g, 58 mmol) were dissolved in dry ethanol (400 ml). Lithium ethoxide (1M, 54 ml, 54 mmol) was added and the mixture was stirred at room temperature for 4 h. Water (200 ml) was added and the product collected by filtration. The product was recrystallised from toluene (250 ml) in the presence of a trace of iodine yielding 1,4-distyrlybenzene (6.0 g, 80%) as colourless crystals. As the melting point and the }^{1}H \text{ NMR spectrum were in agreement with those reported} \]
in the literature\textsuperscript{9,16} no further analysis was carried out, mp 263 °C (lit.\textsuperscript{16} 268 °C) \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 200 MHz) \( \delta \) 7.55 (m, 8H), 7.35 (m, 6H), 7.14 (s, 4H).

\subsection*{5.5.6 \textit{(2,3,4,5,6-Pentafluorobenzyl)triphenylphosphonium bromide (46)}}

\begin{center}
\begin{tikzpicture}
\end{tikzpicture}
\end{center}

Triphenylphosphine (2.02 g, 7.7 mmol) and pentafluorobenzylbromide (2.0 g, 7.7 mmol) were dissolved in dry toluene (50 ml) and heated for 1.5 h. The mixture was allowed to cool and a white solid collected by filtration. The product was washed twice with toluene (5 ml) and dried under vacuum yielding \textit{(2,3,4,5,6-pentafluorobenzyl)triphenylphosphonium bromide (3.45 g, 85\%)} as a white solid. As the elemental analysis and the \textsuperscript{19}F NMR spectrum were in agreement with those reported in the literature\textsuperscript{17} no further analysis was carried out. Found C 57.37\%, H 3.21\% C\textsubscript{25}H\textsubscript{17}BrF\textsubscript{5}P requires C 57.38\%, H 3.27\%. \textsuperscript{19}F NMR (CDCl\textsubscript{3}, 188 MHz) \( \delta \) -136.41 (m, 2F), -151.14 (m, 1F), -160.10 (m, 2F).

\subsection*{5.5.7 \textit{1,4-Bis(2,3,4,5,6-pentafluorostyryl)-2,3,5,6-tetrafluorobenzene (45)}}

\begin{center}
\begin{tikzpicture}
\end{tikzpicture}
\end{center}

\textit{(2,3,4,5,6-Pentafluorobenzyl)triphenylphosphonium bromide (1.2 g, 2.3 mmol)} and LiCl (0.2 g) were dissolved in DMF (10 ml). KO\textsubscript{tBu} (1 M, 2.3 ml, 2.3 mmol) was added. After stirring for 3.5 h tetrafluoroterephthalaldehyde (0.24 g, 1.15 mmol) was added. The mixture was stirred for further 15 h at room temperature and quenched by addition of aqueous hydrochloric acid (2 M, 2 ml). All solvents were removed under reduced pressure and the product redissolved in chloroform (200 ml). The mixture was washed with aqueous hydrochloric acid (2 M, 100 ml) and the aqueous layer extracted with chloroform (100 ml). The combined organic fractions were washed three times with water (100 ml) and dried (MgSO\textsubscript{4}). The MgSO\textsubscript{4} was rinsed with toluene (30 ml). The solvents were removed under reduced pressure. The
product was purified by column chromatography (silica gel, toluene: hexane 1:20) yielding \(1,4\text{-bis(2,3,4,5,6-pentafluorostyryl)-2,3,5,6-tetrafluorobenzene}\) (0.35 g, 57%) as a light yellow powder. Column chromatography with hexane only (a large amount of solvent (2 L) was required) gave a white powder, mp 190-192 °C. Found C, 50.28%; H, 1.09%; M(MS, EI) 534 (M+). Calculated for \(\text{C}_{22}\text{H}_{4}\text{F}_{14}\): C, 49.46% H, 0.75%; M 534. \(^1\text{H NMR} (\text{C}_{7}\text{D}_{8}, 300 \text{ MHz}) \delta 7.20 (s, 4\text{H}, \text{CH}=\text{CH}); \) \(^1\text{F NMR} (\text{C}_{7}\text{D}_{8}, 188 \text{ MHz}) \delta -142.95 (\text{m, } 4\text{F}), -143.93 (\text{s, } 4\text{F}), -154.70 (\text{m, } 2\text{F}), 162.96 (\text{m, } 4\text{F})\) (see appendix page 157).

5.6 References

6 Overall Conclusions and Proposal for Future Work

6.1 Conclusions

Several synthetic routes to fluorinated conjugated polymers were investigated. The McMurry reaction was found unsuitable for this aim since it led to side reactions and defects in the case of fluorinated aromatic aldehydes and ketones. The Horner Wittig reaction was used successfully to prepare a fluorinated block copolymer, which consisted of alternating oligo(ethylene oxide) units and fluorinated distyrylbenzene units. The polymer was fractionated and the high molecular weight fraction showed a degree of polymerisation of 17. All double bonds in the conjugated unit had a trans-configuration. To our knowledge this is the first example of a poly(p-phenylene vinylene) derivative in which all four available aromatic positions are substituted with fluorine atoms.

