Insights into the self-assembly of pi-conjugated systems

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Cooperative supramolecular polymerization of π-conjugated systems

Abstract. An overview is presented of cooperative supramolecular polymerizations of π-conjugated systems. After a short description of the thermodynamic aspects of cooperative supramolecular polymerizations, examples of π-conjugated systems are given that assemble according to this mechanism. In the majority of the examples the exact mechanistic details have not been ascertained, however, based on the reported results the assembly of these systems can be categorized as being cooperative in nature. Special attention is given to the influence of different parameters on the supramolecular polymerization process.
1.1 Introduction

During the last century the understanding of synthetic organic chemistry has been developed to such an extent that virtually every molecule encountered in Nature can potentially be synthesized. However, the synthetic availability of these molecules does not necessarily mean that the synthetic and natural occurring molecules will behave in a functionally identical manner. It is the supramolecular arrangement of these molecules that is crucial for obtaining the desired functionality.

An example of a complex supramolecular architecture found in Nature is the photosynthetic unit (Figure 1.1). In this unit, the chlorophyll chromophores, which are π-conjugated molecules, are organized in a specific supramolecular manner to allow the transfer of the absorbed solar energy to the reaction center.¹ A sequence of electron transfer steps yields a charge separated state that is extremely long lived which enables the catalysis of a range of redox reactions finally leading to the production of oxygen and glucose from water and carbon dioxide.¹ Inspired by this photosynthetic reaction, a promising field of applications for supramolecular systems based on π-conjugated systems is photocatalysis. Already numerous examples exist where chromophores can act as photocatalysts for example for degradation reactions ²,³ and for the splitting of water into oxygen and hydrogen.⁴⁶ The combination of self-assembled structures as collectors of solar energy and as a possibility to transport the absorbed energy along the aggregate by careful placement of multiple different chromophores within the assembly could potentially create an object with a function similar to the photosynthetic unit. However, in order to achieve such a degree of control over the position of multiple different chromophores within the same aggregates, an increased knowledge about the subtleties influencing the supramolecular polymerization of π-conjugated molecules is a necessity.

![Figure 1.1. Schematic picture of a photosynthetic unit (right) and the organization of the chromophores in the reaction center (left), where the arrow indicates an energy transfer reaction.¹ ⁷](image)

Besides application as photocatalysts, the semiconducting properties of π-conjugated oligomers allow these systems to be used in electronic applications, like for example solar cells or light emitting diodes.⁷ The use of covalent polymers as the active material in these devices is a rapidly growing area, where the first products have become commercially available.⁷ Recently, the field of supramolecular electronics has been created, where the opto-electronic properties of self-assembled π-conjugated
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For example applications like transistors or light emitting diodes are considered. Furthermore doping of the assemblies can create conductive supramolecular wires. For photovoltaic applications, the careful placement of different chromophores within the self-assembly can create an electron transfer route to transport the photogenerated electrons and holes to their respective electrodes by making a junction between p- and n-type materials.

For supramolecular polymers, the self-assembly of single component systems is a widely studied subject. Supramolecular polymers are built up of monomers that are held together by reversible and highly directional non-covalent interactions, like for example hydrogen bonds and $\pi-\pi$ interactions. The self-assembly of the monomers gives rise to polymeric properties in dilute and concentrated solutions as well as in the bulk. Recently, an attempt has been made to classify the present systems according to their supramolecular polymerization mechanism in analogy to the classification of covalent polymerizations proposed by Carothers in 1931. Three mechanisms can be distinguished being the isodesmic, ring-chain and cooperative supramolecular polymerizations corresponding to step, ring-opening and chain polymerization, respectively. For the isodesmic mechanism each monomer addition has the same equilibrium constant. Numerous examples based on $\pi$-conjugated materials have been shown to assemble via the isodesmic model through temperature- and concentration-dependent measurements. Structures formed via the ring-chain mechanism can yield large macrocycles in equilibrium with linear supramolecular polymers. The isodesmic and ring-chain assembly mechanism are well understood and documented; by contrast the cooperative mechanism is relatively little known and studied at the present time. Since the isodesmic and the ring-chain mechanisms are not encountered for the molecules that will be discussed in the following Chapters of this thesis, they will not be addressed in detail. In the following sections attention is given to the definition of cooperative supramolecular polymerization, the thermodynamic properties of the process as well as examples from literature. The study of thermodynamic properties of synthetic cooperative systems is less developed than in the case of the other two mechanisms. Therefore, for the majority of the reported examples it was attempted to show that these systems are assembled in a cooperative fashion. Due to the large number of examples in the literature, a selection was made to show the large diversity of $\pi$-conjugated molecules that are demonstrated or are suspected to self-assemble according to the cooperative mechanism. In addition, an attempt was made to assign the origin for the observed cooperativity of the examples discussed; also some remarkable specificities of the self-assembled systems will be highlighted.

1.2 Definition of cooperative supramolecular polymerization

In cooperative supramolecular polymerization the growth of the supramolecular polymer occurs in at least two distinct stages. The first step in the formation of the polymer consists of linear isodesmic polymerization with an association constant $K_n$ for the addition of each monomer. The polymerization process continues until a nucleus of degree of polymerization $s$ is formed. Due to various cooperative effects (vide infra), monomer addition after reaching the degree of polymerization $s$, occurs with an association constant $K_\infty$ that is higher than $K_n$. The supramolecular polymerization continues by linear isodesmic polymerization but the association constant is now $K_\infty$ (elongation phase) rather than $K_n$. 

7
Figure 1.2. Schematic energy diagrams of a cooperative supramolecular polymerization. The left diagram displays the uphill cooperative polymerization having an unstable nucleus, in this case a dimer. The right diagram displays the characteristics of a downhill cooperative supramolecular polymerization having a thermodynamically stable nucleus, in this case a tetramer. The abscissa in each subplot represents the size of the oligomer (i) whereas the ordinate measures the free energy $\Delta G^0_i$ (the free energy of forming an i-mer from monomers) in arbitrary units.

For cooperative (nucleated) supramolecular polymerizations a distinction can be made between uphill and downhill nucleated supramolecular polymerizations (Figure 1.2). The difference between these mechanisms lies in the thermodynamic stability of the nucleus. In uphill polymerizations, the Gibbs free energy of the nucleus is higher in energy than the monomer showing its thermodynamic instability (Figure 1.2, left). However, in downhill polymerization the nucleus is lower in Gibbs free energy than the monomer, and thus thermodynamically stable with respect to the monomer (Figure 1.2, right). The position of the nucleus with respect to the monomer depends highly on the chosen reference state and therefore on the concentration. As a result interconversion between the two mechanisms depicted in Figure 1.2 is possible. In the remainder of this Chapter, the discussed systems will be referred to as cooperative, however, the nature of the nucleation as described above is not clear in all cases and thus it will not be addressed in great detail.

Based on current understanding, three different effects are responsible for the cooperative growth of supramolecular systems; electronic effects (both short range polarization and long range electronic effects), structural effects (both helix formation and allosteric effects) and the hydrophobic effect. At the nucleus these effects can create an additional beneficial interaction (vide infra) which results in an increase in the driving force to elongate the polymer by subsequent monomer addition. An attempt is made to classify the examples from the literature with respect to each of these effects, however, as will be discussed, an unambiguous assignment is not possible.
1.3 Thermodynamic aspects of cooperative supramolecular polymerization

In contrast to isodesmic, also referred to as equal-$K$ supramolecular polymerization, the cooperative mechanism is characterized by at least two different association constants in the assembly pathway (Scheme 1.1). As a result, these supramolecular polymerizations are characterized by a critical concentration or temperature at which the supramolecular polymer starts growing.

A large variety of models exist to describe the concentration- and temperature-dependent properties of cooperative polymerizations. In this case the model developed by Van der Schoot is taken as an example to illustrate the characteristics of cooperative supramolecular polymerizations. In thermally activated equilibrium polymerizations, only a small portion of the monomers is active and is able to polymerize. The remaining monomer is in an inactive state and is unable to grow into long supramolecular polymeric species. The active and inactive states of the monomer are in thermal equilibrium and the equilibrium strongly favors the inactive state. It should be noted that this model treats the nucleation (activation) step as a unimolecular reaction from inactive to active species, in this case denoted as monomer, with equilibrium constant $K_a$. Such a polymerization is described by the following reaction scheme (Scheme 1.1):

\[
\begin{align*}
M & \xrightleftharpoons{K_a} M^* \\
M^* + M & \xrightleftharpoons{K_e} M^*M \\
M^*M + M & \xrightleftharpoons{K_e} M^*M_2 \\
\vdots & \\
M^*M_i + M & \xrightleftharpoons{K_e} M^*M_{i+1}
\end{align*}
\]

Scheme 1.1. Reaction equations describing the cooperative supramolecular polymerization mechanism

In Scheme 1.1 the activated species $M^*$ (the nucleus) reacts only with non-activated monomers $M$ to form dimers, but $M^*$ does not participate in the successive chain elongation steps. In the model analyzed by Van der Schoot, the monomeric activation step is described by a dimensionless activation constant $K_a$, while the subsequent elongation of the polymers is described by a temperature-independent elongation enthalpy ($\Delta H_e$) and the concentration-dependent elongation temperature $T_e$. For supramolecular polymers that polymerize upon cooling, the elongation enthalpy is negative (i.e. $\Delta H_e < 0$) and thus these systems exhibit a so-called ceiling temperature. Therefore, at temperatures above $T_e$ the polymers are unstable and thus only monomers are present.

The observed critical elongation temperature, $T_e$, separates two polymerization regimes. Above this temperature, most of the molecules in the system are in an inactive state (nucleation regime). By approaching the $T_e$ the activation equilibrium is shifted to favor the activated monomer. At the critical elongation temperature the amount of activated monomer is such that the equilibrium describing the elongation steps is shifted to the right and elongation of the nucleus can occur that eventually will result in supramolecular polymers with a high degree of polymerization (DP). For low values of $K_a$, implying low and relatively high concentration of activated and non-activated monomers, respectively, hardly any polymeric species are present at temperatures above the critical temperature.
Below the critical temperature the fraction of polymerized material increases abruptly (Figure 1.3a and 1.3b) and the transition becomes sharper as $K_a$ becomes smaller. Thus the dimensionless activation constant $K_a$ can be seen as a measure of the cooperativity parameter $\sigma$ encountered in concentration-dependent supramolecular polymerizations.\textsuperscript{27, 28} The number-averaged degree of polymerization ($\langle DP_N \rangle$) in Figure 1.3b at temperatures below $T_c$ starts to show an exponential growth. Furthermore, higher $DP$'s can be reached when the cooperativity is increased ($K_a$ is decreased). Similarly, a higher enthalpy release $\Delta H_e$ in the elongation regime, corresponding to a higher equilibrium constant for elongation ($K_e$), will lead to more favorable chain growth (Figure 1.3c) and higher $DP$'s (Figure 1.3d).

In contrast to isodesmic supramolecular polymerizations, the shape of the curves that describe the fraction of aggregated material as a function of temperature are clearly non-sigmoidal.

\textbf{Figure 1.3.} Temperature-dependent properties of cooperative supramolecular polymerizations illustrated using the mean-field thermally activated equilibrium model as analyzed by Van der Schoot:\textsuperscript{30} a) Fraction of polymerized material, $\phi$, and (b) number-averaged degree of polymerization, $\langle DP_N \rangle$, as a function of the dimensionless temperature $T/T_\text{c}$ for 4 values of $K_a$, with $\Delta H_e = -60$ kJ/mol. c) Mole fraction of polymerized material, $\phi$, and (d) number-averaged degree of polymerization, $\langle DP_N \rangle$, as a function of the dimensionless temperature for 3 values of $\Delta H_e$ with $K_a = 10^{-4}$. 

\[ T_c \]

$T_c$. Below the critical temperature the fraction of polymerized material increases abruptly (Figure 1.3a and 1.3b) and the transition becomes sharper as $K_a$ becomes smaller. Thus the dimensionless activation constant $K_a$ can be seen as a measure of the cooperativity parameter $\sigma$ encountered in concentration-dependent supramolecular polymerizations.\textsuperscript{27, 28} The number-averaged degree of polymerization ($\langle DP_N \rangle$) in Figure 1.3b at temperatures below $T_c$ starts to show an exponential growth. Furthermore, higher $DP$'s can be reached when the cooperativity is increased ($K_a$ is decreased). Similarly, a higher enthalpy release $\Delta H_e$ in the elongation regime, corresponding to a higher equilibrium constant for elongation ($K_e$), will lead to more favorable chain growth (Figure 1.3c) and higher $DP$'s (Figure 1.3d). In contrast to isodesmic supramolecular polymerizations, the shape of the curves that describe the fraction of aggregated material as a function of temperature are clearly non-sigmoidal.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.3.png}
\caption{Temperature-dependent properties of cooperative supramolecular polymerizations illustrated using the mean-field thermally activated equilibrium model as analyzed by Van der Schoot: a) Fraction of polymerized material, $\phi$, and (b) number-averaged degree of polymerization, $\langle DP_N \rangle$, as a function of the dimensionless temperature $T/T_\text{c}$ for 4 values of $K_a$, with $\Delta H_e = -60$ kJ/mol. c) Mole fraction of polymerized material, $\phi$, and (d) number-averaged degree of polymerization, $\langle DP_N \rangle$, as a function of the dimensionless temperature for 3 values of $\Delta H_e$ with $K_a = 10^{-4}$.}
\end{figure}
1.4 Heterogeneous versus homogeneous nucleation

Nucleation plays a dominant role in cooperative processes, especially at low concentrations. The nucleation can either be homogeneous or heterogeneous in nature. For one-dimensional supramolecular polymers, homogeneous nucleation is only observed in those cases where secondary interactions responsible for the polymerization are complementary. When some of these interactions are in conflict with each other, the homogeneous nucleation can be hampered and is often taken over by heterogeneous nucleation.\(^3\) In a heterogeneous nucleation, the nucleus forms at a preferential site such as a phase boundary or on impurities like dust. Typically, nucleation via a heterogeneous mechanism requires less energy than homogeneous nucleation. For example, the deliberate addition of nanoparticles (copolymer particles, cerium oxide particles, quantum dots and carbon nanotubes) enhances the probability of the appearance of a critical nucleus for nucleation of protein fibrils from human β\(_2\) microglobulin.\(^3\) Heterogeneous nucleation can also occur when it is catalyzed by the surface of an existing supramolecular polymer (secondary nucleation). Initially, nuclei are formed from monomers, but after the creation of a certain amount of supramolecular polymer, the secondary pathway takes control of the growth. The introduction of foreign objects and the study of the kinetics of the supramolecular polymerization can discriminate between homogeneous and heterogeneous nucleation.\(^3\)

1.5 Examples of cooperative supramolecular polymerization

In this section examples will be discussed that are shown or suggested to polymerize via a cooperative supramolecular polymerization mechanism. For each of the examples an attempt has been made to assign the origin of the cooperativity, which can be categorized in three main classes, being electronic, structural or hydrophobic effects. Since multiple effects can contribute to the origin of cooperative growth, it is not always clear which effect is the major contributor.

The supramolecular polymerization of merocyanine dyes (Scheme 1.2) has been studied in detail by Würthner and co-workers. Polymerization is achieved by the antiparallel association of the dipole moments in the monomers (schematically depicted in Figure 1.4a,b), since the extremely high dipole moment of 17 Debye allows for a high dimerization constant of \(K_{\text{dim}} > 10^6 \text{ M}^{-1}\) in tetrachloromethane, as determined with UV/Vis absorption spectroscopy.\(^3\) In alkane solvents of lower polarity, like methylcyclohexane, the dimerization constant was increased to values exceeding \(10^8 \text{ M}^{-1}\). Dimerization of bifunctional merocyanine dye 1 results in the formation of small oligomeric structures at low concentration in apolar solvents as well as in solvents with higher polarity, like tetrachloroethane, as evidenced by viscosity measurements. These oligomeric structures (Figure 1.4a) further assemble into fiber-like aggregates, for which force field calculations suggested that these aggregates consist of six linear intertwined oligomers (Figure 1.4c,d).\(^3\) X-ray diffraction on the supramolecular fiber-like polymers showed an interaction with an additional neighboring molecule, besides the one already present in the original oligomer. As a result the \(\pi-\pi\) interactions increased and
the absorption maxima was hypsochromically shifted. This polymer is referred to as the H-type aggregate.

![Scheme 1.2. The molecular structure of the merocyanine dyes.](image)

The formation of this H-type polymer was studied by temperature-dependent and solvent polarity-dependent UV/Vis spectroscopy. By increasing the amount of methylcyclohexane (MCH) in a tetrahydrofuran (THF)/MCH mixture a sharp increase in intensity at the absorption maximum of the H-type aggregate and a sharp decrease in both the monomer and oligomer bands could be observed. This sharp change is indicative of a cooperative supramolecular polymerization process. Direct evidence was obtained by temperature-dependent measurements, where also a sharp non-sigmoidal transition was observed. An increase in concentration allowed the bundling of the supramolecular polymer that grew to such an extent that solvent gelation could be achieved (Figure 1.4e). By the addition of a monofunctional dye that can acts as a chainstopper, the reversible nature of the polymerization was revealed by a drop in the viscosity with increasing amounts of chainstopper.\(^{34}\) Intriguingly, the introduction of chirality in 2 allowed the visualization of two distinctly different H-type supramolecular polymers showing opposite helicity and a difference in thermodynamic stability.\(^{36}\) By synthesizing the enantiomer 3 and the use of the already available achiral derivative, ‘Sergeant-Soldiers’ and ‘Majority-Rules’ experiments could be performed.\(^{37, 38}\) Chiral amplification was followed as a function of time by circular dichroism (CD) and UV/Vis spectroscopy. The Sergeant-Soldiers experiments revealed an increasing amplification rate upon increasing the amount of chiral sergeant present in the system.\(^{37}\) The kinetic data of the Majority-Rules experiments for the three types of assemblies that were formed, could be analyzed in great detail due to the kinetic stability of each type of supramolecular polymer.\(^{38}\) Prior to chiral amplification, the kinetic data of the transition from the oligomers to the first H-type aggregate showed a so-called ‘lag phase’ in the UV/Vis traces indicative for a nucleated supramolecular polymerization. After formation of the H-type aggregate, an autocatalytic amplification of chirality was revealed, which the authors attributed to the autocatalytic generation of secondary nuclei with preferred helicity that grew into larger domains.
In total, both the thermodynamic analysis as well as the kinetic analysis strongly suggests a nucleated supramolecular polymerization mechanism for the merocyanine dyes. The supramolecular polymerization is driven by a dipole-dipole interaction (Figure 1.4a), which suggests that the cooperativity is most likely the result of the formation of a large net-dipole over the whole supramolecular polymer that should strengthen the interaction between the merocyanine dyes. However, from the data it is difficult to distinguish if the cooperativity is related to the formation of this dipole or that it is associated with the intertwining of the six oligomeric strands (a structural effect) or a combination thereof.

Very recently, Würthner and co-workers have reported on the cooperative supramolecular polymerization of perylene bisimide chromophores. Instead of only using the π–π interactions as driving force for the supramolecular polymerization for these perylene bisimide structures, they elegantly designed the system in such a way that an additional hydrogen bonding interaction was incorporated. The concentration-dependent UV/Vis and CD studies revealed a critical concentration for the supramolecular polymerization, and the UV/Vis absorption data could be analyzed with the $K_2$–$K$ model giving $K_2 = 13 \text{ L mol}^{-1}$ and $K = 2.3 \times 10^6 \text{ L mol}^{-1}$ ($\sigma = 10^{-5} \text{ to } 10^{-6}$). By careful analysis of the atomic force microscopy (AFM), scanning tunneling microscopy (STM) and optical data they showed that helical fibers were formed suggesting an allosteric effect for the cooperativity. However, the dipole moment of the dimer was around 20% higher (8.8 D) than for the monomers (6.1 D), which can indicate an electronic contribution to the cooperativity.

The supramolecular polymerization of chiral oligo(p-phenylenes vinylenes) 4–6 (abbreviated as OPV, Scheme 1.3) equipped with an ureidotriazine self-complementary quadruple hydrogen bonding unit in alkane solvents was investigated by our group using temperature-dependent optical and chiroptical techniques in solution.
Chapter 1

The enantiomeric purity of the chiral side tails was expressed at the supramolecular level leading to one-handed helical structures, as evidenced by the bisignated circular dichroism spectrum at room temperature. At high temperature these molecules were shown to exist in their monomeric form or as hydrogen-bonded dimers,\textsuperscript{41, 42} which have been studied in detail with STM\textsuperscript{42, 43} and $^1$H NMR spectroscopy.\textsuperscript{41} At low temperatures AFM and small angle neutron scattering (SANS) showed the presence of supramolecular polymers that were fiber-like in nature.\textsuperscript{42}

![Diagram of supramolecular polymers and scheme 1.3](image)

\textbf{Scheme 1.3. Oligo(p-phenylene vinylene) derivatives.}

To probe the supramolecular polymerization, temperature-dependent CD and UV/Vis spectroscopy were employed, which resulted in a sharp non-sigmoidal transition (Figure 1.5). The non-sigmoidal growth process strongly indicates the presence of a cooperative supramolecular polymerization mechanism, which was analyzed by the model developed by Van der Schoot (\textit{vide supra}). For 5 an enthalpy release ($\Delta H_b$) of $-56$ kJ mol$^{-1}$ and a $K_a$ value of $10^{-4}$–$10^{-5}$ were determined in dodecane. The presence of a cooperative transition was further confirmed by a sharp non-symmetric peak in the temperature-dependent heat capacity at constant pressure measurements.

![Figure 1.5. Degree of aggregation, $\phi$ based on UV/Vis, CD and PL spectroscopy for 5 and the schematic representation of the supramolecular polymerization of 4–6.](image)

By combining the chiroptical data with the optical data, it was suggested that disordered pre-aggregates precede the formation of chiral supramolecular polymer (Figure 1.5). The gradual increase in the UV/Vis absorption in this temperature domain indicated an isodesmic supramolecular polymerization for the formation of the pre-aggregates, while after the introduction of a helical twist,
the supramolecular polymerization towards long polymers seems to be more thermodynamically favorable. This behavior is typical for a cooperative supramolecular polymerization. By using the models described in the previous section a degree of polymerization at the $T_c$ could be determined which interestingly coincided with the number of molecules necessary to complete one helical turn. A closer look at the molecular structure in the polymerized material indicates that the molecule should be flat to be incorporated in the stack. However, in their monomeric or hydrogen-bonded dimeric form the OPV segment most likely has a non-zero dihedral angle with the ureidotriazine unit. In order to obtain the monomeric structure that is able to polymerize, the dihedral angle needs to be reduced to zero and hence a thermodynamically less favorable conformation should be reached. It is likely that this allosteric property makes 4–6 supramolecularly polymerize according to the cooperative mechanism. Additionally, interactions between non-neighboring monomers upon formation of the helix could also contribute to the cooperativity.

Chiral hexa-OPV substituted benzene 7 displayed a similar behavior in dilute solution, having a sharp change in the temperature-dependent CD and UV/Vis absorption in methycyclohexane. In contrast to the OPV derivatives 4–6, the $T_c$ of 7 is observed at the same temperature for both techniques, which excludes the formation of achiral pre-aggregates. A much higher degree of cooperativity and enthalpy release was observed for this system when compared to the OPV ureidotriazine derivatives. The values were so high that they could not be resolved with the model developed by van der Schoot. This increase was related to the higher number of OPV units in the molecule. Furthermore, these molecules could not be disassembled at 90 °C at a concentration of $2 \times 10^{-7}$ M in heptane, showing a remarkable increase in stability when compared to their hydrogen-bonded hexameric counterparts. It is likely that the OPVs are arranged perpendicular with respect to the central benzene in the molecularly dissolved state of 7. A rotation around this bond to reduce the dihedral angle is necessary to achieve the preferred structure that can supramolecularly polymerize. This means that a thermodynamic barrier needs to be overcome to achieve polymerization, resulting in a cooperative supramolecular polymerization mechanism.

Aida and co-workers reported on the supramolecular polymerization of amphiphilic hexa-peri-hexabenzocoronenes (HBC) 8–17 (Scheme 1.4) in THF and THF/water mixtures, where the HBC core was used to produce conductive graphene-like nanotubes.

![Scheme 1.4. The hexa-peri-hexabenzocoronenes studied by Aida and co-workers.](image-url)
The HBCs formed a stacked bilayer structure (Figure 1.6) were the alkyl tails are interdigitated in the center of the bilayer and the ethylene glycol tails are located at the periphery, allowing the aggregate to be soluble in polar solvents like THF and water. In related studies, they were able to covalently fix the supramolecular assemblies by redox-mediated polymerization, photo dimerization of coumarine and ring-opening metathesis polymerization. By aid of the latter Aida and co-workers were able to trap the intermediate nanocoil structure before the more stable nanotube was formed, showing that HBC’s can form different types of self-assembled structures. The formation of the nanotube or nanocoil depends highly on the solvent and the reaction time of the polymerization, where the nanotube proved to be the thermodynamically stable product.

![Figure 1.6. Schematic picture of the supramolecular polymer based on the HBC motif.](image)

More recently, an elaborate study revealed the effect of the side groups on the supramolecular polymerization of the HBCs by the synthesis of 9–17. A decrease in length of the ethylene glycol chains as performed for 9–12 did not hinder the self-assembly, but decreased the solubility of the supramolecular polymer in THF. This showed that the ethylene glycol is not essential for guiding the self-assembly towards nanotube formation. In contrast the length of the alkyl tail did show a significant influence, where the dodecyl 8, tridecyl 14 and hexadecyl 13 yielded nanotubular assemblies, while the octyl 15 and branched 3,7-dimethyloctyl derivative resulted in ill-defined aggregates. It was concluded that a certain alkyl length was needed to allow for the crystallization of the aliphatic tails by interdigitation thereby enabling nanotube formation. The most striking result from this study was the drastic influence of the phenyl group that is used to attach the ethylene glycol tails to the HBC core. Removal of this phenyl group as done for 17 yields ill-defined structures and hence the phenyl proved to be crucial to drive the supramolecular polymerization towards nanotube/coil formation. No report has been made about the specific mechanism of supramolecular polymerization, but given the long length of the polymer and the dependence of the polymerization on the phenyl group, a cooperative mechanism is highly plausible. Again, a rotation around the phenyl could likely be the reason for the cooperativity and therefore this system is different from the isodesmic supramolecular polymerization of the HBC as reported by Müllen and co-workers. In addition the supramolecular polymers studied by Müllen et al. are purely one dimensional, while the nanotubes of Aida and co-workers are considered to be quasi two dimensional. Therefore, besides the
allosteric effect, the difference in dimensionality of the polymeric structure could also account for the cooperative nature of the supramolecular polymerization.

The chiral amplification of the HBC (Scheme 1.5) in the form of the Majority-Rules\textsuperscript{53} and Sergeant-Soldier\textsuperscript{54} effect has been reported. Due to the high solubility of chiral HBC derivatives 18 and 19 in THF, nanotube and nanocoil formation of the chiral compound could only be achieved in methyl-THF.\textsuperscript{53} The chirality of the structures was confirmed with circular dichroism spectroscopy, while transmission electron microscopy (TEM) images showed right-handed coils for 18, and left-handed coils for 19. Mixing the two components did not alter the nanotube formation.\textsuperscript{53} Differential scanning calorimetry on the mixtures, showed that the transition of the nanotube in a liquid crystalline mesophase occurred at lower temperatures for the mixture when compared to the pure enantiomers. This indicates that the stability of the mixtures is less than that of the pure components. A clear non-linear relationship in the CD effect versus the enantiomeric ratio could be observed, showing chiral amplification as a result of the Majority-Rules effect.

![Scheme 1.5. HBCs used for the chiral amplification studies](image)

The Sergeant-Soldier effect was investigated using 8 as the soldier and either 20 or 21 as the sergeant.\textsuperscript{54} The supramolecular polymerization of 20 and 21 by themselves only yielded ill-defined objects, however, the coassembly with 8 resulted in nanocoil formation having a preferred handedness. Full chiral amplification was achieved at 10 mol\% of 20 or 21.\textsuperscript{54} Exclusive formation of nanocoils was achieved until 50 mol\% of sergeant, while at higher percentages the presence of ill-defined assemblies appeared.

The group of Rowan and Nolte reported on the surface patterning of porphyrin trimers 22 (Scheme 1.6) via supramolecular polymerization and dewetting,\textsuperscript{55} where the polymerization was driven by a combination of hydrogen bonding and π–π interactions. They showed an impressive control over the formation of highly ordered line patterns on a surface as evidenced by AFM. In a later stage they also investigated in detail the supramolecular polymerization in solution by temperature- and concentration-dependent \textsuperscript{1}H NMR, CD and UV/Vis spectroscopy.\textsuperscript{56} Concentration-dependent \textsuperscript{1}H NMR in chloroform enabled the determination of a critical concentration of ~0.2 mM for the supramolecular polymerization of 22, while in hexane, disassembly of the polymer could not be visualized by this technique. The appearance of a critical concentration strongly indicates the presence of a cooperative mechanism for the supramolecular polymerization. Concentration-dependent UV/Vis spectroscopy in hexane and cyclohexane of 23 showed clear isosbestic points indicative for the presence of two different species (monomers and aggregates). However, with CD spectroscopy different CD signatures were observed showing the presence of different organizations. Remarkably, in hexane a face-to-face
type packing was obtained, while in cyclohexane solutions the UV/Vis absorption indicated that the porphyrins were arranged in a head-to-tail and a face-to-face type organization. These results stress the importance of the solvent on the supramolecular polymerization and the presence of multiple organizations.

Scheme 1.6 Porphyrin trimers.

Since hydrogen bonding is present in these structures, it would seem likely that electronic effects account for the cooperativity in the system. However, the position of the porphyrin with respect to the amides is likely to be most stable when the porphyrin plane is coplanar with the amide. Therefore, an allosteric effect, expressed as a rotation of the porphyrin around the phenyl-porphyrin bond, can also add to the cooperativity. At this point, it is unclear to what extent the allosteric and electronic effects contribute to the cooperativity observed in this system.
Cooperative supramolecular polymerization of \( \pi \)-conjugated systems

Scheme 1.7. The molecular structure of oligo(p-phenylene vinylene) and oligo(p-phenylene ethynylene) derivatives.

Ajayaghosh et al. studied the gel-formation as well as the supramolecular polymerization in dilute solution of linear \( \pi \)-systems and have recently extensively reviewed this work.\textsuperscript{57, 58} Using the hydrophobicity of cholesterol derivatives, OPV trimers equipped with one or two cholesteric groups, \textsuperscript{24–29} (Scheme 1.7), showed supramolecular polymerization in decane solutions.\textsuperscript{59} The packing arrangement depends on the number of cholesteric units that are attached; \textsuperscript{24–26} showed H-type assembly, whereas \textsuperscript{27–29} revealed J-type aggregation by UV/Vis spectroscopy. In addition, opposite chirality was observed for the two structures.\textsuperscript{59} These interesting features could make it worthwhile to study the supramolecular polymerization mechanism in more detail. For now this system is thought to be a cooperative supramolecular polymerization mainly by the fact that the \( \pi \)-conjugated system and the cholesterol unit have to be combined in order to drive the supramolecular polymerization.

Another system concerns an oligo(p-phenylene ethynylene) (OPE) derivative \textsuperscript{30} bearing a benzylic alcohol group at its telechelic positions.\textsuperscript{60} The combination of \( \pi-\pi \) interactions and hydrogen bonding allows supramolecular polymerization into ribbon-like structures that eventually form vesicles. The necessity of hydrogen bond formation was confirmed by the fact that no polymeric structures could be obtained for \textsuperscript{31}. Initially a kinetically stable assembly of \textsuperscript{30} was formed that underwent slow transformation into a thermodynamically more stable supramolecular polymer. Temperature-dependent UV/Vis spectroscopy showed a sharp change in intensity at a specific temperature that was followed by a second transition at higher temperature (Figure 1.7). The sharp change indicates a cooperative supramolecular polymerization; however, it is difficult to assign the cooperativity to the formation of linear polymer or to vesicle formation.
Figure 1.7. Temperature-dependent UV/Vis absorption for 30 in decane (1.1 × 10^{-5} M). The inset shows the fraction of polymerized material, α, versus the temperature, as derived from the absorption at 380 nm.\(^{60}\)

This group also studied the chiral amplification via the Sergeant-Soldier principle for OPEs (achiral 30 and chiral 32) and OPVs (achiral 33 and chiral 34). In the first case compound 32 was not assembled in alkane solvents, and therefore a CD effect could not be observed. Intimate mixing between 30 and 32 was achieved by annealing at high temperatures, where the molecules were molecularly dissolved. Cooling down the solution yielded mixed assemblies as indicated by the appearance of a CD effect. Strikingly, the co-assemblies showed the formation of helical fibers instead of vesicle like assemblies which are normally observed for pure 30. Also in the case of the OPV derivatives 33 and 34, chiral amplification was shown, where CD spectroscopy and AFM studies revealed at low incorporation of 34 (less than 22 mol%) a left-handed helical polymer, while at high incorporation right-handed helices could be detected.

Scheme 1.8. The chiral OPE and achiral and chiral OPV derivatives.

Already in the early seventies independent studies have been reported about the aggregation properties of cationic and anionic porphyrins.\(^{61, 62}\) The group of Pasterнак investigated the effects of templates, like DNA, on the supramolecular polymerization of water soluble porphyrins.\(^{63}\) Additionally, they have also reported a kinetic study concerning the supramolecular polymerization of water soluble porphyrin 35 (Scheme 1.9).\(^{64}\)
Cooperative supramolecular polymerization of π-conjugated systems

Scheme 1.9. Water soluble porphyrin derivatives.

The polymerization of 35 yielded J-type aggregates in acidic aqueous media (pH ~ 1) as was revealed by UV/Vis spectroscopy. The strong cohesive interaction of water promotes the supramolecular polymerization by the hydrophobic effect.65 Injection of a concentrated solution of molecularly dissolved 35 into acidic water facilitated the polymerization, however, in this case the kinetics were too fast to be recorded (Figure 1.8).64

Figure 1.8. The supramolecular polymerization kinetics of 35 at the same porphyrin concentration (4.5 × 10⁻⁶ M in 0.3 M HCl aqueous solution), dependent on the method of mixing (a) addition of highly concentrated porphyrin solution to the acidic water, (b) same as (a) but a lower initial porphyrin concentration was used, (c) similar to (b), but now the solution was stirred.64

By lowering the injection concentration the assembly rate was significantly slowed down so that it could easily be studied. Stirring of the solution after injection increased the rate and the smoothness of the curve. In the last two examples there is a clear concentration-dependent lag phase before the supramolecular polymerization is initiated, and therefore it can be concluded that a nucleated mechanism is operative in the polymerization of 35.64 By fitting the kinetic traces to an autocatalytic nucleation model, a nucleus size of ~ 5–6 molecules could be determined, where the size of the nucleus seemed independent of the initial porphyrin concentration (Figure 1.8). In contrast, the rate of polymerization is highly dependent on this concentration. Since nucleus formation is the rate determining step, it was suggested that prenuclear species are more rapidly produced at higher porphyrin concentration and hence the overall polymerization rate is enhanced.
An elaborate light scattering study showed a decreased polymerization length at higher concentration, which was explained by the formation of an increased number of nuclei. In order to demonstrate the importance of the nucleation on the supramolecular polymerization, a small amount of seeds was added to a solution of 35, and the kinetics were probed. A significantly faster polymerization rate was obtained for the solution containing the small amount of seeds, suggesting that the supramolecular polymerization is indeed nucleated.

Although not explicitly stated, Purello and co-workers found a similar supramolecular polymerization mechanism, since they used a stretched exponential for the description of the supramolecular polymerization kinetics of 35 and 36 (Scheme 1.9) in the presence of phenyl aniline. Further evidence was obtained from experiments showing the ability of the porphyrin system to memorize the chirality of the polymer after its depolymerization. This was explained by the presence of small undetectable chiral seeds that are able to nucleate the polymerization into helical structures with one single handedness.

The group of Ribó is well known for their work on the chiroptical response of supramolecular polymers based on water soluble porphyrins. A very recent contribution from this group showed the effect of an unidentified chiral contaminant in the solvent that proved to be able to induce the chirality in the supramolecular polymer of the disodium salt of 35 by acting as a nucleation site. Both examples show that a heterogeneous nucleation event initiates the self-assembly.

Monsù Scolaro and co-workers have also reported on the nucleating effects in the supramolecular polymerization of 37 (Scheme 1.9) in water containing NaCl. Furthermore, similarly as described by Pasternack et al., a decrease in polymer length upon increasing the concentration of 35, was observed using light scattering. More recently, the supramolecular polymerization was attempted in chlorinated organic solvents, like dichloromethane, by the addition of acids.

By equipping π-conjugated segments with ethylene glycol dendrons, supramolecular polymerization was achieved in water. M. Lee and co-workers synthesized a large variety of oligo(p-phenylene) derivatives (Scheme 1.10) that were shown to polymerize into cylindrical micelles, coiled coils (43 and 44) and more recently an elegant example of supramolecular capsules with gated pores was reported. Light scattering experiments in combination with UV/Vis spectroscopy showed the supramolecular polymerization of 40 and 41 in water, while transmission electron microscopy allowed the visualization of the cylindrical micelles.
Cooperative supramolecular polymerization of π-conjugated systems

Scheme 1.10. Oligo(p-phenylene) derivatives studied by Lee and co-workers.

By introducing a twist in the aromatic part, as was done for 42, supramolecular polymerization could not be achieved, thus showing the importance of π–π interactions for the polymerization and indicating an allosteric effect that can contribute to the cooperativity. For 43 and 44, the enantiomeric purity is expressed at a supramolecular level as visualized by CD spectroscopy. In addition for 43 helical fibers were observed with transmission electron microscopy; however, in this case the helicity of the fibers was different from the handedness determined by CD spectroscopy. This was explained by the formation of a superhelix again hinting towards a polymerization driven by a structural change. The presence of the hydrophobic effect and the notion of the presence of an allosteric effect in the supramolecular polymerization of these molecules, indicates that the formation of the polymers most likely proceeds via a cooperative mechanism.

1.6 Aim and outline of the thesis

The review of the literature shows that a large variety of π-conjugated molecules can self-assemble; however, the determination of the supramolecular polymerization mechanism has rarely been investigated in detail. Additionally, the influence of the self-assembly protocol to obtain a certain supramolecular organization is not yet well understood. An increased understanding of the parameters that influence the self-assembly of π-conjugated systems is a necessary step to achieve control over the position of the chromophores. Therefore, the focus of this thesis will be to explore these parameters with the final aim to create supramolecular assemblies having chromophores at predetermined positions.

A covalent approach was used in Chapter 2 to attach chromophores to a helical foldamer scaffold in order to nicely position the components in a three dimensional organization. The results showed that separation of these chromophores by a helical bridge hampered the uniform description of the charge transfer phenomena within current theory. In Chapter 3, attention is turned to cooperative supramolecular polymerization of π-conjugated systems, in this case chiral oligothiophenes. It was
shown that the self-assembly can be characterized by having a heterogeneous nucleation event due to very small amounts of impurities. Furthermore, the cooling rate and assembly protocol drastically influenced the supramolecular organization, revealing a complex energy landscape for the self-assembly. Chapter 4 describes the elucidation of the internal structure of the thiophene assemblies by applying a combination of magnetic field alignment, small angle X-ray scattering and linear birefringence revealing a picture of cylindrical structures where the thiophenes are arranged in the tangential direction (short axis) of the cylinder. In Chapter 5 circular dichroism was used to investigate the organization of chiral and achiral oligo(phenylene vinylene) (OPV) derivatives. Large apparent CD effects were observed for achiral derivatives that are a consequence of linear dichroism caused by alignment of the self-assembled fibers in solution. Coassemblies of the chiral and achiral molecules having different conjugation length showed the formation of enriched clusters of the separate components, in which the level of enrichment depends highly on the preparation method. In Chapter 6 the self-assembly of star shaped hexa(OPV)benzene derivatives is discussed, where special attention is given to the influence of reduced dynamics on the self-assembly process. As a result of the reduced dynamics two types of aggregates (A1 and A2) were present where a transition between the two aggregates could be observed. The A1 type of assembly became increasingly dynamic with the addition of good solvent. Size exclusion chromatography (SEC) could be applied to study the self-assembly and revealed a surprisingly high monomer content upon the addition of a good solvent. Coassembly of the enantiomers, revealed that the transition from the first type of aggregate to the second type was significantly decreased in rate. The results suggested that the transition was facilitated by the formation of enantiomerically pure clusters of the star shaped molecules. In the epilogue, the influence of these parameters on the design and synthesis of complex supramolecular architectures is discussed.

1.7 References

Cooperative supramolecular polymerization of \( \pi \)-conjugated systems


17. This mechanism is equal to the exponential growth mechanism as proposed by Dill: De Young, L. R.; Fink, A. L.; Dill, K. A. Acc. Chem. Res. 1993, 26, 614-620


Cooperative supramolecular polymerization of π-conjugated systems

Covalently organizing chromophores on a foldamer scaffold and its electron transfer properties

Abstract. The synthesis and characterization of four quinoline-derived foldamers with increasing oligomeric length is reported; namely a dimer O2P, tetramer O4P, pentamer O5P and nonamer O9P functionalized with on one end an oligo(p-phenylene vinylene) (OPV) and on the other end a perylene bisimide (PB) chromophore. ¹H NMR confirms the formation of the expected folded structures in both toluene and chloroform solution. The structural predictability and rigidity of the oligomeric series enabled the investigation of the effect of a helical bridge and chromophore position on the photoinduced processes in the electron OPV-PB donor-acceptor pair in chloroform and toluene. The helical properties of the bridge ensured that the chromophore separation distance through space is different from the separation distance through the bridge. For all foldamer-solvent combinations studied, excitation of either OPV or PB results in nearly quantitative quenching of the fluorescence indicating a fast charge separation reaction between the OPV and PB. Femtosecond photoinduced absorption measurements confirmed the fast formation of a charge separated state. The recombination reaction involves a combination of direct decay to the ground state and the formation of an intermediate triplet state, with their balance depending on the foldamer-solvent combination. Molecular orbital calculations rationalize the fast photoinduced charge separation, by revealing that the bridging foldamer mediates the charge transfer from donor to acceptor via the superexchange mechanism. Remarkably low attenuation factors ($\beta_{CS} \approx 10^{-2} \text{ Å}^{-1}$) were obtained using either through space or through bridge separation distance. However, in these calculations only three of the four foldamers show the expected linear behavior between the logarithm of the charge separation rate constant and the distance between the chromophores. The combined results show that when a helical bridge is separating the charge transfer couple, it is not suitable to use a uniform description of the charge separation phenomena.
2.1 Introduction

Photoinduced charge-transfer processes are crucial for the function of the photosynthetic unit. In particular, the three dimensional organization of the individual molecules within the photosynthetic unit imposed by the surrounding protein matrix enables the formation of charge separated states with extraordinary long lifetimes. In order to understand and mimic these biological photophysical processes, artificial model systems have been designed in which the distance dependence for charge separation and charge recombination reactions is studied in donor–bridge–acceptor molecules. In these examples, the chromophores are either placed on top (cofacial) or next to each other (colinear) in a covalent fashion. For instance a cofacial positioning of the chromophores is achieved by using helical DNA, peptides, aromatic foldamers or a nonhelical rigid linker as a scaffold to attach the chromophores. Colinear interactions are obtained by connecting the chromophores to rigid bridges that can either be composed of conjugated or saturated moieties. As a consequence of the rigidity of these bridges, in all cofacial and colinear positioning, the chromophore position is fixed and the distance between the chromophores through space is similar to the distance through the bridge. Depending on the properties of the bridge and the way the chromophores are attached to the bridge, charge transfer may proceed via a superexchange or a charge hopping mechanism. In the superexchange mechanism the bridge solely serves to facilitate the interaction between the donor and acceptor wave functions. In the hopping mechanism the electron is located at the bridge for a short period of time during which the charge transfer occurs. The effectiveness of the bridge in mediating the charge transfer process is expressed in the attenuation factor $\beta$. Typical attenuation factors found are $\beta = 0.6 – 1.2 \, \text{Å}^{-1}$ for hydrocarbon bridges, $\beta = 0.32 – 0.66 \, \text{Å}^{-1}$ for conjugated polyphenylenes, $\beta = 0.04 – 0.2 \, \text{Å}^{-1}$ for polyenes and $\beta = 0.04 – 0.17 \, \text{Å}^{-1}$ for polyynes. A lower attenuation factor indicates that the bridges can more effectively mediate the charge transfer reaction.