In order to study the influence of fluorine substituents on conjugated polymers the non-fluorinated equivalent was synthesised. The Wittig reaction was used as polycondensation method. 50% of the double bonds in the distyrylbenzene unit had a cis-configuration and 50% had a trans-configuration. The degree of polymerisation was 10. Both polymers were soluble in chloroform and free-standing films could be cast from solution.

The electron affinity and the ionisation potential in both polymers were determined by a combination of cyclic voltammetry, UV photoelectron spectroscopy and UV-absorption spectroscopy. The substitution of hydrogen by fluorine in the block copolymer increased the electron affinity and the ionisation potential by 0.85 eV. However, the optical band-gap was the same in both polymers (3.0 eV). The photoluminescence quantum efficiency of the fluorinated and the non-fluorinated block copolymers were 17% and 34%, respectively.

Light emitting diodes based on both devices were prepared. Indium tin oxide was used as the anode in these devices and aluminium or calcium was used as the cathode. The fluorinated block copolymer showed very poor characteristics as emissive layer in light emitting devices. However, the polymer proved to be a good electron-carrier due to its high electron affinity.
Single layer LEDs based on the non-fluorinated block copolymer exhibited luminances over 2000 cd/m². The luminescence efficiency was as high as 0.5 cd/A, corresponding to an internal quantum efficiency of 1.1%. The onset of luminescence was at 6.5 V. The polymer emitted in the yellow-green region of the visible light. A light emitting cell based on a complex of this polymer with lithium triflate showed a reduced threshold for luminescence.

In a further project a self-assembling J aggregate based on aryl-fluoroaryl interactions was synthesised. The molecule contained two terminal fluorinated benzene rings and two central non-fluorinated benzene rings, all connected by vinylene bridges. This oligo(p-phenylene vinylene) aggregated in a ‘brickwall’ motif as shown by X-ray crystal structure analysis. 16 H···F interactions per molecule were observed in the crystal structure. A photochemically induced [2+2] reaction in the solid state was demonstrated.

6.2 Future Work

Several aspects of this work deserve further investigation. The preparation of non-fluorinated block copolymers with varying content of cis- and trans-double bonds is desirable in order to investigate the effect of the conformation on the optical and electronic properties. The effect of such conformational changes on the photoluminescence and electroluminescence efficiency is of particular interest. Such polymers could be prepared by isomerisation of the described block copolymer or by new synthetic routes (e.g. Heck reaction).

Some further work on light emitting cells is required in order to increase the stability of the devices. Since demixing of the polymer and lithium triflate occurred under the concentration used, whether or not lower concentrations of lithium triflate lead to increased stability and a further decrease in turn-on voltage should be examined.

The organisation in the fluorinated block copolymers should be further investigated. X-ray diffraction might show the degree of crystallinity in the polymer.

Finally, the optical properties of the oligo(p-phenylene vinylene) derivative with two fluorinated terminal aromatic ring need to be investigated. A thin film of the
material needs to be prepared in which the molecules aggregate in the ‘brickwall’ motif. A narrow and intense absorption and emission is expected for a J aggregate.
Appendix
Determination of the Photoluminescence Quantum Efficiency

The quantum efficiency $\eta$ is the ratio of the number of photons emitted and the number of photons absorbed. Three different experiments are used to determine the photoluminescence. In the first experiment the integrating sphere is empty. In the second experiment the sample is placed in the sphere and the laser beam is aimed at the wall of the sphere. In the third experiment the laser is aimed at the sample. In each experiment the intensity of light at the excitation wavelength is measured ($L_a$, $L_b$, $L_c$). Also, in the second and third experiment the intensities of the emitted light are determined ($P_b$, $P_c$).

When a photon hits the sample it can be absorbed, transmitted, or reflected. The absorption coefficient $A$ is the ratio of the number of photons that are absorbed by the sample to the total number of photons hitting the sample. In the case of experiment three the intensity $L_c$ is decreased relative to the intensity in experiment two $L_b$ due to the absorption by the sample. The absorption coefficient can therefore be calculated in the following way:

$$L_c = L_b (1 - A)$$

And therefore:

$$A = 1 - \frac{L_c}{L_b}$$

The total number of photons that hit the detector in experiment three is given by $P_c + L_c$. Two parts contribute to this: The first part is the number of photons that are emitted from the sample, which is the product of the quantum efficiency, the intensity of the incident beam and the absorption coefficient. $\eta L_a A$. The second part is due to the light that is reflected or transmitted by the sample. This part can be calculated by using the intensities measured in experiment two since the beam is not aimed at the sample in this case