The use of bridges to spatially organize chromophores in more of a three dimensional situation, where the chromophores are positioned in both a cofacial and a colinear arrangement has rarely been explored. Examples include the investigation of chromophores within constrained molecular assemblies or connected at ortho, meta or para positions by rigid aromatic molecular linkers. In both cases the chromophores are held at a relatively short distance from each other by nonhelical bridges. These studies revealed that the effect of chromophore orientation on the charge transfer process, if any, depends highly on the system in hand. One hurdle in studying the effect of chromophore positioning in both a cofacial and colinear arrangement lies in the difficulty to achieve large distances between the electron donor and acceptor and to simultaneously be able to control and tune their relative orientations. It was hypothesized that helical foldamers possessing stable and predictable conformations may be promising candidates, where the helicity of the bridge can be used as a scaffold to organize chromophores in space. Indeed, chemists have designed and synthesized a large variety of oligomeric and polymeric molecules that adopt predefined helical or extended conformations that are commonly used as peptide mimics, the sizes of which sometimes approach those of small proteins.

Here, the synthesis and characterization of a series of helical aromatic oligoquinoline amide-based foldamers that can act as helical bridges between an electron donor, an oligo(p-phenylene vinylene) (OPV) and an electron acceptor, a perylene bisimide (PB) is reported. This charge transfer couple has
been selected since the photophysics of the individual compounds and the charge-transfer pair have been thoroughly studied.\textsuperscript{16,17} The oligoquinoline amide foldamers feature remarkably high structural robustness and predictability in a variety of apolar, polar and protic solvents and in the solid state as determined with extensive NMR and single-crystal X-ray diffraction studies.\textsuperscript{18} For example, the characteristic time of helix handedness inversion in chlorinated or aromatic solvents lies in the 100 ms range for a quinolinecarboxamide tetramer and in the 2 hours range for an octamer.\textsuperscript{18} In DMSO, \textsuperscript{1}H NMR experiments show that the helical structure of an octamer is stable up to 120 °C.\textsuperscript{15a,18} These beneficial properties are expected to enable the exact positioning of the chromophores in order to vary and control not only the distance between the donor and the acceptor, but also their relative orientation in space. As a result of the helicity of the foldamers the distance between the chromophores either through space or through the bridge is different. For this reason it is likely that the charge transfer pathways will depend on the foldamer that is studied. Four different foldamer sequences were synthesized ranging from dimer to nonamer that are all equipped with the same electron donor (OPV) and electron acceptor (PB) rigidly connected to the quinoline foldamer (Figure 2.1). These molecules were designed to cover a well-defined array of distances and orientations between the chromophores. With a variety of optical techniques it was shown that excitation of the PB leads to the formation of a charge separated state. Remarkably low attenuation factors are obtained by either using the distance through space ($\beta_{CS} = 0.05 \text{ Å}^{-1}$) or through the bridge ($\beta_{CS} = 0.02$ or 0.06 $\text{ Å}^{-1}$). Molecular orbital calculations revealed electronic coupling through the bridging foldamer, where the degree of electronic interaction depends highly on the foldamer studied. These results show that the bridge is most likely mediating the charge separation between the chromophores. However, the calculations performed to ascertain the attenuation factor is each time based on only three foldamers whilst a fourth one deviates. The current theoretical description that dictates an exponential relationship between the charge transfer rates and the distance between the donor and acceptor, being either the distance through space or through a bridge, seems to be insufficient to uniformly describe the charge separation phenomena when a helical bridge is separating the charge transfer couple.

\textbf{2.2 Molecular design and synthesis}

The calculation of the energy-minimized structures of all oligomers from dimer to nonamer by molecular mechanics enabled the selection of a series of foldamers where both the orientation as well as the distance could be varied.\textsuperscript{19} To minimize the complexity of the calculations, the aliphatic tails of the chromophores were shortened. In order to reduce the synthetic effort, it was decided to select four different foldamers for this study. The analyses of the optimized structures revealed that the four foldamers listed in Figure 2.1 cover a wide variety of orientations and distances between the chromophores, and were for that reason synthesized. In O\textsubscript{2}P the center-to-center donor–acceptor distance through space ($R_{DA}$) between the chromophores is calculated to be 15 Å and the angle between them is $\alpha_{DA} = 115^\circ$. The separation through the bridge ($R_{Bridge}$) is calculated as the shortest distance across the quinoline units, resulting in $R_{Bridge} = 18$ Å for O\textsubscript{2}P. The tetramer O\textsubscript{4}P ($R_{Bridge} = 33$ Å) and nonamer O\textsubscript{9}P ($R_{Bridge} = 69$ Å) both place the donor under a small angle with respect to the acceptor ($\alpha_{DA} = 28^\circ$ for O\textsubscript{4}P and $\alpha_{DA} = 15^\circ$ for O\textsubscript{9}P) separated by 6 Å and 14 Å, respectively, which can suggest
that the charge separation pathways can be similar for these two compounds. The structures of O2P and O9P show that the distance through space between the chromophores is similar in the two foldamers, while the distance through the bridge (18 versus 69 Å) differs considerably. Therefore, a comparison between the results for these two foldamers should yield more insight in the effect of chromosome orientation and charge separation pathway. In the pentamer O5P a shorter through bridge separation distance than in O9P is achieved (40 versus 69 Å), while the through space distance between the chromophores is increased to 22 Å since the chromophores are almost radially opposed \( (\alpha_{DA} = 166^\circ) \).

<table>
<thead>
<tr>
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<th>( R_{DA} ) (Å)</th>
<th>( R_{Bridge} ) (Å)</th>
<th>( \alpha_{DA} ) (°)</th>
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<tbody>
<tr>
<td>O2P</td>
<td>15</td>
<td>18</td>
<td>115</td>
</tr>
<tr>
<td>O4P</td>
<td>6</td>
<td>33</td>
<td>28</td>
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<tr>
<td>O5P</td>
<td>22</td>
<td>40</td>
<td>166</td>
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<tr>
<td>O9P</td>
<td>14</td>
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Figure 2.1. Molecular formula of the four foldamers with appended chromophores (top left) described in this study. Table with the distance through space \( (R_{DA}) \) or through bridge \( (R_{Bridge}) \) and dihedral angle \( (\alpha_{DA}) \) between the chromophores (top right), and top views down the foldamer helix axis (left) and side views (right) of their energy minimized conformations (bottom). The helical backbones are shown in gray, the OPV units in blue and the PB units in red. The alkyl chains of OPV and PB units were replaced by methyl groups during energy minimization. The top views clearly show the similar orientations of the chromophores in O4P and O9P.

The synthesis of O2P, O4P, O5P and O9P starts from the previously reported, perylene bisimide 1,21 OPV 22 and quinoline derivatives.30b The synthesis of O2P begins with a peptide based \( \alpha- \) (Benzotriazol-1-yl)-N,N,N',N'-tetramethylyuronium hexafluorophosphate (HBTU) activated coupling of 1 with nitro quinoline-dimer carboxylic acid 5 resulting in 6 with 60% yield after column chromatography. Catalytic hydrogenation in chloroform with 10% Pd on carbon converts the nitro derivative of 6 to amine 7 in quantitative yield. Subsequent acylation of 7 with 2 and purification by recycling size exclusion chromatography (SEC) eventually yields 17 mg (30%) of O2P as an orange solid. Although this synthetic route is in principle generally applicable to synthesize all foldamers, in practice, the hydrogenation conditions caused the degradation of the perylene-nitro-tetramer. By
using protective group chemistry as depicted in Scheme 2.1, this troublesome hydrogenation could be circumvented.

- The starting materials

- The synthesis of O2P

- The synthesis of O4P

- The synthesis of O5P and O9P

Scheme 2.1. Chromophoric precursor perylene bisimide amine 1, OPV3-acid chloride 2 Quinoline tetramer 3 and octamer 4 nitro esters and the synthetic scheme of O2P, O4P, O5P and O9P. For synthetic details, the reader is referred to section 2.5.
To this end, the tetramer amine-ester was protected with a BOC group by treatment with di-tert-butyl dicarbonate that resulted in the protected amine 9. Subsequent hydrolysis of the methyl ester of 9 and activation of the corresponding carboxylic acid 10 to acid chloride 11 under mild conditions by using a chloroenamine was followed by a reaction with PB amine 1 resulting in 12 after column chromatography. Removal of the BOC-group with trifluoroacetic acid in dichloromethane yielded 13 quantitatively and subsequent coupling with 2 under basic conditions resulted in tetramer O4P as an orange solid after purification by column chromatography and recycling SEC.

For the synthesis of O5P and O9P a more convergent synthetic strategy (Scheme 2.1) was applied which is based on the chain extension of a foldamer with one monomeric unit that already contains the OPV chromophore. Although this synthetic scheme seems applicable for the synthesis of all the foldamers, it is hampered by the synthetic availability of the starting compounds. The synthetic strategy used to synthesize the starting foldamers is based on connecting even numbers of oligomers making dimer, tetramer (3) and octamer (4) readily available.\textsuperscript{14-23} The synthesis of the monomeric building blocks starts with an acid chloride coupling of 2 with amine 14 (70%). Subsequent hydrolysis of the ester and activation with a chloroenamine ultimately yielded monomeric building block 17. This compound can be attached to either the tetramer (3) or octamer (4) amine. Chain extension of 3 and 4 with one monomeric unit 17 resulted in pentamer 18 and nonamer 19, respectively. The esters were hydrolyzed to their corresponding acids (for pentamer compound 20 and for nonamer compound 21) with sodium hydroxide in a THF/methanol mixture and the carboxylic acids were activated with a chloroenamine to the acid chlorides 22 and 23. PB amine 1 was coupled to the acid chlorides which resulted in pentamer O5P and nonamer O9P that were intensively purified by recycling SEC. All intermediate compounds have been analyzed with \textsuperscript{1}H NMR and/or MALDI-TOF MS, while additional SEC and \textsuperscript{13}C NMR measurements were performed for the final products. However, the amount of material present for O5P and O9P after reaction and purification was only a couple of milligrams, which is insufficient for a \textsuperscript{13}C NMR.

As shown by the \textsuperscript{1}H NMR spectra in Figure 2.2, the amide protons involved in intramolecular hydrogen bonds are shifted downfield and appear as sharp signals, as expected for folded oligoquinolines.\textsuperscript{18} Upon increasing the oligomer length, these protons shift upfield, indicating an increase of ring current effects associated with aromatic stacking in the helical structure. A similar trend is observed for the aromatic signals. For example, a signal assigned to an OPV resonance is found at \(\delta = 6.2\) ppm in O2P and O4P, at \(\delta = 6.1\) ppm in O5P and at \(\delta = 5.8\) ppm in O9P. In toluene-ds, the shielding effect seems to be more important for the amide protons resulting in a larger upfield shift. An important observation is the splitting of a number of signals of O4P, O5P and O9P in CDCl\(\text{3}\) and toluene-ds, revealing the presence of two diastereomers in solution with a 1:1 ratio of P and M helices.\textsuperscript{18} The result is in contrast with previous reports about quinoline amide foldamers appended with chiral residues, which did show a preference for the helical handedness.\textsuperscript{20,24} The stereocenters carried by the OPV are located further away from the helix which most likely hampers any significant interactions with the helical backbone that would favor one particular handedness. The exchange between the P helix and the M helix is slow on the NMR time scale (milliseconds), and thus, the two species appear as two sets of signals.\textsuperscript{24} Only for the shorter oligomer O2P, the exchange is fast and the average NMR signals of the diastereomers are observed. The lack of preference in helical handedness is confirmed by the circular dichroism spectra that are essentially non existent.\textsuperscript{25} Since the helical
diastereoisomers only differ by the P or M helical sense of the quinoline oligomer, the position of the chromophores with respect to the helix and with respect to each other is expected to remain the same. Thus the P and M helices may be considered as enantiomers for the purpose of this study. This assumption is validated by molecular modeling, which shows no change of the conformation when the stereochemistry of the OPV is inverted while the handedness of the helix is conserved.25

![Figure 2.2. 1H NMR (500 MHz) spectra of the amide region for the four different foldamers in CDCl3. One of the four amide resonances of O4P splits into two (as marked by * and #) corresponding to helical diastereomers. The same occurs to four of the five amide resonances of O5P and several resonances of O9P.](image)

2.3 Photophysical characterization

UV/Vis spectroscopy. To study the effect of solvent polarity on the charge transfer processes, the photophysical studies were performed in toluene and chloroform, since the structure of the quinoline foldamers is well established in both solvents.18 The UV/Vis absorption spectrum of each foldamer is shown in Figure 2.3 and can roughly be divided into three regions: a quinoline part (300–400 nm), an OPV part (350–450 nm), and a PB part (450–550 nm), as observed from the spectra of the individual chromophores in chloroform (Figure 2.3c). The quinoline part shows a progressive increase in molar absorption coefficient upon elongation as a result of the increase in quinoline content. The OPV and PB part only show small fluctuations in molar absorption coefficient that are likely caused by changes in electronic structure and environment, as also observed by 1H NMR. The difference between the absorption spectra of O4P when compared with the sum spectrum of the reference compounds indicates the existence of some electronic interaction in the ground state. The structure and spectral position of the vibronic bands of PB are similar for all foldamers and are indicative for a molecularly dissolved chromophore. Even at high concentration (c = 5.0 × 10⁻⁴ M) the spectrum displays this characteristic vibronic progression and therefore ensures that further photophysical analysis is not hampered by any aggregation phenomena.25 Decreasing the solvent polarity by using toluene instead of chloroform did not affect the shape of the absorption spectra or the position of the absorption
maxima of the foldamers. Irrespective of the concentration, O5P and O9P show an overall decrease in molar absorption coefficient in toluene when compared to chloroform. Again the change in molar absorption coefficient is likely related to the differences in electronic structure and environment of the foldamers in the two solvents as also observed by 1H NMR.

**Figure 2.3** UV/Vis absorption spectra of O2P (black), O4P (red), O5P (green) and O9P (blue) in chloroform (a) and toluene (b). The spectra of Tetramer (black), OPV-ref (red) and C13-PB-P (blue) reference compounds in chloroform (c) and their molecular structures (d). The inset in (c) shows the sum spectrum of the reference compounds (black) and of O4P (red).

**Fluorescence spectroscopy.** In order to evaluate the photophysical processes in these systems, steady-state emission spectra of the foldamers were recorded after excitation of either the PB (495 nm) or the OPV (400 nm) chromophore. Irrespective of excitation wavelength and solvent, the quantum yields of fluorescence for the PB are strongly diminished (Table 2.1). Although C13-PB-P does not have an amide functionality at the para position of the phenyl group, previous results of a compound having an urea functionality showed similar photophysical properties to C13-PB-P. This indicates a highly efficient charge transfer reaction between the OPV and the PB. Excitation spectra recorded at the residual emission band of the PB (577 nm) show contributions of all chromophores, revealing that both the quinoline foldamer and the OPV chromophore contribute to an energy transfer reaction to the PB.

Time-resolved fluorescence spectroscopy showed significant quenching of the singlet excited state of the PB (577 nm) after excitation at λex = 400 nm. Analysis of the decay traces resolved rise times (positive amplitude) that are shorter than the instrument response (30 ps) and short decay times
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(Table 2.1) close to the instrument response. The rise times are attributed to energy transfer from OPV to PB, while the decay times result from the charge transfer step. Although the low fluorescence intensity and very short decay times hinder accurate determination of the quenching factors, the results obtained from these decay times show reasonable correlation with the values from steady-state fluorescence. Photoinduced absorption spectroscopy will provide a more direct route to probe the charge transfer rates.

Table 2.1. Fluorescence quantum yields and decay times from steady state and time-resolved fluorescence, and quenching factors derived thereof.

<table>
<thead>
<tr>
<th></th>
<th>Chloroform</th>
<th>Toluene</th>
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<tr>
<td></td>
<td>$\Phi$ (%)</td>
<td>$Q$</td>
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<tr>
<td>O2P</td>
<td>$&lt; 1$</td>
<td>$&gt; 100$</td>
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<tr>
<td>O4P</td>
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<td>O5P</td>
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<tr>
<td>O9P</td>
<td>$&lt; 1$</td>
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</table>

$^a$ Fluorescence quantum yield ($\Phi$) and quenching factor ($Q$) from steady state fluorescence using C13-PB-P as a reference ($\Phi$ (C13-PB-P) = 0.99), $\lambda_{exc} = 495$ nm.$^{28}$

$^b$ Emissive decay time ($r$) and quenching factor ($Q$) from time-resolved fluorescence measurements using C13-PB-P as a reference ($r$(C13-PB-P) = 4.2 ns).$^{28}$

Photoinduced absorption spectroscopy. In order to elucidate if charge transfer is responsible for the observed fluorescence quenching, femtosecond photoinduced absorption spectroscopy was employed. With this technique, the rate of charge separation and charge recombination can be measured. A representative transient, of O4P in chloroform, is shown in Figure 2.4a, while the lifetime traces at two distinct wavelengths are given in Figure 2.4b.

Figure 2.4. a) Femtosecond photoinduced absorption measurements of O4P in chloroform and b) the corresponding lifetime traces at 911 nm (circles) and 961 nm (squares). The line is the fit through the data (Optical Density (OD) = 0.5 at $\lambda_{exc} = 525$ nm in a 2 mm quartz cell).

After excitation of the solution at $\lambda_{exc} = 525$ nm (PB chromophore), the transient absorption measurements in the near-infrared regime initially show a broad band (900-1100 nm) that sharpens in
time into a band with a maximum at 961 nm. Reference experiments showed that the broad band relates to the 
$S_1 - S_n$ absorption of the PB, while the absorption at 961 nm has been previously assigned to the absorption of the radical anion. In addition, the radical cation of the OPV trimer ($\lambda_{\text{max}} = 1630$ and 725 nm) and the quinoline radical anion ($\lambda_{\text{max}} \approx 710$ nm) and cation ($\lambda_{\text{max}} = 620$ nm) do not absorb in the measured wavelength regime. Both bands are observed in all transient absorption spectra of the different foldamers, irrespective of the solvent used. This indicates that in all systems excitation of the PB results in a charge separated state where the OPV acts as the electron donor and the PB as acceptor. The absence of signatures characteristic for the quinoline in the photoinduced measurements and the fact that the quinolines are not able to be oxidized or reduced by the chromophores, as determined from cyclic voltammetry that did not yield any reduction or oxidation waves for the quinolines, strongly suggest that charge transfer between OPV and PB occurs via the superexchange mechanism. The time constants of charge separation ($\tau_{\text{CS}}$) and recombination ($\tau_{\text{CR}}$) have been extracted from the traces at two different wavelengths (Figure 2.4b). The traces at both wavelengths were simultaneously fitted with 3 different time constants, $\tau_s$, $\tau_x$, and a time constant of $\sim 2$ ps to account for solvent reorganization, including the restriction that all three time constants should yield the same result for both wavelength traces. For details about the fitting procedure the reader is referred to section 2.5. The results of the fits are summarized in Table 2.2. Since no additional time constants were necessary for the fit, it is assumed that the two diastereoisomers present in a 1:1 ratio show virtually identical photophysics and behave as enantiomers, as expected from molecular mechanics calculations which revealed similar structural features for the diastereoisomers.

Table 2.2. Time constants for charge separation (CS) and charge recombination (CR) in chloroform and toluene for O2P, O4P, O5P and O9P from femtosecond photoinduced absorption measurements.

| Foldamer | Chloroform | | | Toluene | | |
|-----------|-------------|-----------|-------------|-----------|-----------|
|           | $\tau_s$ (ps) | $\tau_x$ (ps) | $\tau_s$ (ps) | $\tau_x$ (ps) | |
| O2P       | 20          | 240        | 20          | 1150       | |
| O4P       | 35          | 320        | 30          | 400        | |
| O5P       | 70          | 2140       | 110         | 1060       | |
| O9P       | 50          | 740        | 90          | 460        | |

From Table 2.2 it is clear that charge separation is always faster than charge recombination. The short time constants for charge separation indicate that the formation of the charge separated state is much faster than the intrinsic decay of the PB acceptor-reference chromophore (C13-PB-P, Figure 2.3d). This compound has a fluorescence quantum yield of near unity and its decay to the ground state proceeds in 4.2 ns. Therefore, the observed low fluorescence quantum yields of the order of 1% for these systems are in line with the 100 fold reduction of the decay rate (40 ps versus 4.2 ns). As expected and in correspondence to the fluorescence measurements, charge separation is at a similar rate or somewhat slower in toluene than in the more polar solvent chloroform, indicating that it occurs in the Marcus normal region. There is no direct correlation between the through bridge distance ($R_{\text{bridge}}$) and charge separation rates, confirming that the bridge is indeed folded. As expected for these folded structures, the rates do not follow the general trends normally observed for studies in which chromophores are oriented either in a cofacial or colinear fashion. It is striking that the difference in
charge separation lifetime between the two solvents is largest for the longer oligomers. When plotting the logarithms of the rate constants ($k = 1/\tau$) for charge separation and charge recombination against the distance through space between the chromophores ($R_{Da}$), the three points belonging to O4P, O5P and O9P are on a straight line while the shortest oligomer O2P deviates. The slope of this line yields the attenuation factor $\beta_{CS} = 0.05 \text{ Å}^{-1}$ for charge separation in both solvents (Figure 2.5a) and $\beta_{CR} = 0.13 \text{ Å}^{-1}$ for charge recombination in chloroform (*vide infra*). From the molecular structure it is clear that the helical bridge is not $\pi$-conjugated; however, the attenuation factor for charge separation is much lower than normally observed for charge separation through a conductive $\pi$-conjugated bridge (0.32 - 0.66 Å⁻¹) and is in the range of polyynes (0.04 – 0.17 Å⁻¹). This surprisingly fast charge transport in the system indicates the presence of strong electronic interactions between the donor, acceptor, and bridge in the excited state and suggests a charge separation reaction that is mediated by the bridging foldamer. For that reason the logarithm of the charge separation rate constant in chloroform was also plotted against the distance through the bridge (Figure 2.5b). From this plot it is clear that either O5P or O9P deviates from the straight line that is formed by the data from the remaining molecules. The attenuation factor obtained in this way is again very low, $\beta_{CS} = 0.02 \text{ Å}^{-1}$ when discarding O5P and $\beta_{CS} = 0.06 \text{ Å}^{-1}$ when discarding O9P (Figure 2.5b), and remarkably similar to the result when the through space chromophore separation is used. Although the attenuation factor seems to be independent of the distance that is used to calculate it, one should remember that for all three methods a different foldamer is discarded from the calculations. Therefore, a uniform theoretical description of the charge separation by using either the separation distance through space or through bridge is not possible when using helical bridges to separate the chromophores.

![Figure 2.5](image-url)

**Figure 2.5.** Dependence of the charge separation rate constant in chloroform with the separation distance through space (a) or bridge (b). The black and gray values give the attenuation factors obtained directly from the linear fit (black; discarding O5P or gray; discarding O9P).

To shed more light on the low attenuation factor and the deviation of one of the foldamers with respect to the three others when calculating $\beta$, AM1 calculations were performed using SPARTAN (Wavefunction Inc.). Within a frontier molecular orbital (FMO) description, excitation with, e.g., 530 nm corresponds to local PB excitation and in the acceptor-reference compound C13-PB-P this corresponds to the HOMO-LUMO transition. The O2P, O4P, O5P, and O9P systems show analogous
electronic transitions. But, whereas the LUMO of these systems is very similar to the LUMO of the reference and entirely localized on the PB, the highest occupied molecular orbital that has a contribution on the PB unit also has a significant, but varying, electron delocalization into the foldamer bridge (Figure 2.6). Of course, there are additional lower lying doubly occupied orbitals that have a more pronounced PB contribution, but the delocalized orbitals depicted in Figure 2.6 will contribute to the “local PB excitation” and enhance the electronic coupling in the excited state between PB and OPV units. The HOMO-acceptor orbitals considered in Figure 2.6 serve to visualize how the π-systems of the separate foldamer units mix into the large aromatic PB localized orbital resulting in electron delocalization of the PB orbital over the foldameric part in an oscillating mode. Within a FMO description, excitation of the PB is followed by charge separation which can be viewed as a HOMO acceptor-HOMO donor interaction.

The relevant HOMO-acceptor orbital of O9P is shown in Figure 2.6d (in fact this is the HOMO-7 of the whole O9P system), the corresponding HOMO-donor orbital is mainly localized on the OPV but also has substantial orbital coefficients on the foldamer bridge (just like the HOMO-7 of the system, but not as extensive). The interaction of the HOMO and HOMO-7 strongly suggests electronic coupling through the foldamer bridge, and therefore, it is likely that the helical bridge mediates the charge transfer process. These calculations further support that charge separation through the bridge is achieved via the superexchange mechanism. In a similar way the charge recombination can be described by a LUMO-acceptor/HOMO-donor interaction. The fact that the LUMO of all four foldamers is very similar and localized on the PB correlates with the much higher attenuation factor for charge recombination that is derived from the experiments.

The electronic coupling through the foldamer bridge as visualized by the MO calculations occurs to a different extent for all foldamers and is expected to slightly modulate the molar absorption coefficients of the different systems (see UV/Vis in Figure 2.3). Because of the presence of only two bridge units in O2P, a significant amount of electronic coupling between the electron donor and acceptor exists which can account for the surprisingly fast charge separation reaction in this system (Figure 2.5a). This may explain the deviation of O2P from the other three oligomers when the distance

![Figure 2.6. Visualization of the highest doubly occupied molecular orbitals of the foldamers with a contribution on the PB unit for O2P (a), O4P (b), O5P (c) and O9P (d). These orbitals contribute to the locally PB excited state and give evidence of coupling with the bridge.](image-url)
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through space is used to obtain the attenuation factor (Figure 2.5a). This enhanced electronic coupling also makes it difficult to compare O2P with O9P and with that to ascertain the effect of chromophore orientation on the charge transfer processes. From the MO calculations it becomes apparent that although the number of monomeric units is higher in the nonamer O9P, the electronic coupling is more pronounced than in O5P, where it is almost absent (Figure 2.6c versus 2.6d). For this reason it seems more likely that in O9P the charge separation is mediated by the bridging foldamer and that O5P is the molecule that deviates when the distance through the bridge is used to determine the attenuation factor (Figure 2.5b).

The charge recombination rate decreases with increasing distance between the chromophores in the series O4P, O9P and O5P in both chloroform and toluene, while O2P deviates which is most likely caused by the enhanced electronic interaction between the donor and acceptor through the bridge. Similar to the charge separation rate, charge recombination in O4P and O2P is faster in the more polar solvent. This behaviour is characteristic of the Marcus inverted region for charge recombination\(^{33}\) which is normally observed for these chromophores when recombination occurs to their ground state.\(^{16}\) In contrast to the shorter oligomers, O9P and O5P in chloroform show a slower charge recombination reaction than in toluene which contradicts the expected behavior for a recombination reaction in the Marcus inverted region. This suggests that the molecules do not recombine directly to the ground state but that recombination proceeds via an intermediate higher-lying energy state, for instance a triplet state. From Figure 2.7 it becomes clear that the energy levels of the singlet charge separated state in toluene are somewhat higher than in chloroform. The difference in energies of the singlet charge separated state for the different foldamers as shown in Figure 2.7 follows from the different distances between the centers of the radical cations and anions in the charge separated state. The energies of the different triplet levels were obtained from previous studies.\(^{35}\) Since the energies of the charge separated states are all higher in energy than the PB triplet, charge recombination may result in the formation of PB triplets.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2.7}
\caption{Energy-level diagram for the chromophores and the corresponding charge separated states in the foldamers (the equation for the Gibbs energy of photoinduced electron transfer was used to calculate the energy levels of the charge separated states, see section 2.5) in chloroform (left) and toluene (right).}
\end{figure}
To probe whether charge recombination into triplet excited states occurs, near steady-state photoinduced absorption spectroscopy was employed to visualize the presence of the triplet state on the PB; the lowest triplet state in the system (Figure 2.7). In order to visualize the PB-triplet, C13-PB-P was sensitized with a fullerene derivative (PCBM) that produces the triplet state almost quantitatively while its higher-lying triplet state enables an energy transfer to the triplet state of C13-PB-P.

**Figure 2.8.** Near steady-state photoinduced absorption of O2P (black), O4P (red), O5P (green) and O9P (blue) in chloroform (a) and toluene (b) (λ_{exc} = 528 nm). The laser line is masked for clarity. The dashed curve are the results for a mixture of PCBM and the perylene bisimide reference, upon excitation of PCBM (λ_{exc} = 351 nm).

Excitation of the PB chromophore in each of the foldamers results in a spectrum (Figure 2.8) consisting of 2 small bands at λ = 504 nm (2.46 eV) and λ = 470 nm (2.64 eV) that are typical for the T-T\textsubscript{n} absorption of the PB.\textsuperscript{35a} Irrespective of the solvent, the shorter oligomers, O2P and O4P, showed marginal amounts of triplet formation, while for the longer oligomers, O5P and O9P, higher triplet yields of at least 20\% were obtained.\textsuperscript{36} The triplet excited state lifetime of the foldamers corresponds to that measured for C13-PB-P. The measurements show that, indeed, charge recombination to the triplet excited state occurs. This can explain the apparent absence of Marcus inverted region behavior for the charge recombination of O5P and O9P excited states. However, further investigation is necessary to determine why for these two systems charge recombination is faster in toluene than in chloroform. Recombination from a singlet charge separated state to a local triplet excited state can only occur if one of the electrons inverts its spin. Two mechanisms are known to describe the formation of triplet states from singlet charge separated states; radical pair and spin–orbit intersystem crossing.\textsuperscript{37} In radical pair intersystem crossing the spins in the singlet charge separated state dephase and evolve into the triplet charge separated state, followed by a charge recombination to a local triplet excited state (in this case that of the PB). In spin–orbit intersystem crossing charge recombination from the singlet charge separated state to the local triplet excited state occurs in one step involving a change in orbital magnetic momentum that is needed for the spin flip. It is noted that the energy of the charge separated state of O4P is the lowest of all. Since the radical cation and radical anion in O4P are close in space, it can be expected that the exchange energy in O4P is larger than for the other oligomers and places the energy of the triplet charge separated state below the triplet energy of PB. This would inhibit the radical pair mechanism from producing the PB triplet state as observed experimentally in
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chloroform and to lesser extent in toluene. However, at this point the distinction between the radical pair and the spin-orbit intersystem crossing mechanism cannot be made. Additional time resolved electron spin resonance measurements might be able to clarify the mechanism that is responsible for the formation of the PB triplet.

2.4 Conclusion

Electron donating (OPV) and electron accepting (PB) chromophores were successfully organized in predetermined three dimensional positions by covalent attachment to rigid helical scaffolds. This allowed the study of photoinduced charge transfer which could either occur through space or through the bridge. Molecular orbital calculations revealed significant electronic interactions through the bridging foldamer. With a variety of optical techniques it was shown that excitation of the PB leads to the formation of a charge separated state and that formation of triplet states can significantly contribute in the recombination pathway. All rates for charge separation were high and resulted in a surprisingly low attenuation factor, which is far below the value generally found for π-conjugated bridges. Attenuation factors were obtained by assuming charge separation through space or through bridge, but each time one different foldamer needed to be discarded because it did not correlate with the behaviour of the other three. Therefore, a uniform description in terms of the current theory does not hold when a helical foldameric biomimetic bridge is used as a scaffold to organize the chromophores. Whereas in Förster energy transfer theory the angle between the transition dipole moments of the photoactive units is explicitly taken into account, a similar orientation factor is less straightforward in charge transfer theory. The attenuation factor currently describes only the influence on the electronic coupling of the intervening medium at varying distance but at constant orientation. Such insights are relevant for the investigation of charge transfer processes in both synthetic as well as biological donor-bridge-acceptor systems.

2.5 Experimental Section

**General methods.** $^1$H NMR and $^{13}$C NMR spectra were recorded on a 400 MHz NMR (Varian Mercury, 400 MHz for $^1$H NMR and 100 MHz for $^{13}$C NMR) or a 500 MHz NMR (Varian Unity Inova, 500 MHz for $^1$H NMR and 125 MHz for $^{13}$C NMR) and Buker DMX 300. For $^1$H NMR and $^{13}$C NMR, chemical shifts are reported in ppm downfield from tetramethylsilane (TMS). Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. and used were without purification. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry has been performed on a PerSeptive Biosystems Voyager-DE PRO spectrometer. For recycling SEC, an apparatus consisting of a Shimadzu LC-10AD VP Liquid Chromatograph, a Shimadzu SPD-10AV VP UV/Vis detector, and two JAIGEL columns (2.5 H and 2 H) from Japan Analytical Industry was used with HPLC grade chloroform as the eluent, while the flow rate was 3.5 mL/min. UV/vis spectra were recorded on a Perkin Elmer Lambda 900 UV/vis/NIR spectrometer, CD spectra on a Jasco J-815 spectropolarimeter and steady-state fluorescence spectra on an Edinburgh Instruments FS920 double-monochromator luminescence spectrometer equipped with a Peltier-cooled red-sensitive photomultiplier. The emission spectra were corrected for the wavelength dependence of the detection system. Time-correlated Single Photon Counting measurements were performed using an Edinburgh Instruments LifeSpec-PS spectrometer comprising a 400 nm picosecond laser (PicoQuant PDL 800B) operated at 2.5 MHz and by detection with a Peltier-cooled Hamamatsu micro-channel plate photomultiplier (R3809U-50). The data were deconvoluted with an instrument response function recorded using dispersed light and fitted to a mono or a multiexponential function using the Fluofit package (Picoquant, Berlin). All solvents were of AR quality. Dichloromethane was...
freshly distilled over potassium/sodium, DIPEA over CaH₂, DMF was dried over 4Å molsieves. Other reagents used were purchased from Acros and Aldrich and have been used without further purification. For near steady-state PIA, the solutions contained $c = 5 \times 10^{-4}$ M and were prepared in a glovebox with less than 5 ppm oxygen in its atmosphere. The PIA spectra were recorded between 2.0 and 2.7 eV by exciting with a mechanically modulated cw Ar ion laser ($\lambda = 361$ nm or $\lambda = 528$ nm, 275 Hz) pump beam and monitoring the resulting change in transmission of a tungsten-halogen probe light through the sample ($\Delta T$) with a phase-sensitive lock-in amplifier after dispersion by a grating monochromator and detection, using Si, InGaAs, and cooled InSb detectors. The pump power incident on the sample was typically 25 mW with a beam diameter of 2 mm. The PIA (-$\Delta T/T = ad$) was directly calculated from the change in transmission after correction for the photoluminescence, which was recorded in a separate experiment. Photoinduced absorption spectra and photoluminescence spectra were recorded with the pump beam in a direction almost parallel to the direction of the probe beam. The solutions were studied in a 1 mm near-IR grade quartz cell at room temperature. Femtosecond photoinduced absorption experiments were performed with a Spectra-Physics Hurricane Titanium:Sapphire regenerative amplifier system. The full spectrum setup was based on an optical parametric amplifier (Spectra-Physics OPA 800C) as the pump. The residual fundamental light, from the pump OPA, was used for white light generation. The polarization of the pump light was controlled by a Berek Polarization Compensator (New Focus). The Berek Polarizer was always included in the setup to provide the Magic-Angle conditions. The probe light was double-passed over a delay line (Physik Instrumente, M-531 DDD) that provides an experimental time window of 3.6 ns with a maximal resolution of 0.6 fs/step. The OPA was used to generate excitation pulses at 530 nm. The laser output was typically 3.5-5 µJ pulse$^{-1}$ (130 fs FWHM) with a repetition rate of 1 kHz. The samples were placed into cells of 2 mm path length (Hellma) and were stirred with a downward projected PTFE shaft, using a direct drive spectro-stir (Spectrocell). This stir system was also used for the white light generation in a 2 mm water cell. For femtosecond transient absorption in the NIR region a Control Development NIR-256L-1.7T1-USB, optical spectrometer system, InGaAs detector with 512 element arrays responding to wavelengths range from 900-1700 nm, was used. Detection light was generated with a sapphire plate. For time resolved photoinduced absorption spectroscopy, samples were dissolved in spectroscopic solvents and filtered (0.4 µm PVDF HPLC-filters) to remove particles and potential aggregates. The samples had an absorbance of ca. 0.3 – 0.7 (2 mm) for femtosecond transient at the excitation wavelength. The UV/Vis absorption spectra of the samples were measured before and after the laser experiments and were found to be virtually identical, thus ruling out any possible degradation or chemical change of the samples. All photophysical data reported here have a 5 to 10 % error limit, unless indicated otherwise. The experiments were performed at room temperature. Cyclic voltammograms were recorded in an inert atmosphere with 0.1 M tetrabutyl ammonium hexafluorophosphate (TBAPF₆) in dried dichloromethane as supporting electrolyte. The working electrode was a platinum disc (0.2 cm$^2$) and the counter electrode was a silver electrode. The samples were measured using an Ag/AgCl reference electrode using a µAutolab II with a PCSTAT30 potentiostat. The used distances and angles have been determined using the optimized MM2 calculated structures. The distance through the bridge has been determined from the structures, while taking the shortest distance through the bridge.

**Synthesis and characterization.**

**Nitro-dimer-Perylene (6).** HBTU (30.4 mg, 0.08 mmol, 1.5 eq), HOBT (7.2 mg, 0.0533 mmol, 1 eq), N,N-diisopropylethylamine (44 µL, 5 eq) were added to a solution of 5 (28.4 mg, 0.053 mmol, 1 eq) in DMF (1 ml) and stirred for 30 min at room temperature in an inert atmosphere. The solution was added in a dropwise manner to a suspension of 1 (35.4 mg, 0.053 mmol, 1 eq) in DMF (0.5 ml) and CHCl₃ (2 mL). The solution was stirred for 24 hrs under an inert atmosphere at room temperature after which toluene (10 ml) was added and the organic layers were washed with a saturated NaHCO₃ solution (10 ml). After the organic layer was dried over Na₂SO₄ and filtered, the solvent was evaporated. The compound was purified further with column chromatography (SiO₂, 7.5 % ethyl acetate in chloroform, TLC in 10% ethyl acetate in CHCl₃). After precipitation in cold methanol 40 mg (64 %) as a red solid material was obtained. $^1$H NMR (CDCl₃, 400 MHz): δ (ppm) 11.65 (s, 1H, NH), 10.25 (s, 1H, NH), 8.88 (dd, 1H, ArH), 8.62-8.74 (m, 8H, ArH), 8.55 (dd, 1H, ArH), 8.27 (dd, 1H, ArH), 8.09 (dd, 1H, ArH), 7.92 (s, 1H, ArH), 7.91 (s, 1H, ArH), 7.84 (d, J = 8 Hz, 2H, ArH), 7.72-7.62 (m, 2H, ArH), 7.19 (d, J = 8 Hz, 2H, ArH), 5.17 (q, 1H, CH), 4.17 (d, J = 9 Hz, 2H, CH₂), 4.12 (d, J = 9 Hz, 2H, CH₂), 2.40-2.20 (m, 4H, CH₂ and CH), 1.85 (kw, 2H, CH₂), 1.50-1.10 (m, 32 H, CH₂ and CH₃), 0.95 (t, 6H, CH₃). MALDI-TOF MS (calc MW = 1178.37; C₂₂H₁₇N₄O₆): 1177.38 [M⁺].

**Amine-dimer-perylene (7).** 10 % Pd/C (2 mg) was added to a solution of 6 (20 mg, 0.017 mmol, 1 eq) in CHCl₃ (20 mL) and subsequently put under H₂ (60 psi) and shaken for 19 hrs resulting in 20 mg (100 %) of 7 as a red solid. $^1$H NMR (CDCl₃, 400 MHz): δ (ppm) 11.95 (s, 1H, NH), 10.05 (s, 1H, NH), 8.88 (dd, 1H, ArH), 8.74-8.62 (m,
7.54 (d, J = 8 Hz, 2H, ArH), 7.38-7.27 (m, 2H, ArH), 6.98 (d, J = 8 Hz, 2H, ArH), 5.17 (q, 1H, CH), 4.13 (d, J = 9 Hz, 2H, CH₂), 4.09 (d, J = 9 Hz, 2H, CH₂), 2.40-2.30 (m, 4H, CH₂ and CH₃), 1.85 (kw, 2H, CH₂), 1.70-1.10 (m, 34 H, CH₂ and CH₃), 0.95 (t, 6H, CH₃). MALDI-TOF MS (calc MW = 1148.38; C₆₇H₄N₆O₈S): 1147.47 [M⁺].

OPV3-dimer-Perylene (O2P), N,N-diisopropylethylamine (25 μL, 5 eq) and acid chloride 2 (26 mg, 0.029 mmol, 1 eq) was dissolved in dry CHCl₃ (1 mL) under an inert atmosphere. Amine 7 was dissolved in dry CHCl₃ (1 mL) and slowly added to the reaction mixture. The reaction was allowed to run for 17 hrs under an inert atmosphere after which the reaction was stopped by addition of saturated solution of NaHCO₃ (10 mL). The aqueous phase was extracted with CHCl₃ (3 × 10 mL). The combined organic layers were dried over Na₂SO₄, filtered and the solvent was evaporated. The residue was further purified using silica column chromatography (eluents: 1 % Methanol in CHCl₃, biodegradable STH) resulting in 44 mg (80 %) O2P.

Recycling SEC afforded 17 mg extremely pure O2P as an orange solid. ¹H NMR (CDCl₃, 500 MHz): δ (ppm): 12.05 (s, 1H, NH); 11.85 (s, 1H, NH); 9.60 (s, 1H, NH); 9.10 (d, 1H, ArH); 8.95 (s, 1H, ArH); 8.75 (2 d, J = 8 Hz, 8H, ArH); 8.50 (d, J = 8 Hz, 1H, ArH); 7.85 (s, 1H, ArH); 7.70 (dd, J = 8 Hz, 1H, ArH); 7.65 (dd, J = 8 Hz, 1H, ArH); 7.60 (2H, ArH); 7.55 (d, J = 16 Hz, 1H, CH=CH); 7.52 (d, J = 16 Hz, 1H, CH=CH); 7.50 (d, J = 8 Hz, 2H, ArH); 7.35 (d, J = 16 Hz, 1H, CH=CH); 7.19 (s, 1H, ArH); 7.16 (d, J = 16 Hz, 1H, CH=CH); 7.11 (d, 2H, ArH); 7.09 (d, J = 16 Hz, 1H, CH=CH); 6.75 (s, 1H, ArH); 6.25 (s, 1H, ArH); 5.05 (q, 1H, NCH₂); 4.2-3.4 (m, 16H, OC₃H₇); 2.4–0.2 (m, 97H, C₂H₅O). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 164.0; 163.6; 163.5; 163.0; 160.5; 151.8; 151.2; 151.0; 150.5; 150.4; 150.1; 150.0; 138.5; 138.2; 137.6; 135.5; 134.9; 134.5; 134.2; 133.8; 133.6; 132.7; 126.6; 126.5; 125.5; 125.1; 123.6; 123.2; 123.1; 122.9; 122.4; 122.2; 121.7; 121.3; 119.1; 118.5; 118.3; 117.0; 116.3; 115.6; 115.4; 110.1; 109.9; 109.5; 108.3; 99.2; 75.9; 75.5; 75.4; 74.7; 74.3; 73.6; 73.4; 54.8; 35.2; 35.0; 34.4; 32.4; 31.9; 30.3; 29.2; 28.2; 28.0; 26.9; 26.6; 26.4; 26.3; 25.7; 22.3; 19.3; 18.9; 16.8; 16.7; 16.4; 16.0; 14.30; 11.6; 11.5; 11.4; 10.8. MALDI-TOF MS (calc MW = 1987.60; C₆₇H₄N₆O₈S): 1987.09 [M⁺].