$$(1-A)(L_b + P_b)$$

and therefore:

$$L_c + P_c = (1-A)(L_b + P_b) + \eta L_a A.$$ 

which can be rearranged to:

$$L_c + P_c = L_c + (1-A) P_b + \eta L_a A.$$ 

$$\eta = \frac{[P_c - (1-A) P_b]}{L_a A}$$

---

*de Mello, J.C; Wittman, H. F; Friend, R. H. Advanced Materials 9, 1997, 230*
9-Pentafluorophenyl-10-phenyl-1,2,3,4-tetraphenylpentantrane (2)

$^1$H NMR spectrum

$^{13}$C NMR spectrum ($^1$H decoupled)
9-Pentafluorophenyl-10-phenyl-1,2,3,4-tetraphenylpenanthrene (2) (cont.)

$^{13}$C NMR spectrum ($^{19}$F decoupled)

$^{19}$F NMR spectrum
1,2-Diphenyl-1-pentafluorophenyl-2-(2,3,4,5-tetrafluorophenyl)ethene (mixed with pentafluorobenzophenone)
GC-MS results for reaction 2.4.2 showing 9-pentafluorophenyl-10-phenyl-1,2,3,4-tetraphenylpenanthrene (2) and 1,2-diphenyl-1-pentafluorophenyl-2-(2,3,4,5-tetrafluorophenyl)ethene
1,17-Bis(diethoxy-4-methly-2,3,5,6-tetrafluorophenyloxy) - 3,6,9,12,15-pentaoxaheptadecane (10)

$^1$H NMR spectrum

$^{13}$C NMR spectrum

$^{19}$F NMR spectrum
1,3-Bis(diethoxy-4-methy-2,3,5,6-tetrafluorophenylxy)-2,2-dimethylpropene (11)

$^1$H NMR spectrum

$^13$C NMR spectrum

$^{19}$F NMR spectrum
1,3-Bis(diethoxy-4-methyl-2,3,5,6-tetrafluorophenoxoxy)-2-ethylhexane (12)

$^1H$ NMR spectrum

$^{13}C$ NMR spectrum

$^{19}F$ NMR spectrum
11,17-Bis(4-formyl-2,3,5,6-tetrafluorophenyloxy)
-3,6,9,12,15-pentaoxaheptadecane (13)

$^1$H NMR spectrum

$^{13}$C NMR spectrum

$^{19}$F NMR spectrum
1,3-Bis (4-formyl-2,3,5,6-tetrafluorophenyl)oxy)- 2,2-dimethylpropane (14)

$^1$H NMR spectrum

$^{13}$C NMR spectrum

$^{19}$F NMR spectrum
1,3-Bis(4-formyl-2,3,5,6-tetrafluorophenyloxy)-2-ethylhexane (15)

\(^1\)H NMR spectrum

\(^{13}\)C NMR spectrum

\(^{19}\)F NMR spectrum
2,3,5,6-Tetrafluoroterephthalaldehyde tetra-acetate (17)

\[ 
\text{\textsuperscript{1}H NMR spectrum} 
\]

\[ 
\text{\textsuperscript{13}C NMR spectrum} 
\]

\[ 
\text{\textsuperscript{19}F NMR spectrum} 
\]
2,3,5,6-Tetrafluoroterephtalaldehyde (18)

$^1$H NMR spectrum

$^{13}$C NMR spectrum

$^{19}$F NMR spectrum
1,4-Bis(dibromomethyl)-2,3,5,6-tetrafluorobenzene (19)

$^1$H NMR spectrum

$^{13}$C NMR spectrum

$^{19}$F NMR spectrum
5,6,28,29,30,31,32,33-Octafluoro-8,11,14,17,20,23,26-heptaoxatricyclo[22.2.2.2\textsuperscript{4,7}]tritriaconta-1(30),2,4(33),5,7(32),27(31),25-heptaene (20)

\textsuperscript{1}H NMR spectrum

\textsuperscript{13}C NMR spectrum

\textsuperscript{19}F NMR spectrum
Polymerisation via the McMurry reaction

$^1$H NMR spectrum
1,8-Di-(4-methyl-2,3,5,6-tetrafluorophenyloxy)octane (25)

$^1$H NMR spectrum

$^1$C NMR spectrum

$^{19}$F NMR spectrum
1,8-Di-(4-bromomethyl-2,3,5,6-tetrafluorophenyloxy)octane (26)

$^1$H NMR spectrum

$^{13}$C NMR spectrum

$^{19}$F NMR spectrum
1,8-Bis-(4-triphenylphosphoniummethylen-2,3,5,6-tetrafluoro-phenyloxy) octane dibromide (27)