Boc-protected Quinoline tetramer ester (9). To a solution of tetramer amine ester 8 (180 mg, 0.18 mmol, 1 eq) in dioxane (3 mL) was added Boc anhydride (130 mg, 0.6 mmol) and a catalytic amount of DMAP (10 mg). The reaction mixture was stirred at 40°C for 16 hours. The solvent was removed and the crude product was purified by chromatography on silica-gel eluting with DCM/MeOH 99:1 v:v to provide the expected acid 9 (67 mg, 0.1 mmol, 2.5 eq) and DIPEA (95 μL, 0.55 mmol, 14 eq) was dissolved in a mixture of dried DCM/CHCl₃/THF (3.5 mL) under nitrogen. The acid chloride was then added in the amine mixture through a
canula at 0°C. The reaction mixture was stirred at 0°C for 30 minutes then at room temperature for 16 hours. The reaction mixture was washed once with a saturated NaHCO₃ solution, once with water, once with a 1N HCl solution and then with a saturated NaCl solution. The organic phase was dried over NaSO₄, filtered, evaporated and then the crude product was purified by chromatography on silica gel eluting with DCM/MeOH (99/1, v:v) to afford 47 mg of a red solid 12 (68%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 12.33 (1H, s); 11.98 (1H, s); 11.25 (1H, s); 9.28 (1H, s); 9.21 (1H, d, J = 7.6 Hz); 8.79-8.64 (11H, m); 8.25 (1H, s); 8.13 (1H, d, J = 8.3 Hz); 8.00 (3H, d, J = 7.4 Hz); 7.85 (1H, d, J = 8.1 Hz); 7.66 (2H, t, J = 8.1 Hz); 7.52-7.42 (3H, m); 7.34 (1H, t, J = 8.1 Hz); 7.27-7.16 (2H, m); 7.10 (1H, s); 7.01 (1H, s); 5.20 (1H, m); 4.38-4.27 (2H, m); 4.17-3.93 (6H, m); 2.54-2.24 (6H, m); 1.89 (2H, m); 1.32-1.18 (44H, m); 0.84 (6H, m).

Perylene tetramer amine (13). Compound 12 (21 mg, 12 μmol, 1 eq) was dissolved in a 1:1 (volumetric ratio) mixture of trifluoroacetic acid and CH₂Cl₂ and stirred at room temperature for 3 hours after which the solvent was evaporated. The residue was redissolved in CH₂Cl₂ (10 mL) and washed with 5 mL saturated NaHCO₃ solution. The organic layer was dried over NaSO₄, filtered and after evaporation of the solvent 17 mg (86 %) 13 was obtained as a red solid. The compound was immediately used for the next reaction.

OPV Tetramer Perylene (O4P). Acid chloride 2 (20 mg, 22 μmol, 2 eq) was dissolved in dry CH₂Cl₂ (0.25 mL) and added via a canula under an inert atmosphere to a solution of 13 (17 mg, 10 μmol, 1 eq) and N,N-diisopropylethylamine in dry CH₂Cl₂ (0.2 mL). The solution was stirred for 20 hrs at room temperature after which the reaction was stopped by addition of a saturated solution of NaHCO₃ (10 mL). The aqueous phase was washed with CHCl₃. The combined organic layers were dried over NaSO₄ and the solvent was evaporated. The solid material was purified by silica chromatography (eluent: CHCl₃) yielding 22 mg of O4P. After purification with recycling SEC 5 mg O4P was obtained as an orange solid. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 12.05 (s, 1H, NH); 11.95 (2s, 1H, NH, diastereoisomers); 11.45 (s, 1H, NH); 11.15 (s, 1H, NH); 9.15 (s, 1H, NH); 8.7-8.5 (m, 12H, ArH); 8.3-7.9 (m, 7H, ArH); 7.7-7.5 (m, 5H, ArH and CH=CH); 7.4-7.0 (m, 12H, ArH and CH=CH); 6.8 (s, 1H, ArH); 6.35 (2s, 1H, ArH, diastereoisomers); 5.3 (q, 1H, NCH); 4.4-3.6 (m, 20H, OCH); 3.0-0.2 (m, 111H, CH and ArCH₃). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 163.7; 163.1; 162.4; 161.3; 160.7; 160.2; 151.8; 151.2; 150.9; 150.6; 149.6; 149.1; 148.6; 138.2; 137.7; 137.2; 134.9; 134.6; 133.5; 131.9; 130.1; 129.6; 127.9; 127.2; 126.5; 125.1; 123.5; 122.3; 121.5; 118.5; 117.3; 116.8; 116.4; 76.1; 75.4; 74.6; 35.1; 32.4; 31.8; 29.7; 29.3; 28.3; 27.0; 26.3; 22.6; 19.4; 16.8; 14.1; 11.5; 16.8; 14.1; 11.5; 10.7. MALDI-TOF MS (calc. MW = 2470.31, C₁₅₁H₁₁₁N₁₁O₁₀) = 2470.63 [M⁺]

Saponification of oligomers: The OP oligomer esters (1 eq) and NaOH (2.5 eq) were dissolved in a mixture THF/MeOH (10:1 v:v). The reaction mixture was stirred at 40°C for 16 hours and neutralized with acetic acid. The solvents were evaporated, the crude mixture was diluted in DCM and washed three times with water. The organic phase was dried over NaSO₄, filtered and evaporated. The crude product was purified by chromatography on silica gel eluting with DCM/MeOH 99:1 v:v to provide a solid only characterized by ¹H NMR.

Formation of acid chlorides. The different acids (1 eq) were dissolved in anhydrous DCM under inert atmosphere. Chloroanamine (excess) was added and the reaction mixture was stirred at room temperature for 10 minutes to 16 hours depending on the compound. The solvent was removed then the crude was dried in vacuo for 4 hours. The acid chlorides (not characterized) were used without further purification.

Couplings: In a round bottom flask, the acid chloride (1 eq) was dissolved in dried DCM under nitrogen atmosphere. In a second round bottom flask, the amine (excess) and DIPEA (5.5 eq) were dissolved in dried DCM (or in THF, depending on the compound) under nitrogen. The acid chloride was then added in the amine mixture through a canula at 0°C under an inert atmosphere. The reaction mixture was stirred at 0°C for 30 minutes then at room temperature (2 hours for OPV monomer 15, 16 hours for the others). The reaction mixture was washed once with a saturated NaHCO₃ solution, once with water, once with a 1N HCl solution and then with a saturated NaCl solution. The organic phase was dried over NaSO₄, filtered, evaporated then the crude was purified by chromatography on silica gel.
OPV Monomer acid (16). 15 (76 mg, 0.068 mmol, 1 eq) was dissolved in a mixture THF/MeOH (2.0 mL/ 0.2 mL) and KOH (12 mg, 0.204 mmol, 3 eq) was added. The reaction mixture was stirred at room temperature for 2 hours, and then neutralized with acetic acid (100 μL). The solvents were evaporated, the crude mixture was diluted in DCM and washed three times with water. The organic phase was dried over NaSO₄, filtered and evaporated to provide a solid characterized by 1H NMR and used without further purification (70 mg, 95% yield).

1H NMR (CDCl₃, 300 MHz) δ (ppm): 11.65 (1H, s); 9.04 (1H, d, J = 7.7 Hz); 8.00 (1H, d, J = 8.3 Hz); 7.77 (1H, s);7.73-7.68 (2H, m); 7.62 (1H, m); 7.54 (1H, m); 7.51 (1H, s); 7.48 (1H, m); 7.42 (1H, s); 7.20 (1H, s); 7.19 (1H, s); 7.10 (1H, s); 6.73 (1H, s); 4.23 (1H, m); 4.11 (2H, d, J = 6.3 Hz); 4.06-3.74 (11H, m); 2.32 (1H, m); 2.25 (3H, s); 1.96 (7H, m); 1.67-0.95 (31H, m).

OPV Monomer acid chloride (17). According to the general procedure of acid chloride formation, OPV monomer acid 16 (23 mg, 0.021 mmol, 1 eq) was dissolved in anhydrous DCM (0.5 mL). Chloroamine (9 μL, 0.063 mmol, 3 eq) was added and the reaction mixture was stirred at room temperature for 2 hours (23 mg, yield 99%).

OPV Pentamer ester (18). The acid chloride 17 (23 mg, 0.021 mmol, 1 eq) dissolved in DCM (100 μL) and the amine 4 (25 mg, 0.025 mmol, 1.2 eq) dissolved in DCM (300 μL) were coupled following the general couplings procedure with DIPEA (20 μL, 0.116 mmol, 5.5 eq). The crude was submitted to silica gel chromatography using DCM/MeOH 99:0.5 v:v, following by a second purification on silica gel with a chromatotron using heptane/DCM from 30:70 to 0:100 v:v to provide 27 mg of the product (61% yield). 1H NMR (CDCl₃, 400 MHz) δ (ppm): 11.83 (1H, s); 11.76 (1H, s); 11.74 (1H, s); 11.47 (1H, s); 11.21 (1H, s); 8.68 (1H, d, J = 7.4 Hz); 8.27 (1H, d, J = 7.7 Hz); 8.17-8.78 (7H, m); 7.78-7.61 (4H, m); 7.54-7.10 (11H, m); 7.00 (1H, s); 6.84 (1H, s); 6.82 (1H, s); 6.76 (1H, s); 6.51 (1H, s); 6.05 (1H, s); 4.42 (1H, m); 4.34-4.15 (5H, m); 4.10-3.74 (23H, m); 3.64 (3H, s); 3.16 (3H, s); 2.84-0.69 (82H, m).

OPV Pentamer acid chloride (19). According to the general saponification procedure, NaOH (1 mg, 0.024 mmol, 2.5 eq) was added to a solution of 18 (21 mg, 0.010 mmol, 1 eq) in a mixture THF/MeOH (280/28 μL). The crude was submitted to silica gel chromatography using DCM/MeOH 99:1 v:v to provide 20 mg of the product (56% yield). 1H NMR (CDCl₃, 400 MHz) δ (ppm): 11.19 (1H, s); 11.16 (1H, s); 11.12 (1H, s); 11.09 (1H, s); 8.69 (1H, d, J = 7.4 Hz); 8.38 (1H, d, J = 7.7 Hz); 8.17-7.94 (10H, m); 7.82-7.30 (7H, m); 7.12-7.09 (4H, m); 7.02 (1H, s); 6.95 (1H, s); 6.87 (1H, s); 6.76 (2H, m); 6.62 (1H, s); 6.06 (1H, s); 4.42 (1H, m); 4.19 (6H, m); 3.98 (8H, m); 3.91-3.81 (14H, m); 3.64 (3H, s); 2.65-0.71 (82H, m).

OPV Nonamer acid chloride (20). According to the general procedure of acid chlorides formation, OPV pentamer acid 20 (20 mg, 0.010 mmol, 1 eq) was dissolved in anhydrous DCM (0.2 mL). Chloroamine (4 μL, 0.030 mmol, 3 eq) was added and the reaction mixture was stirred at room temperature for 16 hours (21 mg, yield 100%).

OPV Nonamer ester (21). The acid chloride 20 (53 mg, 0.047 mmol, 1 eq) dissolved in DCM (0.3 mL) and the amine 4 (100 mg, 0.052 mmol, 1.1 eq) dissolved in DCM (1 mL) were coupled following the general couplings procedure with DIPEA (45 μL, 0.259 mmol, 5.5 eq). The crude product was submitted to silica gel chromatography using DCM/EtN₃ 99:1 v:v, following by a second purification on silica gel with a chromatotron using heptane/DCM from 30:70 to 0:100 v:v to provide 80 mg of the product (56% yield). 1H NMR (CDCl₃, 300 MHz) δ (ppm): 11.36 (1H, s); 11.26 (1H, s); 11.16 (1H, s); 10.84 (1H, s); 10.80 (1H, s); 10.77 (1H, s); 10.75 (1H, s); 10.72 (1H, s); 10.61 (1H, s); 8.13 (1H, d, J = 7.7 Hz); 8.06-7.58 (13H, m); 7.48 (2H, s); 7.37-6.91 (14H, m); 6.81 (1H, s); 6.75 (2H, s); 6.74 (1H, s); 6.58 (1H, s); 6.52 (1H, s); 6.40 (2H, s); 6.32 (1H, s); 6.19 (1H, s); 6.14 (1H, s); 5.77 (1H, s); 4.09-3.46 (44H, m); 2.95 (3H, s); 2.56-1.83 (26H, m); 1.79-0.78 (68H, m); 0.71-0.56 (12H, m).

OPV Nonamer acid chloride (22). According to the general procedure of acid chlorides formation, OPV Nonamer acid 21 (30 mg, 0.010 mmol, 1 eq) was dissolved in anhydrous DCM (1 mL). Chloroamine (4 μL, 0.030 mmol, 3 eq) was added and the reaction mixture was stirred at room temperature for 16 hours (31 mg, yield 99%).

OPV Pentamer Perylene (OSP). According to the general couplings procedure, perylene amine 1 (16 mg, 0.024 mmol, 2.5 eq) and the DIPEA (10 μL, 0.053 mmol, 5.5 eq) were dissolved in THF (2 mL) then added in a solution of acid chloride 22 (20 mg, 0.010 mmol, 1 eq) in DCM (200 μL). The crude was submitted to silica gel
chromatography using DCM/MeOH 99.5:0.5 v:v, following by a second purification on silica gel with a chromatotron using again DCM/MeOH 99.5:0.5 v:v. Finally, the compound was precipitated in MeOH and recovered by centrifugation to provide 13 mg of the product (55% yield) which was further purified by recycling SEC. 1H NMR (400 MHz, CDCl3) δ (ppm): 11.8, 11.7, 11.5, 11.2, (5H, NH): 9.0 (1H, NH); 8.7 (8H, ArH); 8.3 (1H, ArH, d); 8.2-7.9 (11H, ArH); 7.7-6.0 (23H, ArH); 5.2 (1H, q); 4.2-3.6 (22H, OCH2); 2.6-0.4 (117H, alkyl H). MALDI-TOF MS (calc. MW = 2721.41, C50H36N6O3): 2721.57 [M].

**OPV Nonamer Perylene** (O9P). According to the general couplings procedure, perylene amine 1 (16 mg, 0.052 mmol, 2.5 eq) and the DIPEA (10 μL, 0.053 mmol, 5.5 eq) were dissolved in THF (2 mL) then added to a solution of acid chloride 23 (30 mg, 0.010 mmol, 1 eq) in DCM (1 mL). The crude was submitted to silica gel chromatography using DCM/MeOH 99.5:0.5 v:v, followed by a second purification on silica gel with a chromatotron using again DCM/MeOH 99.5:0.5 v:v. Finally, the compound was precipitated in MeOH and recovered by centrifugation to provide 13 mg of the product (36% yield) which was subsequently purified by recycling SEC. 1H NMR (400 MHz, CDCl3) δ (ppm): 11.3-10.5 (9H, NH); 8.8-8.6 (9H, NH + ArH); 8.2-6.8, 6.4-6.1, 5.9 (50H, ArH); 5.2 (1H, q); 4.2-3.4 (30H, OCH2); 2.6-0.4 (146H, alkyl H). MALDI-TOF MS (calc. MW = 3680.83, C222H369N30O3): 3680.10 [M⁺].

**Scheme 2.2.** The synthetic procedure for the tetramer model compound.

**Tetramer nitro-amide (25).** To a solution of the tetramer nitro-ester 24 (200 mg, 0.194 mmol, 1 eq) in a mixture THF/MeOH (3.6/0.4 mL) was added aqueous methylamine (1 mL, 28.9 mmol, 149 eq). The reaction mixture was stirred at 40°C overnight. The completion was monitored by TLC (DCM/MeOH 99/1 v:v). The mixture THF/MeOH (3.6/0.4 mL) was added aqueous methylamine (1 mL, 28.9 mmol, 149 eq). The reaction mixture was stirred overnight at room temperature. The solvents were removed and dichloromethane (20 mL) and water (20 mL) were added. The aqueous layer was extracted 3 times (20 mL) with DCM and the combined organic layer was dried over Na2SO4, filtered and concentrated under vacuum. The crude was submitted to silica-gel chromatography eluting with DCM/MeOH 99/1 v:v to afford 96 mg (90% yields) of the expected compound.

**Tetramer amine-amide (26).** To a solution of the tetramer nitro-ester 24 (16 mg, 0.010 mmol, 1 eq) in DCM (1 mL). The crude was submitted to silica gel chromatography eluting with DCM/MeOH 99/1 v:v to afford 165 mg (85% yields) of the expected compound. 1H NMR (CDCl3; 400 MHz) δ (ppm): 12.32 (1H; s); 11.66 (1H; s); 11.32 (1H; s); 8.58 (1H; d; J=8.3 Hz); 8.35 (1H; d; J=7.6 Hz); 8.16 (1H; d; J=7.6 Hz); 8.04 (2H; d; J=8.8 Hz); 7.94 (1H; d; J=8.0 Hz); 7.85 (1H; s); 7.78 (1H; t; J=8.3 Hz); 7.62 (1H; d; J=8.1 Hz); 7.57 (1H; t; J=8.1 Hz); 7.51 (1H; s); 7.40 (1H; t; J=7.6 Hz); 7.29-7.22 (3H; m); 6.91 (1H; s); 6.80 (1H; s); 4.30-4.23 (4H; bm); 3.90 (4H; m); 2.53 (3H; d; J=4.6 Hz); 2.51-2.28 (4H; m); 1.30-1.18 (24H; m).

**Tetramer amine-amide (27).** The tetramer amine-amide 26 (102 mg, 0.010 mmol, 1 eq) was dissolved in ethyl acetate (5 mL) in a Parr container. Pd on carbon was added (10 mg) and air was replaced by H2. The reaction mixture was shaken under H2 atmosphere (2 bars) overnight. After completion, the crude was filtered through celite and the organic phase was concentrated to afford quantitatively (86 mg) the amine. 1H NMR (CDCl3; 400 MHz) δ (ppm): 12.48 (1H; s); 11.75 (1H; s); 11.68 (1H; s); 9.00 (1H; d; J=7.7 Hz); 8.41 (1H; d; J=7.7 Hz); 8.06-7.99 (3H; m); 7.88 (1H; d; J=8.3 Hz); 7.75 (1H; t; J=7.2 Hz); 7.74 (1H; s); 7.61 (1H; t; J=8.1 Hz); 7.53 (1H; d; J=7.6 Hz); 7.34 (1H; s); 7.31-7.23 (3H; m); 7.02 (1H; t; J=7.9 Hz); 6.93 (1H; s); 6.78 (1H; s); 5.96 (2H; d; J=7.4 Hz ); 4.30-4.19 (4H; bm); 3.90 (4H; m); 2.59 (3H; d; J=4.9 Hz); 2.50-2.27 (4H; m); 1.26-1.19 (24H; m).

**Scheme 2.2.** The synthetic procedure for the tetramer model compound.
Specification of the fitting equation and procedure for the time traces of the femtosecond photoinduced absorption measurements

$S_1$-$S_n$ absorption should show an exponential decay corresponding to $-e^{-t/\tau_{CS}}$.

PB$^+$ absorption should show an exponential rise (CS) and exponential decay (CR) corresponding to $e^{-t/\tau_{CS}} - e^{-t/\tau_{CR}}$.

At 961 and 911 nm both the $S_1$-$S_n$ absorption and the PB$^+$ absorption contribute to the signal, therefore, the two equations should be added to each other. The difference in contribution at each wavelength can be corrected by using pre-exponential factors. The offset in $t$ and $\Delta$ absorbance direction will be corrected by introducing $t_0$ and $y_0$ in the equations. An additional exponential term is added to account for the solvent reorganization. Therefore, the fitting equation for the two wavelengths will result in:

911 nm:

$$y = y_0 + A_1 e^{-t/\tau_{CS}} + A_2 e^{-t/\tau_{CR}} - A_3 e^{-t/\tau_{CS} \tau_{CR}} + A_4 e^{-t/\tau_t}$$

961 nm:

$$y = y_{0.2} + A_{1.2} e^{-t/\tau_{CS}} + A_{2.2} e^{-t/\tau_{CR}} - A_{3.2} e^{-t/\tau_{CS} \tau_{CR}} + A_{4.2} e^{-t/\tau_t}$$

This equation is used to simultaneously fit the two curves with taking the lifetimes and a fixed $t_0 = 1.31$ the same for the two wavelengths.

Prediction of the Gibb’s free energy for electron transfer. The semi-quantitative model described by Weller can be used to estimate the Gibb’s free energy ($\Delta G_0$) for electron transfer on the basis of the relative permittivity ($\varepsilon$) of the solvent:

$$\Delta G_0 = -e[E_{\text{ex}}(D) - E_{\text{red}}(A)] + E_{00} + \frac{e^2}{4\pi\varepsilon_s\varepsilon_0 R_{cc}} + \frac{e^2}{8\pi\varepsilon_0} \left( \frac{1}{r^+} + \frac{1}{r^-} \right) \left( \frac{1}{\varepsilon_{\text{ref}}} - \frac{1}{\varepsilon_s} \right)$$

in which $E(S_i)$ is the energy of the lowest singlet excited state, $e$ and $\varepsilon_0$ are the elementary charge and the vacuum permittivity, $E^\text{r}(D/D^\text{r})$ and $E^\text{a}(A/A^\text{a})$ are the redox potentials of the electron donating and accepting part of the molecule measured in a solvent with relative permittivity $\varepsilon_{\text{ref}}$, $R_{cc}$ is the center-to-center distance of the two charges, and $r^+$ and $r^-$ are the radii of the positively and negatively charged species. The results were obtained by using the following parameters: a solvent-dependent $E(S_i)$, from the emission maximum of C13-PB-P, $E^\text{r}(D/D^\text{r}) = +0.915$ V, and $E^\text{a}(A/A^\text{a}) = -1.040$ V vs. Fe/Fe$^\text{r}$ in dichloromethane, and $r^+ = r^- = 4.7$ Å, and $R_{cc} = R_{DA}$ in Å which is stated in the main text.

2.6 References and notes


Chapter 2


When the edge-to-edge distance was used, the attenuation factor was $K_{\text{att}} = 0.09 \, \text{s}^{-1}$ when discarding OSP from the fit.
Chapter 2


36 During the experiments evidence emerged that the chemical stability of the compounds were limited as a result of the triplet formation. This hampered the exact determination of the triplet quantum yields.


40 This compound exists as a mixture of diastereoisomers (chirality from the helix and the OPV). Here only the $^1$H NMR spectrum of one of the two diastereoisomers is reported.


The role of purity and cooling protocol on the self-assembly of oligothiophenes

Abstract. The self-assembly of chirally substituted, ultra-high purity oligothiophenes (sexi- and septithiophenes) was investigated using temperature-dependent UV/Vis and CD spectroscopy. It was shown that the self-assembly can be characterized by heterogeneous nucleation due to very small quantities of impurities and evidence emerges that only in their most pure form are the thiophenes likely to self-assemble homogeneously. The impurities, present in less than 0.1 %-molar concentration, enable the supramolecular polymerization to start at higher temperatures than is the case for the highest purity samples studied, whilst different supramolecular morphologies are obtained. Also the cooling rate influences both the supramolecular organization and the rate of ordering; e.g. a clear example of stereomutation is encountered for septithiophene assemblies. Hence, by applying different self-assembly protocols, the oligothiophenes can be guided towards a variety of supramolecular organizations. The findings indicate a complex energy landscape for the supramolecular polymerization of oligothiophenes.
3.1 Introduction

Semi-conducting π-conjugated polymers and oligomers are promising materials for applications in flexible plastic and organic electronic devices.\(^1\) Especially thiophene-based structures display intriguing properties.\(^2\) Hence, oligo- and polythiophene synthesis and device fabrication have been intensively optimized and remarkable sensitivities are observed for the device performance dependent on the molecular structure and the morphology determined by the fabrication protocol.\(^3\) Following the rapid development of the use of semi-conducting polymers for bulk plastic electronics, the use of self-assembled π-conjugated oligomers has created the field of supramolecular electronics.\(^4\) This makes the self-assembly behavior of these oligomers and polymers a topic of increasing interest;\(^5\) it is the exact control of the intermolecular orientation of the molecules in the aggregate or bulk that determines the overall performance of the device.\(^1\) This was demonstrated for the anisotropic mobility in regioregular 3-alkyl-polythiophenes.\(^6\) The observed macroscopic differences could be assigned to morphological mutations that in turn are the result of differences in the self-assembly pathways. A striking example is the observed stereomutation of chiral polythiophenes by changing the cooling rates from the melt.\(^7\) An increased knowledge of the self-assembly of thiophene derivatives would lead to a better understanding of the origin of the observed subtleties that show an influence on the molecular organization.

In the past, manifolds of self-assembled structures have been produced by a variety of preparation methods.\(^8\) With the exception of a few examples,\(^9,10\) it is usually assumed that molecular components self-assemble into the thermodynamically most stable aggregate.\(^11,12\) It is only recently that kinetically controlled aggregates have been taken into account.\(^9,12\) Previously, it was shown that the self-assembly of π-conjugated (p-phenylene vinylene) oligomers in alkane solvents is governed by a nucleation-growth mechanism (see Chapter 1) and the presented results show that in that case the nucleation is homogenous in nature.\(^13\) The group of Pasternack\(^14\) and Purrello\(^15\) independently showed the ability of seeds to nucleate the supramolecular polymerization of porphyrin derivatives. Nucleation was achieved onto seeds consisting of pre-assembled molecules eventually yielding supramolecular polymers. In addition, Purrello et al. showed that the seeds were able to retain a memory of the chirality in its previously self-assembled structure and transfer this chirality to new monomers that are assembling onto the seed.\(^15\)

![Scheme 3.1](image)

**Scheme 3.1.** The molecular structure of T6 (R, R chiral) and T7 (S, S chiral).
Here, a detailed study of the aggregation of chiral oligothiophenes is presented, where the resulting structures can act as models for the polymers but in addition are intriguing nanoscopic objects themselves. The self-assembly of chiral oligothiophenes T6 and T7 (Scheme 3.1) was selected because it was previously established that the self-assembly was a sensitive function of the experimental protocol adopted. The molecules comprise a π-conjugated α,α'-linked sexi (T6) or septi (T7) thiophene derivative carrying enantiomerically pure chiral oligo(ethyleneoxide) side-chains at both the α- and ω-position. The synthesis of the thiophenes has been performed in the group of prof. W. J. Feast at Durham University. The self-assembly can be probed by temperature-dependent ultraviolet/visible absorption (UV/Vis) and circular dichroism (CD) spectroscopy. These techniques in combination with dynamic light scattering (DLS), atomic force microscopy (AFM) and scanning electron microscopy (SEM) have shown that these molecules can self-assemble into inter alia, spherical capsules constructed of a monolayer of oligothiophenes. The CD spectra of n-butanol solutions of T6 and T7 showed a right-handed helical arrangement for T6 (R,R-chirality) and T7 (S,S-chirality). This difference is explained by the number of thiophene rings in the molecule that determines the curvature in the all anti-conformation of the thiophene rings and by the chirality of the side-chains. In case of T6, different types of aggregates such as plates and fibers are observed depending on the experimental protocol adopted. First the stability and purification of T6 and T7 is addressed before the effect of the purity and cooling protocol on the self-assembly of both T6 and T7 will be discussed. It was shown that these oligothiophenes all self-assemble by a cooperative mechanism and evidence emerged of a nucleation that is mostly heterogeneous in nature. In addition a complex energy landscape is revealed for the self-assembly of T6 and T7.

3.2 Purification and stability of oligothiophene derivatives

Before turning to the study of the supramolecular polymerization, the stability and purity of T6 and T7 were investigated. After standard purification, the purity of T6 that was used in previous studies, batch 1, was about 98 % (based on the peak area in analytical size exclusion chromatography (SEC) assuming equal extinction coefficients). However, the application of recycling SEC enabled T6 to be obtained in a much purer form (Figure 3.1).

![SEC profiles](image-url)

*Figure 3.1. a) SEC profile of T6, batch 1 in chloroform (λ = 450 nm) and b) recycling SEC profile of T6 recorded at λ = 525 nm in chloroform (T = 293 K) c) T7 before purification using analytical SEC (λ = 447 nm, T = 323 K)*

After purification of T6 by recycling SEC, three fractions were collected, one with a longer retention time than T6 (fraction 1), one with the same (fraction 2) and one with a shorter retention time...
Fraction 2 was determined to have a purity of 99.9% by analytical SEC (Figure 3.3, sample B). The MALDI-TOF mass spectra of fractions 1 and 3 (Figure 3.2a and c, respectively) showed multiple peaks, while fraction 2 revealed the molecular ion (1078.23; calc. 1078.25; Figure 3.2b) and the sodium adduct of T6. This purity grade will be referred to as sample B in the remaining of this Chapter (vide infra). The mass spectrum of fraction 1 showed a regular pattern with mass differences of 44 and 58 units corresponding to loss of ethylene oxide (44) and methoxy terminated ethylene oxide (58) units. The mass differences suggest decomposition of the ethylene oxide side-chains and all the peaks in the MALDI-TOF mass spectrum can be ascribed to this phenomenon. The MALDI-TOF mass spectrum of fraction 3 showed a similar pattern of peaks as for fraction 1, but also masses corresponding to species formed by dimerization of T6 fragments. Furthermore, a mass corresponding to a dioxygen adduct of a T6 dimer was detected (2M+ + 32; 2186.40, calc. 2186.47). When fraction 3 was subjected to SEC analysis, fractions with longer retention times were obtained (Figure 3.2d), revealing that the dimers decomposed into smaller fragments.

When stored as a solid under a nitrogen atmosphere for 18 h, no degradation was observed in a purified sample of T6. In contrast, storage in air at room temperature led to the appearance of additional peaks in the analytical SEC trace and irradiation with light accelerated the degradation process. The fact that T6 only decomposes in the presence of air indicates that oxidative processes are the source of degradation (data not shown). Most likely, singlet oxygen is either formed through...
energy transfer from the thiophene-core to triplet ground state oxygen or via a dioxygen-thiophene charge transfer complex. The presence of dimers could be due to non-covalent π-dimerization or covalent crosslinking. Most probably singlet oxygen initiates the shortening of the solubilizing side-chains, by a mechanism analogous to that postulated for the degradation of oligofluorenes. Where, in the case of oligofluorenes the side-chain degradation clearly initiates the backbone degradation, in the case of T6 backbone initiation and side-chain initiation cannot be discriminated.

In the case of T7 (Figure 3.1c, purity of 77%), purification by recycling SEC could not be achieved due to the low solubility in chloroform at room temperature. Therefore, this material was purified with high temperature analytical SEC. The low scale of this purification technique hampered further investigation of the impurities, although it still allowed the purification of T7 to 98% purity (Figure 3.8a).

3.3 The self-assembly of oligothiophenes

First the effect of impurities on the self-assembly of T6 was investigated. By shortening the collection times for fraction 2 during the recycling SEC of batch 1, three samples with increasing purities were obtained; assigned as sample A (99.6%), sample B (99.9%) and sample C (99.9+%) (Figure 3.3).

![Normalized intensity (AU) vs. time (min) for T6 samples]

**Figure 3.3.** 100 × zoom in of the SEC traces of different T6 samples: batch 1 (dashed), sample A (black), sample B (dark gray) and sample C (light gray) at λ_{max} = 450 nm.

By using temperature-dependent UV/Vis and CD spectroscopy, solutions of samples of A, B, and C in n-butanol (c =2.6 × 10^{-5} M) were cooled from 333 K to 273 K at a rate of 60 K/hr (Figure 3.4a,c) and both UV/Vis and CD intensities were monitored simultaneously at λ = 415 nm, which is close to the maximum in both absorption and CD (Figure 3.4b,d). The cooling curves are not sigmodial, but show a sudden non-sigmoidal change in both UV/Vis and CD intensity at a specific temperature. This temperature of elongation (T_e) is indicative of a cooperative self-assembly process. Since the T_e for both UV/Vis and CD techniques is the same, the self-assembly proceeds immediately from monomers via helical nuclei to helical assemblies. The cooling curves could not be fitted with the one-dimensional nucleation-growth model used previously (see Chapter 1). The deviation of the curves
is most likely to be a consequence of the formation of large capsules and cylinders (vide infra) resulting in linear dichroism (LD). The shape of the cooling curves is different for all three samples when using the same assembly protocol, showing that a tiny amount of impurity has a decisive influence on the supramolecular polymerization. The most pure sample C shows the lowest $T_e$ while the least pure sample A shows the highest $T_e$ ($T_e$ (C) = 305 K < $T_e$ (B) = 306 K < $T_e$ (A) = 309 K, Figure 3.4a). Although the sign of the CD effect appears positive at long wavelengths and negative at short wavelengths, the envelopes and intensities of the CD spectra of samples A – C at 273 K (Figure 3.4b) differ quite dramatically. In the UV/Vis spectra the absorption maximum shifts hypsochromically as the solution temperature is lowered and the H-type self-assembly occurs. Light-scattering is observed in both UV and CD spectra at long wavelengths where the chromophore does not absorb; this scattering is due to the size of the assemblies (vide infra). Interestingly, the scattering is the lowest in case of the most impure sample (sample A), implying that this sample gives rise to the smallest scattering entities. These combined results clearly demonstrate the heterogeneous character of the nucleation in the self-assembly process.

Next, the reversibility of the self-assembly processes was investigated (Figure 3.5). Remarkably, heating the first formed solution of the self-assembled T6 structures to just above the $T_e$ and then slowly cooling the solution for the second time results in a less intense CD effect in the case of the two
The role of purity and cooling protocol on the self-assembly of oligothiophenes

least pure samples A and B, while for the most pure sample C the CD effect fully recovers. However, when in a third heating-cooling cycle the solution of sample B was heated to a higher temperature (353 K) well above $T_e$, the system becomes fully reversible. This effect can be attributed to “seeds” that are only fully disassembled above 333 K and shows that the reversibility of the system is highly dependent on the applied superheating. The T$_6$ molecules did not show any degradation in solution during the measurements, however, standing for eight days lowers the purity of sample B (99.9 %) to that of sample A (~ 99 %).

Figure 3.5. CD cooling curves of T$_6$ samples A, B and C in n-butanol either starting from 333 K or 353 K and being the 1$^{st}$, 2$^{nd}$, or 3$^{rd}$ cooling run ($\lambda = 415$ nm, $\Delta T/\Delta t = -60$ K/hr, $c = 2.6 \times 10^{-5}$ M)

The effect of cooling protocols on the self-assembly process of sexithiophenes. Different CD cooling curves (Figure 3.7a) and full spectra (data not shown) were obtained when subjecting a solution of the most pure sample C to different cooling rates; e.g. quenched, 60 K/hr, 4 K/hr, and 1 K/hr. The full spectra show presence of scattering at long wavelengths for T$_6$ at 273 K after slow cooling, while the scattering is disappeared in the quenched sample coinciding with an increase in intensity of the absorption band. The CD spectra at 273 K after 4 K/hr and 1 K/hr have a different appearance; however, after correcting for the absorption intensities similar $g_{abs}$ values are obtained, possibly indicating that the thermodynamic most favored state is reached under these conditions for this sample. In the cooling curves (Figure 3.7a), an increase in $T_e$ can be observed for lower cooling rates which further supports the fact that a more thermodynamic stable state is reached for lower cooling rates. The CD spectra recorded at 273 K for the sample obtained by cooling at 60 K/hr could not be generated via a superposition of spectra obtained from the quenched sample and the sample cooled at 1 K/hr. The origin of this discrepancy can be differences in selective scattering (e.g. difference in assembly size), linear dichroism or changes at the molecular level. At this point no distinction can be made between these possibilities.

Tapping mode atomic force microscopy (TM–AFM) of drop cast assemblies of T$_6$ obtained by cooling solutions of sample B at 4 K/hr yields capsules in the middle of the evaporated sample while at the edges large cylinders are visible using optical microscopy (Figure 3.6). Cooling at 60 K/hr gave much smaller assemblies (~5 μm) than cooling at 6 K/hr (~ 100 μm). The larger assembly size for the slowly cooled solution could contribute to the increase in light scattering observed in the spectroscopic measurements.
Figure 3.6. Tapping mode AFM images in the middle of an evaporated drop of n-butanol containing T6 assemblies, on a glass substrate (a, b) and optical microscopy images at the edge of that drop (~50 x enlarged) (c, d). Different cooling speeds were applied to obtain the assemblies: 60 K/hr (a, c) or 4 K/hr (b) and 6 K/hr (d) (c = 2.6 x 10^{-5} M, sample B).

A solution of T6 (sample C) was also subjected to a stepwise cooling routine (Figure 3.7b) to investigate the reorganization of the self-assembled structures during their formation. Here, the solution was annealed for 5 minutes at a sequence of temperatures, after which cooling was resumed at 60 K/hr. During the annealing step, both UV/Vis and CD spectra were recorded in order to investigate changes in the helical supramolecular organization of the sexithiophenes.

Figure 3.7. a) Cooling curves with 60 K/hr, 4 K/hr and 1 K/hr (c = 2.6 x 10^{-5} M, λ = 415 nm). b) Stepwise cooling curve in CD of T6 in n-butanol (gray, left axis) (c = 2.6 x 10^{-5} M, ΔT/Δt = 60 K/hr, λ = 415 nm) and temperature profile (black, right axis). CD spectra (c) and UV/Vis spectra (d) of the solution at different points in the self-assembly process during stepwise cooling (T = 333 K (solid), 308 K (dashed), 305 K (dotted), 289 K (dash-dot) and 273 K (dash-dot-dot). The inset in c shows the enlarged CD spectrum at T = 308 K.
The step-wise annealing of a T6 solution of sample C in n-butanol results in a higher Te (309 K as opposed to 305 K), and a lower CD intensity (λ = 415 nm at 273 K) than continuous cooling. The overall shape of the CD cooling curve and the envelope of the CD spectrum obtained at 273 K closely resemble those reported for cooling at 4 K/hr and 1 K/hr (for cooling curves see Figure 3.7a). During annealing, the UV/Vis and the CD intensities change. While the alteration in UV/Vis only results in a progressive decrease in intensity (data not shown), the fluctuations in CD are highly irregular. Three district regimes can be distinguished. In the first regime from 309 - 307 K each annealing step (5 minutes annealing at each 0.5 K step) results in an increase in the CD effect. A weak CD effect is observed (Figure 3.7c, CD spectrum at 308 K is shown in the insert), while no significant differences in the UV/Vis spectrum are visible when compared to that of the molecularly dissolved solution (333 K). The second regime, between 307 and 304 K shows no significant change in the CD intensity at 415 nm during annealing, while in the third regime, from 304 – 273 K, the CD intensity decreases during annealing (5 minutes annealing at each 2 K step). This decrease is a result of similar fluctuations in LD (data not shown) caused by a change in convective flow in the cuvette during annealing (see Chapter 5).28 The CD spectra in the second and third regime resemble the spectrum after continuous cooling at 4 K/hr and not the one obtained after cooling continuously at 60 K/hr, in spite of the presence of LD during stepwise cooling. Furthermore, when applying a stepwise cooling method, the LD cooling curve is positive, while for continuous cooling at 60 K/hr a negative LD is observed. These results show that annealing in the different temperature regimes of the self-assembly process causes differences in the supramolecular organization.

The self-assembly of septithiophenes. The self-assembly of septithiophene T7 (98 % pure, Figure 3.8a) in n-butanol (2.6 × 10⁻⁵ M) was also investigated using temperature-dependent CD and UV/Vis spectroscopy. The sharp non-sigmoidal increase in the temperature-dependent CD curve shows that T7 also polymerizes according to the cooperative mechanism (Figure 3.8b). However, due to the limited range of purity grades that were available for T7 and its enhanced photolability, the effect of the impurities on the supramolecular polymerization could not be investigated.

![Figure 3.8. a) SEC of the purified sample of T7 where the inset shows the enlargement of the peak basis (λ = 254 nm, T = 323 K in chloroform) and b) CD cooling curve of a solution of T7 in n-butanol (c = 2.6 × 10⁻⁵ M, λ = 425 nm, ∆T/∆t= -60 K/hr)](image-url)
The shape of the CD spectrum after cooling is positive at long wavelengths and negative at short wavelengths, which is what would be expected for T7 having S, S chirality (Figure 3.9a). The spectra at 273 K did not contain any form of scattering and linear dichroism artifacts, implying that the observed CD spectra are a result of the supramolecular arrangement of the molecules. Therefore, more emphasis was put on the effect of the cooling protocol on the supramolecular polymerization of T7.

**Figure 3.9.** a) CD spectra of T7 after quenching in an ice batch (black), 60 K/hr cooling (gray), the same codes and concentration were used for (b) (c = 2.6 × 10^{-5} M, T = 273 K). b) UV/Vis spectra of T7 (T = 273 K). Time-dependent CD (c) and UV/Vis (d) spectra during annealing where the arrow indicates the time increments (c = 2.6 × 10^{-5} M, Δt = 5 min, T = 320 K).

To evaluate the effect of the cooling rate on the self-assembly process of T7 a solution was heated to 363 K and quenched in an ice bath. The UV/Vis spectrum was similar to that obtained after cooling at 60 K/hr, however, the CD spectrum at 273 K was completely different (Figure 3.9a,b). Remarkably, the CD signature is a mirror image of the spectrum obtained after cooling at 60 K/hr indicating different helicity for the two samples. Intrigued by this difference in helicity a quenched solution was annealed at 320 K to investigate if helix reversal, so called stereomutation, could be observed. Monitoring the CD effect at 5 minutes intervals showed that the CD effect initially decreased and that the stereomutation started after 1 hr and was completed after 4 hrs (Figure 3.9c). The CD effect corresponding to the final state of the annealing process does not resemble the CD effect obtained after cooling the solution at 60 K/hr, implying that for the latter cooling rate the system is not under thermodynamic control. The observed stereomutation with CD spectroscopy is accompanied by a hypsochromic shift and a decrease in oscillator strength in UV/Vis (Figure 3.9d). Thus, the self-
The role of purity and cooling protocol on the self-assembly of oligothiophenes

assembly of T7 showed at least three different types of supramolecular arrangement within the self-assembled structures as evidenced by the combination of CD and UV/Vis spectroscopy. Similar to T6, the different supramolecular arrangements can be obtained by varying the self-assembly protocol. However, the chiroptical changes between the different states are more drastic in the case of T7, showing even the formation of supramolecular structures possessing opposite helical handedness.