$^{1}$H NMR spectrum

$^{19}$F NMR spectrum
1,8-(Bis-2,3,4,5,6,2',3',4',5',6' nonafluorostilben-4-yloxy)octane (28)

\[ \text{1H NMR spectrum} \]

\[ \text{13C NMR spectrum} \]

\[ \text{19F NMR spectrum} \]
Poly(bis(2,3,5,6-tetrafluoro-p-phenylenevinylene)-2,3,5,6-tetrafluoro-p-phenylene-1,10-dioxodecane) (29)

$^1$H NMR spectrum

$^{19}$F NMR spectrum
1,17- Bis(4-methyl-2,3,5,6-tetrafluorophenylxyloxy)-3,6,9,12,15-pentaoxaheptadecane (30)

$^1$H NMR spectrum

$^{13}$C NMR spectrum

$^{19}$F NMR spectrum
2,3,4,5-Tetrafluoroxylene-1,4-bis(triphenylphosphonium bromide) (32)

$^1$H NMR spectrum

$^{13}$C NMR spectrum

$^{19}$F NMR spectrum
F-DSB-\textit{block-SEO} (34)

\textsuperscript{1}H NMR spectrum

\textsuperscript{13}C NMR spectrum

\textsuperscript{19}F NMR spectrum
1,17-Bis (4-formylphenyloxy)-3,6,9,12,15-pentaoxaheptadecane (37)

$^1$H NMR spectrum

$^{13}$C NMR spectrum
H-DSB-block-SEO (39)

$^1$H NMR spectrum

$^1$H NMR spectrum

$^1$C NMR spectrum

$^1$H NMR spectrum

$^1$C NMR spectrum
4,4'-bis(2,3,4,5,6-pentafluorostyryl)stilbene (44)

$^1$H NMR spectrum

$^{19}$F NMR spectrum
Photochemical [2+2] reaction of 4,4'-bis(2,3,4,5,6-pentafluorostyryl)stilbene (44)

$^1$H NMR spectrum

$^{19}$F NMR spectrum
1,4-Bis(2,3,4,5,6-pentafluorostyryl)-2,3,5,6-tetrafluorobenzene (45)

$^1$H NMR spectrum

$^{13}$C NMR spectrum
IR spectra of compounds 13 and 30.

The arrows indicate the absorption for fluorinated aromatics.

1,17-Bis(4-methy-2,3,5,6-tetrafluorophenyloxy)-3,6,9,12,15-pentaoxaheptadecane (30)

1,17-Bis(4-formyl-2,3,5,6-tetrafluorophenyloxy)-3,6,9,12,15-pentaoxaheptadecane (13)
Cyclic voltammetry data

This data was recorded at Cambridge Display Technology (CDT). ITO electrodes were coated with the polymers and the oxidation potential of F-DSB-block-SEO (Figure 1 left), H-DSB-block-SEO (Figure 1 right) and ferrocene (Figure 2) were recorded. The potential of ferrocene relative to the vacuum level is 5.3 V.\(^*\) Taking into account solid state effects for the oxidation the IP of the polymers were calculated as:

\[
\begin{align*}
\text{IP (F-DSB-block-SEO)} & = 6.2 \pm 0.1 \text{ eV and} \\
\text{IP (H-DSB-block-SEO)} & = 5.5 \pm 0.1 \text{ eV.}
\end{align*}
\]

Figure 1 Cyclic voltammetry data for F-DSB-block-SEO (left) and F-DSB-block-SEO (right).

Figure 2 Cyclic voltammetry data for ferrocene.

### List of compounds and abbreviations

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<td>29</td>
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List of compounds and abbreviations

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Abbreviations

- AFM: atomic force microscopy
- AIBN: 2,2'-azobis(2-methylpropionitrile)
- DCM: dichloromethane
- DMF: dimethyl formamide
- DSB: 1,4-distyrylbenzene
- DSS: 4,4'-distyrylstilbene
- EA: electron affinity
- EI: electron impact
- EL: electroluminescence
- FT: Fourier transform
- GC: gas chromatography
- GPC: gel permeation chromatography
- HOMO: highest occupied molecular orbital
- IP: ionisation potential
- ITO: indium tin oxide
- LEC: light emitting cell
- LED: light emitting diode
- LUMO: lowest unoccupied molecular orbital
- MS: mass spectroscopy
- NBS: N-bromosuccinimide
- NMR: nuclear magnetic resonance
- PA: polyacetylene
- PDI: polydispersity index
- PEO: poly(ethylene oxide)
- PFS: 2,3,4,5,6-pentafluorostilbene
- PL: photoluminescence
- PPV: poly(p-phenylene vinylene)
- SEO: sexi(ethylene oxide)
- THF: tetrahydrofuran