3.4 Complex energy landscapes

The remarkable results described above give rise to the questions: why is there such a dramatic influence of impurities and why are so many different supramolecular arrangements found in the self-assembly of both T6 and T7? Proteins are well known to fold into different conformational and aggregated local minima, often called “substates”.\textsuperscript{31,32} The connection of all these local minima creates an energy landscape for the protein folding process. In crystal engineering of small molecules and polymers, similar local energy minima are encountered called polymorphs.\textsuperscript{33,34,35} A particular crystal form is not always the most stable one and conversion between the different polymorphs is possible.\textsuperscript{33} Temperature, cooling rate and the presence of impurities \textit{inter alia} play a significant role in polymorphism.\textsuperscript{36} Impurities, even at the parts per million level can act as seeds for heterogeneous nucleation and can influence the crystallization kinetics and packing of the molecules.\textsuperscript{36,37} It is reasonable to expect that analogues of the polymorphism observed in crystallization and energy landscapes in protein folding will be encountered in the self-assembly of π-conjugated oligomers and polymers. The self-assembly of T6 is highly dependent on the purity of the sample, showing heterogeneous nucleation at even 0.1 mol% concentration of impurity. Only in its most pure form, evidence emerges that T6 can self-assemble homogeneously; however, the smallest traces of impurities give rise to the presence of multiple CD signatures for the T6 assemblies. This behavior shows the existence of a complex energy landscape for the self-assembly of these materials. Previous studies showed that the thiophene segments are most stable in a cofacial parallel orientation with no handedness.\textsuperscript{19} However, the steric hindrance of the chiral substituent in the oligo(ethyleneoxide) side-chain present in the oligomers investigated in this study hinders the optimum packing.\textsuperscript{19} These counteracting forces could ensure that multiple orientations of T6 and T7 are possible, resulting in a multiplicity of local minima in the energy landscape i.e. multiple self-assembled structures. In addition, easy homogenous nucleation is hampered by these counteracting forces, but makes the compounds very susceptible to heterogeneous nucleation with different structures resulting. Also these molecules form nanocapsules and mesoscopic cylinders which are probably the result of a two dimensional self-assembly process leading most likely to "sheets" which wrap into capsules. Initiation of the “wrapping up” process requires non-planar defects in the sheets.\textsuperscript{38} The formation of capsules has been discussed by Nelson whose analysis reveals that at least two defect sites, so called ‘boojums’, are necessary to assemble a spherical object.\textsuperscript{38} Boojums are energetically unfavorable with respect to the other positions in the sphere and in the case of thiophene capsules these boojums are possibly occupied by impurities; similar considerations must apply to cylinders. Systems that do not contain such counteracting forces either at the molecular or supramolecular level, but in which the different forces are complementary, are likely to show a simple energy landscape, with easy to control
self-assembly protocols, without a profound influence of impurities. The oligo(p-phenylene vinylenes) ureidotriazine derivatives are an example of that class of materials (see Chapters 1 and 5).

3.5 Conclusion

In the current work it is demonstrated that modern chromatographic purification techniques, like recycling SEC, allow impurity specification with great precision in oligothiophene semiconductors. The degradation of oligothiophenes can be characterized as an oxidative degradation of the side-chains where oxygen is most likely sensitized by the π-conjugated core. Furthermore, the trace amounts of impurities have a dramatic effect on molecular packing, self-assembly and the size distribution of the assemblies formed. Besides the influence of impurities, the resulting self-assembled structures are also dependent on cooling rate and cooling method employed. These results reveal that self-assembly has remarkable similarities to both the crystallization of molecules on the one hand and to the dynamics of protein folding and aggregation on the other hand. The insights obtained from this study could be relevant to the controlled construction of self-assembled structures and functional materials in general.

3.6 Experimental Section

General methods. The synthesis and characterization of T6 and T7 has already been described.\textsuperscript{19} n-Butanol was purchased from Acros and were used without purification. HPLC-grade chloroform was purchased from Biosolve. UV/Vis, CD and LD spectra were measured on a Jasco J-815 spectropolarimeter where the sensitivity, time constant and scan rate were chosen appropriately. Before starting the studies related to the cooling speeds, the T6 solution was heated for 45 minutes at 353 K. Temperature-dependent CD, LD and UV/Vis measurements were performed with a PFD-425S/15 Peltier-type temperature controller with a temperature range of 263-383 K and adjustable temperature slope on the J-815. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry has been performed on a PerSeptive Biosystems Voyager-DE PRO spectrometer. Size exclusion chromatography was performed on a Shimadzu LC10-AT using two PL Gel 3 μm 100 Å (length per column 300 mm, diameter 7.5 mm) column, a Shimadzu Photodiodearray SPD-M10Avp detector from 250-700 nm and chloroform as eluent with a flow rate of 1 mL/min (T = 293 K). Recycling size exclusion chromatography was performed on a modified Shimadzu LC10-AT using 1 Jaigel 2.5 H (600 * 20 mm) + 1 Jaigel 2 H (600 * 20 mm) column, a Shimadzu SPD-10AVp UV/Vis detector at 450 nm and 510 nm and chloroform as eluent with a flow rate of 3.5 mL/min (T = 293 K). Atomic Force Microscopy images were recorded under ambient conditions using a Digital Instrument Multimode Nanoscope IV operating in the tapping mode regime. Microfabricated silicon cantilever tips (NS) with a resonance frequency of approximately 300 kHz and a spring constant of about 50 Nm\textsuperscript{-1} were used. AFM samples were prepared by dropcasting the solutions on glass. A Zeiss Axiolab microscope was used with a 50× Zeiss objective. The camera is a Sony PowerHAD. The pictures have been captured with a Pinnacle PCTV video capturecard. The sample was deposited on a round glass cover (Menzel, 24 mm).

3.7 References and notes


The role of purity and cooling protocol on the self-assembly of oligothiophenes

19 It should be noted that no additional peaks were observed when monitoring at $\lambda_{\text{max}} = 254$ nm.
27 A different sample, Sample B’, was used which has a similar purity as sample B.
28 Remarkably, the cooling curves for the slowest cooling rates are positive at high temperatures and become negative at lower temperatures, however the full spectra does not change sign.
Elucidation of the internal structure of an oligothiophene assembly

Abstract. The internal organization of sexithiophene (T6) supramolecular polymers in solution has been determined by combining small angle X-ray scattering and birefringence measurements on a magnetically aligned system. For the supramolecular polymerization of T6 under these conditions a cylindrical type of assembly is proposed. The π-π stacking interactions are not present in the long axis of the polymer but in the tangential direction (short axis) of the cylinder. Lateral edge-to-edge interactions between the thiophene molecules are present along the long axis. These observations can be explained by cylinder formation that is due to a wrapping-up process of initially formed sheets consisting of T6.
4.1 Introduction

Self-assembly of organic molecules into larger aggregates is a promising approach for constructing potentially functional nanostructures. In principle, the large diversity of molecular building blocks permits the fabrication of assemblies with a large variation in composition, shape and functionality. In many cases, however, the precise internal molecular arrangement of the nanostructures is unknown, which hampers the development of a deeper understanding of the structure-property relationship that is required to steer the self-assembly process towards nanostructures with desired functionalities and chromophore organization. In particular, it is important to determine the molecular arrangement of supramolecular polymers in the solution where the polymerization takes place. Solution experiments provide a stable environment with well-defined intermolecular interactions, where solvent and temperature dependencies can be readily investigated. Spurious effects that can be present when aggregates are characterized after deposition on a substrate, that are a consequence of molecule-substrate interactions and solvent evaporation effects, are excluded in this way.

To this end the internal structure of an sexithiophene (T6) assembly in a solution of o-dichlororobenzene (ODCB) and n-butanol (1:10 volume ratio) was determined. ODCB was added to the n-butanol since it is a good solvent for π-conjugated systems and enabled the use of a more concentrated T6 solution. Furthermore, it is likely to allow the structures to assemble in their thermodynamically stable minimum (see Chapter 6). The higher concentration allowed an approach for a structural investigation that is inspired by studies on biological structures and combines the virtues of small angle X-ray scattering (SAXS) and linear birefringence with magnetic orientation. SAXS is very powerful for resolving internal aggregate structures, as opposed to e.g. 1H NMR, circular dichroism, UV/Vis absorbance and fluorescence on one hand, which probe short range interactions, and techniques like light scattering and cryo-TEM on the other hand, which probe length scales too large to determine the molecular arrangement. To elucidate the internal structure SAXS and birefringence measurements were performed on magnetically aligned sexithiophene aggregates. Cylindrical aggregates were found in which the sexithiophene molecules are arranged in a lamellar fashion in a radial direction with π-π stacking in the tangential direction of the cylinder.

Scheme 4.1. The molecular structure of T6 having R,R chirality.

As already discussed in Chapter 3, the molecules (T6) comprise a π-conjugated α,α'-linked sexithiophene derivative carrying chiral oligo(ethyleneoxide) side-chains at the α- and α'-position (Scheme 4.1). Previously it has been shown that T6 forms aggregates in protic solvents, with morphologies ranging from spherical structures, needles and rodlike helical assemblies to flat “crêpes”, where the morphology and resulting properties depend on the solvent and fabrication method used. The combination of the purified material (see Chapter 3) and the solvent mixture of ODCB and n-butanol, the boiling points of which are both higher than the elongation temperature $T_e$.
Elucidation of the internal structure of an oligothiophene assembly

for the concentration used, allowed the study of aggregate formation and melting in a reversible way.20 Like all molecules used for self-assembly, sexithiophenes have an anisotropic chemical structure to exploit the directionality in the intermolecular interactions. Such anisotropic molecules are very suitable for magnetic orientation due to their large anisotropy in the magnetic susceptibility.22 Aromatic moieties like benzene and oligothiophenes tend to align with the aromatic plane parallel to the field, which can be used to orient supramolecular polymers in solution up to a high degree.23,24,25,26 Depending on the shape of the assemblies, the thiophenes can be organized either with their short axis along the magnetic field or with their long axis. In the past the magnetic alignment technique has been used to deform spherical structures of T6 in isopropanol into ellipsoidal assemblies.29 In contrast to the ODCB/n-butanol mixture, the formation of the assemblies in isopropanol could not be performed under reversible conditions. However, here, the use of alignment for the elucidation of the internal structure of T6 assemblies in ODCB/n-butanol mixture will be discussed. The consequence of the alignment of the nanostructures is that the combination with the optical anisotropy of the molecular building blocks leads to a strong linear birefringence. This birefringence is a sensitive probe for the molecular organization.27

4.2 SAXS and birefringence

The purity level of T6 used was similar to sample B in Chapter 3 (99.9%), since this is the highest purity grade that could be obtained in significant quantities. To prepare the aggregates, freshly purified material (1 mg) was dissolved in a mixture of 100 µL ODCB and 1 mL n-butanol (c = 8.5 × 10⁻⁴ M). The sample was heated to 353 K for at least half an hour in order to allow full disassembly of all pre-existing aggregates (see Chapter 3), after which the solution was slowly cooled to room temperature. A sharp non-sigmoidal change in intensity at the Tc observed in the temperature-dependent optical and chiroptical measurements (Figure 4.1b) indicates a cooperative supramolecular polymerization mechanism similar to that reported for the lower concentration in pure n-butanol (see Chapter 3).

![Figure 4.1. a) CD spectroscopy at 353 K (gray) and 293 K (black) b) temperature-dependent CD curve (ΔT/Δt = -60 K/hr, λ = 450 nm) and c) UV/Vis absorption at 353 K (gray) and 293 K (black) of T6 in an ODCB/n-butanol 1:10 mixture (1 mg in 1.1 mL total volume; c = 8.5 × 10⁻⁴ M).](image)

The hypsochromic shift in the absorption maximum in UV/Vis and the CD effects (Figure 4.1a,c) resemble the results for sample B cooled down with the same cooling speed as described in Chapter 3. Thus ODCB does not seem to have an influence on the self-assembly, only that its presence allows for
higher concentrations of \textit{T6} in \textit{n}-butanol. A significant amount of scattering can be observed, which indicates the presence of large self-assembled structures. This was confirmed by optical microscopy images displaying micrometer sized anisotropic structures in solution (data not shown). These structures align with their long axis along the magnetic field. Polarized optical microscopy did not give any yield any difference in absorbance with respect to the different axis of the aligned structures.

Structure elucidation was achieved by the combination of SAXS and birefringence. At ten different temperatures below \( T_e \), the birefringence was measured in magnetic fields \((B)\) up to 20 T. SAXS experiments were performed at BM26B at the European Synchrotron Radiation Facility (ESRF) in Grenoble. In this case a magnetic field of \( B = 4 \text{T} \) (1.7 T) was applied perpendicular (parallel) to the X-ray beam.

**Small angle X-ray scattering.** The small angle scattering profile of a \textit{T6} solution in ODCB/\textit{n}-butanol mixture (1:10 v/v) was recorded in a specific \( q \)-range. The 1D SAXS profile of the non-aligned sample in the absence of a magnetic field, displays a \( q^4 \) dependency at small scattering vectors and a sharp peak at \( q = 1.3 \text{ nm}^{-1} \) (Figure 4.2 bottom). The initial \( q^4 \) dependence indicates that the molecules self-assemble into large aggregates characterized by a sharp interface between aggregate and solvent, but the data does not contain any information on the overall shape since the assemblies are too large to be measured in this \( q \)-range. The peak at \( q = 1.3 \text{ nm}^{-1} \) corresponds to a typical periodicity of 4.8 nm, consistent with \textit{T6} molecules organized in a lamellar fashion as depicted in the schematic picture in the inset of the bottom graph of Figure 4.2.

![SAXS results of unaligned T6 aggregates](image)

**Figure 4.2.** SAXS results of unaligned \textit{T6} aggregates \((c = 8.5 \times 10^{-4} \text{ M}, 10:1 \text{ n-butanol/ODCB, } B = 0 \text{T and } T = 293 \text{ K})\). Top panels show SAXS images recorded at two different detector distances \((D = 8 \text{ m and } 1.5 \text{ m})\), with different scattering \( q \) ranges thus probing different length scales. Lower panel shows the resulting cross section. The sharp peak at \( q = 1.3 \text{ nm}^{-1} \) indicates a typical period of 4.8 nm between two \textit{T6} molecules, as indicated in the inset. At the far right a schematic picture of the molecular structure of \textit{T6} is depicted.
The application of a magnetic field of 4 T perpendicular to the X-ray beam showed that the isotropic scattering observed without magnetic field was changed into an anisotropic scattering profile at low $q$-values and to two bright spots that appeared at $q = 1.3$ nm$^{-1}$ (Figure 4.3). These spots are visible in the horizontal plane of the detector, while the magnetic field is applied in a perpendicular direction, e.g. the vertical plane of the detector. The azimuthal width of the bright spots (Figure 4.4a) is inversely proportional to the degree of alignment and decreases for higher magnetic field strengths, while saturating at $B = 4$ T where the alignment is almost complete. The SAXS data taken with $D = 8$ m (top left panel of Figure 4.3), probes the overall shape and the strongly anisotropic scattering pattern indicates the presence of aligned aggregates with a high shape anisotropy. This suggests that the aggregate dimension along $B$ is larger than that perpendicular to $B$; these dimensions will be referred to as the long and short axes, respectively. When combining the observations at the two detector distances, the results show that the 4.8 nm periodicity, visible in the horizontal plane of the detector, is related to the short axis of the supramolecular assembly. Hence, T6 is arranged in a lamellar fashion along the short axis of the structure.

For $B$ parallel to the X-ray beam (Figure 4.3 bottom part), the situation is remarkably different. For the long detector distance (probing the shape of the assembly) a radially symmetric scattering pattern is visible. Normally this would suggest that the assemblies are not aligned, however, from the measurements where the magnetic field is perpendicular to the X-ray beam clear signs of alignment were observed. A possible explanation is that the long axes of the T6 aggregates are aligned parallel to the X-ray beam which hampers any contribution from the long axes of the assemblies to the X-ray scattering profile, yielding an isotropic scattering ring. Also at the shorter detector distances, where the molecular length scale is probed, the scattering ring observed at $q = 1.3$ nm$^{-1}$ did not show any sign
of orientation. In spite of the substantial magnetic orientation at \( B = 1.7 \, \text{T} \), the rotational freedom of the aggregates around the \( B \)-axis could lead to the observation of a ring instead of the bright spots that would be expected for an aligned assembly.

**Birefringence.** Although, the SAXS data reveal evidence about the internal structure of the supramolecular polymer, additional information is necessary to arrive at a more detailed understanding. For that reason the ordering of the T6 supramolecular polymers was evaluated with birefringence (Figure 4.4b). The contribution to the birefringence can be the result of a deformation of the assemblies, as was previously observed,\(^{19}\) and as a result of the anisotropic alignment of the aggregates. Since the optical microscopy and the SAXS data did not reveal any change in the shape of the assemblies, it is likely that the contribution coming from a shape-deformation does not significantly contribute to the observed birefringence.

![Figure 4.4. Left: The magnetic field dependence of the azimuthal width of the scattered X-ray beam \((B \perp \text{X-ray})\), which is inversely proportional to the degree of alignment. Inset: azimuthal intensity at \( q = 1.3 \, \text{nm}^{-1} \), as a function of \( B \). Right: birefringence \((n_{\parallel B} - n_{\perp B})\) as a function of magnetic field for different temperatures. The arrow shows the magnetic field at saturation for an increase in temperature. \((c = 8.5 \times 10^{-4} \, \text{M}, 10:1 \, n\text{-butanol/ODCB})\)](image)

For all temperatures above \( T_c = 328 \, \text{K} \) the birefringence is zero at all magnetic fields, since the molecules are molecularly dissolved and no aggregates are present. At temperatures below the \( T_c \) the magnetic birefringence at a specific temperature increases quadratically with the applied field and saturates at higher fields. Furthermore, lower temperatures yield higher values for the birefringence as a result of an increased number of molecules in the supramolecular polymer. The magnetic field where the signal is saturated shifts to higher field strength for higher temperatures as indicated by the arrow. Since the saturating field strength is directly related to the size of the supramolecular polymers, this observation indicates that the size of assemblies becomes larger at lower temperatures. Note that at room temperature the birefringence saturates at around 4 \( \text{T} \), fully consistent with the X-ray data (Figure 4.4a).\(^{29}\)
4.3 Discussion

The two bright spots in the SAXS of aligned aggregates indicate that the T6 molecules are arranged in a lamellar fashion with a periodicity of 4.8 nm. When combined with the profile at a lower q-range (longer detector distance), it is clear that this periodicity is occurring along the short axis of the assembly. The absence of any other scattering intensity limits the possible structures to a lamellar structure, a herringbone structure or a cylindrical structure (Figure 4.5). The CD effect observed for these supramolecular polymers implies a helical twist between the molecules. For the structures depicted in Figure 4.5, this would mean that the subsequent thiophene molecules would have a twist angle to account for this chirality. However, for clarity, the helical twist between the T6 molecules has been omitted in Figure 4.5.

**Figure 4.5.** a) Molecular structure and schematic representation of T6. b) Three possible T6 aggregate structures with their energetically most favorable orientation in a strong magnetic field B. Lamellar structure: due to the rotational degrees of freedom, there is seemingly no alignment. Herringbone structure: two stage alignment, but at high B the structures align parallel to the field. Cylindrical structure: alignment with the long axis along B. The schematic pictures of the cuvettes show the alignment of the assemblies at high magnetic fields.

Below the schematic picture of the different possibilities in Figure 4.5, the alignment of the supramolecular polymers in a strong magnetic field is schematically depicted. For a lamellar structure the alignment with the magnetic field can be either along the direction of the field or perpendicular to it. However, in this case the SAXS should yield evidence for orientation in both directions, which is not observed (Figure 4.3). Hence the lamellar structure for the assemblies can be excluded.

A herringbone structure orients in two steps, at low magnetic fields it aligns like the lamellar structure, but at high fields it will align with its long axis parallel to the magnetic field, unless the herringbone angle is exactly 45 degrees by coincidence. Such a two-step alignment process is neither compatible with the birefringence data, nor with the SAXS data, where only alignment parallel to the magnetic field was observed in the B = 0 - 4 T range. Furthermore, the distance between the thiophenes is likely to be different from the 4.8 nm observed in SAXS, which is caused by the angle between the molecules as a result of the herringbone structure.
The cylindrical structure consists of T6 molecules that are radially oriented with a tangential $\pi$-$\pi$ stacking, where the head-to-tail molecular packing occurs only along the short aggregate axis. It necessarily aligns with its long axis along the magnetic field, when all thiophene planes are parallel to $B$, yielding the anisotropic scattering patterns presented in Figure 4.3. It is also consistent with the birefringence curve, which is a single S-shaped curve that is typical for aggregates with a cylindrically symmetric susceptibility. The cylindrical structure is the only proposed structure that is consistent with both the SAXS and birefringence data. It should be noted that in this micrometer sized cylindrical structure, a close up of the wall of the cylinder reveals a slightly curved lamellar organization of the thiophenes, where the radial orientation prevents the two-state alignment observed for the other structures.

As mentioned, the cylindrical structure depicted in Figure 4.5 does not account for the helicity observed with CD spectroscopy. SAXS and linear birefringence, the techniques that are predominately used in this Chapter, probe significantly larger length scales than CD spectroscopy which is mainly focused on chirality at the molecular and supramolecular level. Already the incorporation of a slight twist between the T6 molecules in Figure 4.5 can create the observed CD effect. Helical cylindrical nanotubes based on chiral $\pi$-conjugated systems have previously been reported in which two dimensional “sheets” wrap up into cylinders. Most likely, a similar self-assembly process occurs for the chiral T6 molecules. The capsules and cylinders found in diluted $n$-butanol solution (see Chapter 3) have presumably a similar architecture in which impurities may play an important role during the formation of these three dimensional structures.

4.4 Conclusion

The internal structure of an oligothiophene self-assembly in solution was for the first time studied by using its alignment in a magnetic field and analyzing it with small angle X-ray scattering and birefringence. A cylindrical structure is proposed where the thiophenes molecules are arranged along the short axis, while quite remarkably, the $\pi$-$\pi$ stacking is present along the tangential direction of the cylinder. A better understanding of the internal structure of self-assembled systems is an important step towards the use of organic molecules as nano-sized building blocks in functional materials having a well-defined organization of $\pi$-conjugated chromophores.

4.5 Experimental Section

General methods. The synthesis and characterization of T6 has already been described. $n$-Butanol was purchased from Acros, while ODCB was purchased from Aldrich and both were used without purification. HPLC-grade chloroform was purchased from Biosolve. UV/Vis, CD and LD spectra were measured on a Jasco J-815 spectropolarimeter where the sensitivity, time constant and scan rate were chosen appropriately. Temperature-dependent CD and UV/Vis measurements were performed with a PFD-425S/15 Peltier-type temperature controller with a temperature range of 263-383 K and adjustable temperature slope on the J-815. Size exclusion chromatography was performed on a Shimadzu LC10-AT using two PL Gel 3 μm 100 Å (length per column 300 mm, diameter 7.5 mm) column, a Shimadzu Photodiodearray SPD-M10Avp detector from 250-700 nm and chloroform as eluent with a flow rate of 1 mL/min (T = 293 K). Recycling size exclusion chromatography was performed on a modified Shimadzu LC10-AT using 1 Jaigel 2.5 H (600 * 20 mm) + 1 Jaigel 2 H (600 * 20 mm) column, a Shimadzu SPD-10AVp UV/Vis detector at 450 nm and 510 nm and chloroform as eluent with a flow
rate of 3.5 mL/min ($T = 293$ K). The magnetic field induced birefringence was measured with a standard modulation technique,\textsuperscript{10} using a HeNe laser (632.8nm, 1mW output, Melles-Griot) as a source of monochromatic light. The sample was contained in a 5 mm optical cell (Hellma) with a water-based temperature controller (+/- 0.1 °C) keeping the temperature constant at 20 °C. The birefringence was measured by slowly sweeping the magnetic field between 0 and 20 T. The small birefringence of the pure solvent caused by the experimental setup was used as a background. Small angle X-ray scattering (SAXS) measurements were performed at the Dutch-Belgian BM26B beamline at the ESRF in Grenoble (France). An X-ray photon energy of 10 keV and two different sample-to-detector distances (8 m and 1.5 m) were used, in order to explore a wide $q$-range ($0.35$ nm$^{-1} < q < 2.9$ nm$^{-1}$, ($q = 1.014\sin(\theta/2)$) where $q$ is the modulus of the scattering vector, $E$ the energy of the X-rays and $\theta$ the scattering angle). The SAXS images were recorded using a 2D multiwire gas filled detector. The positions of diffracted peaks from standard Silver Behenate and rat tail collagen samples were used in order to calibrate the experimental $q$-range. The samples were contained in 2 mm borosilicate capillaries. Standard data reduction procedures, i.e. subtraction of the empty capillary contribution, correction for the sample absorption etc. were applied. Two different magnets were used for performing SAXS measurements in a magnetic field. A remote controlled superconducting 4 T magnet was used for the measurements with the magnetic field perpendicular to the magnetic field, while a compact 1.7 T permanent magnet was used for the measurements with the magnetic field and the X-rays parallel. The magnetic field intensity was homogeneous all over the studied sample.

4.6 References and notes


29. The birefringence results were the same for assemblies that were assembled with or without a 20 T field showing that the influence of the magnetic field on the supramolecular polymerization is negligible.


Circular dichroism to study the organization of achiral and chiral OPV mixed assemblies

Abstract. This Chapter describes the use of circular dichroism spectroscopy (CD) to study the organization of chiral and achiral oligo(\(\pi\)-phenylene vinylene) (OPV) mixed assemblies. First, the self-assembly of achiral OPV derivatives was addressed. Remarkably, large apparent monosignate CD effects were observed for this inherently achiral system in dilute dodecane solutions. The CD effect could even be increased by shaking the cuvette. Although the solution was transparent, a large linear dichroic effect was observed, indicating an alignment of the self-assembled fibers in solution. An inherent optical imperfection in the CD apparatus, in combination with aligned fibers in solution resulted in a monosignate circular dichroic effect. Stirring of this aligned solution created a bisignate CD effect which was shown to be the result of the vortex flow on the aligned fibers. By changing the solvent to methylcyclohexane, no CD effect was observed and the alignment was circumvented. The organization of mixed assemblies consisting of achiral and chiral OPV derivatives (A-OPV4 and S-OPV3) was studied with CD spectroscopy in methylcyclohexane. The influence of two preparation methods on the organization in the mixed assemblies was addressed. The first preparation method allowed the molecules to be fully mixed at high temperature, while subsequent cooling showed chiral amplification of A-OPV4 by S-OPV3. The study indicated the formation of enriched clusters of one of the two components either within one stack, or as separate stacks. The second method was based on the addition of the shorter oligomer at a temperature where the A-OPV4 assemblies were already present and kinetically inert. In this case the chiral amplification was reduced, indicating the formation of clusters more enriched in one of the two components. These results show that the organization of the chromophores depends on the preparation method and highlights the efficacy of circular dichroism to study the organization of mixed self-assembled objects.
5.1 Introduction

A wealth of multicomponent supramolecular systems have been reported, in which mixing of the components is assumed to be achieved randomly. In these systems the exact self-assembly protocol and its influence on the organization of the different components is scarcely addressed. For inorganic wires much is known about the formation of well-ordered, complex architectures having multiple components where each subunit acts as a nucleus for the next component. This leads to the formation of clustered nanowires, where each cluster is made of a different component having different properties. More recently the self-assembly of polymers has approached a similar level of sophistication by using the same principles. These results indicate that subsequent addition of monomers can lead to nearly pure clusters of one of the different components. Although the detection of the internal organization is standardized for the examples discussed above, for supramolecular polymers it remains a challenge. The design and synthesis of more complex supramolecular systems should pave the way to assemble and integrate multiple components in a perfect fashion to create distinct functional properties, like supramolecular p-n junctions and photosynthetic systems (see Chapter 1).

![Scheme 5.1. The molecular structure of the different oligo(p-phenylene vinylene) ureidotriazine derivatives.](image)

Recently, the self-assembly of chiral oligo(p-phenylene vinylene)s (OPV) equipped with a self-complementary hydrogen bonding array (Scheme 5.1, S-OPV3 and S-OPV4) was reported in dodecane yielding helical nanofibers via the cooperative nucleation-elongation mechanism (Chapter 1) as evidenced from the (chir)-optical data. The circular dichroism and UV/Vis spectra of the self-assembled structures are depicted in Figure 5.1. The negative CD effect at long wavelengths observed in both spectra in Figure 5.1a indicates the formation of a preferred left-handed helical structure. The self-assembly process is characterized by a critical temperature called the temperature of elongation, $T_e$. Above the elongation temperature the OPV molecules exist in their hydrogen-bonded dimeric state, while at lower temperatures the dimers are assembled into elongated helical aggregates. The self-assembly mechanism is independent on the length of the π-conjugated OPV core, however, the longer oligomers showed a stronger tendency to assemble at a similar concentration as indicated by the increased $T_e$. Furthermore, the shorter conjugation length of S-OPV3 allows it to act as an energy donor in an energy transfer reaction to the S-OPV4 acceptor in the mixed self-assembled state. At higher incorporation ratios of S-OPV4, clusters of these molecules are formed in assemblies built up of
the energy donor S-OPV3. Furthermore, the fluorescence lifetime measurements showed that the addition of S-OPV4 to a solution of S-OPV3 at room temperature did not result in any observable energy transfer between the chromophores and hence the stacks do not mix at room temperature. This reveals the reduced dynamic nature of the aggregates at this temperature.

**Figure 5.1.** CD (a) and UV/Vis (b) spectroscopy of S-OPV3 (black) and S-OPV4 (gray) in MCH (c = 2 × 10^{-4} M, T = 293 K).

This Chapter discusses the use of circular dichroism to study the organization of A-OPV4 and S-OPV3 mixed assemblies as a function of the preparation method, while taking the dynamics of the assemblies into account. Circular dichroism was previously used to investigate two component systems with the main aim of studying chiral amplification. Two types of chiral amplification can be discriminated, namely the ‘Sergeant-Soldier’ and the ‘Majority-Rules’ effect. The first effect describes experiments where a small amount of chiral molecules is able to bias the helicity of a large excess of achiral ‘soldier’ molecules, creating a preference for either P or M helicities in the self-assembled state. In ‘Majority-Rules’ experiments a small enantiomeric excess of a chiral compound is able to dictate the helicity of the assemblies formed by the enantiomer that has a lower abundance in solution. Chiral amplification is normally investigated for systems that differ only in the identity of the side-chains (chiral and achiral for the ‘Sergeant-Soldier’; R and S-chiral for ‘Majority-Rules’), while the remainder of the chromophore is the same. Since the only difference between these molecules is the side-chains, the organization of the two components in these examples is assumed to occur randomly. The degree of chiral amplification depends highly on the mixing of the components. Therefore, CD spectroscopy can potentially elucidate the internal organization of self-assembled structures. Chiral amplification studies with molecules not only having different side-chains, but also different molecular structures, have not been reported thus far.

### 5.2 The self-assembly of achiral oligo(p-phenylene vinylene) ureidotriazines

During the studies on chiral and achiral OPV derivatives (Scheme 5.1) it was disclosed that a dilute solution of A-OPV3 (c = 5 × 10^{-5} M) in dodecane showed an unexpected circular dichroic (CD) effect after cooling from 363 K to 293 K at a rate of 60 K/hr (Figure 5.2a). Since the molecule is intrinsically
achiral, the effect should originate from macroscopic phenomena during the self-assembly process of A-OPV3 into fibers after slow cooling. Surprisingly, the CD effect increased further after shaking the fully transparent non-viscous solution in the cuvette. To investigate this observation, the self-assembly of A-OPV3 has been studied in more detail. Upon cooling the A-OPV3 solution from 363 to 293 K, a typical small blue shift of the absorption maximum to $\lambda = 407$ nm with a shoulder at $\lambda = 475$ nm is observed. This indicates that at high temperature the molecules are molecularly dissolved, while at low temperature they are self-assembled into fibers (Figure 5.2b). However, at low temperatures, a small response in the linear dichroism (LD) spectrum is observed that increased slightly after shaking (Figure 5.2c). LD and CD are absent at higher temperatures since the molecules are molecularly dissolved. The atomic force microscopy (AFM) images of dried drop-cast solutions of these self-assembled systems on mica showed thick bundles of long fibers (Figure 5.2d).

The three spectra (UV/Vis, CD and LD) are almost identical in shape (Figure 5.2a-c), while the CD spectra seems to be the mirror image of the LD curves. However, when monitoring the spectra during the temperature-induced self-assembly process (UV/Vis and CD intensity at $\lambda = 475$ nm and the LD intensity at $\lambda = 400$ nm) first the absorbance changes while only at lower temperatures the LD signal arises together with the CD signal (data not shown). Because A-OPV3 molecules form fibrous

![Figure 5.2](image_url)
aggregates with a length that increases upon lowering the temperature (see Chapter 1), this behavior indicates that a certain length of the fibers is needed to induce the LD and CD effects. Hence, the increase in LD is most likely associated with (partial) alignment of OPV fibers in solution due to convective flow caused by temperature differences in the cuvette. Additional measurements show that the alignment is less significant when a smaller cuvette (0.1 versus 1 cm) is used, e.g. when the flow pattern is altered. The flow pattern induced by shaking possibly enhances the alignment obtained by the convective flow. Furthermore, LD and CD spectra of aligned A-OPV3 films show very similar effects as observed in solution (data not shown). Consistent with the LD of aligned films and the convective nature of the flow in the heated cell, the LD measurements show that the A-OPV3 fibers in solution orient preferentially in the vertical direction. The apparent CD effect can be interpreted in terms of an artifact resulting from LD in the partially aligned solution in combination with the inherent optical imperfections of the CD machine, namely linear birefringence (LB) in the photo-elastic modulator and/or other optical elements. These imperfections cause a contamination of the pure left (right) circular polarized light with a linear polarized component in the horizontal (vertical) direction which is then selectively absorbed by the partially aligned A-OPV3 fibers. Consistent with this interpretation, the apparent CD effect arising from alignment due to convective flow (which is in the vertical direction) always shows the same sign. The sign of the apparent CD effect from the aligned film of A-OPV3 can be inverted by rotating the film over 90 degrees along the propagation direction of the light beam. The maximal artificial CD contribution can, in this first approximation, not be larger than the flow induced LD; only CD effects larger than the LD should be considered for molecular structural interpretations.

As a result of discussions with Aida et al., it was recognized that large Cotton effects in CD could be created by stirring solutions of aggregates of dendritic zinc-porphyrins, where the sign and intensity of the signal is proportional to the direction and speed of the created vortex flow in the cuvette. To discriminate this type of vortex flow with the convective flow described above, the aligned A-OPV3 solution was stirred in a clockwise and counter-clockwise direction (Figure 5.3a). Stirring the slowly cooled solution results in extraordinary large bisignate CD effects with the zero crossing at the maximum absorption and where the sign is affected by the stirring direction; in full agreement with the results of Aida and co-workers. After removing the vortex flow, the CD effect goes back to the effect observed for the aligned OPV solution. The shape of the CD effect induced by stirring is very different from that of the effect induced by convective flow as discussed above, suggesting a different origin of the stirring induced effect.

The CD effects caused by vortex flow in the cuvette can be explained in a simple way by using two aligned A-OPV3 films that are rotated with respect to each other. Bisignate CD effects whose sign and intensity depend on the angle of rotation of the second film with respect to the first film (Figure 5.3b) are obtained that are very similar to those induced by stirring. For dye doped cholesteric liquid crystals it has been recognized that macroscopic chirality can induce artificial CD effects that can be explained in the simplest way considering a two layer sample. With the first layer showing linear birefringence (LB) and the second layer showing LD’ (where the prime indicates that the property belongs to the second film) in a direction +/-45° with respect to the first layer, large apparent circular dichroism spectra are observed which are essentially a cross product of the LB and LD’ in the two layers. Similarly, in the case of A-OPV3, the CD signal originates from the macroscopic length scale
and is determined by the relative orientation of the second layer (+/- 45°). The observed bisignate CD effects for stirred solutions of A-OPV3 can now be explained by the vortex flow, aligning the fibers in the front- and backside of the cell under a different angle with respect to the vertical direction and with the LB of the front and the LD’ of the back side of the cell combining to an apparent CD contribution. The LD spectrum of the fibers is monosignate (Figure 5.2c) so that the LB spectrum, which is the Kramers-Kronig transform of the LD spectrum, is expected to be bisignate with a zero-crossing near the maximum of the LD intensity. For the combination of LB and LD into the artificial CD contribution one would therefore expect a bisignate spectral signature, which is consistent with the experiment. 

Figure 5.3. a) CD measurements while stirring a previously slowly cooled (self assembled) A-OPV3 solution in a clockwise (solid) and counter-clockwise (dashed) direction (c = 5 × 10^{-5} M, T = 293 K) b) Schematic picture of the angle φ between film 1 (back) and film 2 (front) (left) and c) the results of this orientation study of aligned films of A-OPV3 (right) for φ = - 45° (solid), φ = 45° (dashed) and φ = 90° (dotted).

From these experiments three different contributions to the observed CD effects of A-OPV3 in a stirred solution could be assessed. The first results from the macroscopic helical arrangement of the assemblies induced by the helical flow pattern in the sample cell leading to a bisignate CD effect originating from the combined LB and LD’ optical responses of the A-OPV3. In addition there can be a minor contribution arising from LD of the A-OPV3 and birefringence in the optical system similar to the monosignate CD effect under convective flow (vide supra). Finally, there might be a contribution from stirring induced chirality on the molecular level for which a bisignate spectral shape is also expected, but this option is discarded because the observed CD effect appears and disappears very rapidly when turning the stirring on and off.

The chiral analogue of A-OPV3, namely S-OPV3, did not show any appearance of a linear dichroic signal in the dodecane solvent. However, since the self-assembly of the chiral analogue S-OPV4 has been studied in great detail before, the influence of shaking, cooling and stirring has also been investigated. The CD spectrum taken at ambient temperature without stirring, (Figure 5.4a, solid curve) is free from the two types of artifacts discussed above and corresponds to those previously reported (Figure 5.1). Furthermore, shaking does not affect the CD spectrum. Under stationary conditions no LD effects are present. A CD cooling curve, similar to that reported previously, is recorded (Figure 5.4b, triangles) having an elongation temperature, T_e, of 339 K (c = 2.4 × 10^{-3} M) as determined with circular dichroism. Following the cooling of the S-OPV4 solution with linear
Circular dichroism shows an increase in LD that starts below ($T = 334$ K) the elongation temperature of the self-assembly. Since the size of the S-OPV4 assemblies is much smaller than A-OPV3, the S-OPV4 fibers are less susceptible to the created flow patterns in the cuvette and hence randomization of the fibers is much faster. Although LD is present during cooling, the CD value at 293 K is only marginally affected (typically 4%). Previously, it has been suggested that S-OPV4 forms bundles of fibers at high concentrations based on AFM data and the additional increase in CD intensity during cooling was ascribed to the lateral interactions of the fibers. When this OPV solution ($c = 2.4 \times 10^{-4}$ M) is monitored by LD, an increase in intensity occurs at the same temperature as the additional increase in CD. This suggests that the deviation from the cooperative self-assembly model is probably caused by the formation of bundled fibers and/or influenced by the alignment of the (bundled) fibers in the convective flow in the cuvette as visualized by linear dichroism. Hence, it can be concluded that for the S-OPV4 convective flows can also give rise to deviations of the chiroptical spectra; however, the magnitude is so low, that all data published previously are only marginally influenced by this phenomenon.

![Figure 5.4](image)

**Figure 5.4.** S-OPV4 dodecane solution (1 cm cuvette, $c = 3 \times 10^{-5}$ M). a) CD-spectra at 293 K without stirring (solid), with clockwise (dashed) and counter-clockwise (dotted) stirring (solution obtained by cooling at 60 K/hr from 363 to 293 K, without stirring) and b) Temperature-dependent CD measurements at $\lambda = 420$ nm ($\Delta T/\Delta t = -60$ K/hr) without stirring (triangles), with clockwise (circles) and counter-clockwise (squares) stirring.

On the other hand stirring a S-OPV4 solution showed again a significant influence on the CD effect and the sign depends on the stirring direction (Figure 5.4a). Similar to A-OPV3, the absorption is not affected by the vortex flow. The CD intensity upon stirring is less intense than for A-OPV3 which is probably a result of the different sizes of the two types of assemblies. The CD intensity was also monitored during cooling at $\lambda = 420$ nm, while the S-OPV4 solution was not stirred or stirred continuously in a clockwise or counter-clockwise direction (Figure 5.4b). The effect of stirring becomes visible 5 K below the elongation temperature. This behaviour again suggests that a certain stack length is needed for the assemblies to be influenced by stirring.

Hence, supramolecular assemblies can be partially oriented by convective flow, shaking, or stirring and this partial orientation induces an artificial contribution to the circular dichroism spectra of both chiral and achiral assemblies. The shape, sign, and intensity of the CD effect depend on the type of
created flow and two different CD effects were observed; one due to convective flow and is based on linear dichroism and one due to vortex flow patterns and is based on linear dichroism and linear birefringence. It is clear that the alignment of supramolecular assemblies in dilute solutions can create artifacts in the chiroptical properties of the system which should be clearly differentiated from the effects originating from chirality at the molecular length scale. A change to a cyclic alkane solvent like methylcyclohexane (MCH) for the assembly of OPVs was sufficient to decrease the contribution of linear dichroism to an absolute minimum, without changing the characteristics of the self-assembly mechanism.\textsuperscript{5,17} Most likely, the size of the assemblies is less in this solvent and the created convective flows do not have a significant effect on fibers of this length.

5.3 Circular dichroism to study the formation of mixed assemblies

Circular dichroism has been explored to study mixed assemblies with equal (A-OPV3/S-OPV3, A-OPV4/S-OPV4) or unequal (A-OPV4/S-OPV3) oligomeric lengths. The investigation of the classical ‘Sergeant-Soldier’ experiment for the OPV3 and OPV4 based systems having equal oligomeric lengths has been performed by Dr. Subi George and the most important observations will be briefly discussed. The ‘Sergeant-Soldier’ experiments for OPV3 and OPV4 systems (Scheme 5.1) have been conducted in MCH. Also in this solvent, all OPV derivatives (Scheme 5.1) self-assemble via the cooperative mechanism.\textsuperscript{17} It should be noted that for the achiral compounds the self-assembly mechanism was probed by UV/Vis spectroscopy. At the same concentration, the stability of the achiral OPVs is higher than that of the chiral derivatives having the same conjugation length, as indicated by a significantly higher \( T_e \).\textsuperscript{17} Furthermore, the stability of the longer achiral OPV oligomers (A-OPV4) is higher than that of the shorter oligomers, similar to the results obtained for the chiral OPV.\textsuperscript{5} Mixing the compounds in the assembled state at room temperature did not reveal any chiral amplification, indicating that the self-assembled structures are kinetically inert at this temperature (\( T = 293 \text{ K} \)) and concentration (\( c = 2 \times 10^{-4} \text{ M} \)). By heating the solution to the molecularly dissolved state intimate mixing of the components was achieved, and subsequent cooling allowed the coassembly of the two components resulting in chiral amplification. In the case of A-OPV3 10 mol\% of the S-OPV3 sergeant was needed for full chiral amplification to be achieved, while for A-OPV4 15 mol\% of S-OPV4 was necessary at a similar concentration. This indicates that S-OPV3 has a stronger influence on the helicity of an achiral ensemble than S-OPV4.

For the exploration of CD spectroscopy to study the organization of mixed assemblies having building blocks that differ not only in side-chain, but also in the oligomeric length; S-OPV3 was taken as the chiral trimer and A-OPV4 as achiral tetramer. As discussed above, the combination of a short chiral oligomer and a longer achiral oligomer can lead to a significant difference in temperature of elongation, in this case being 14 K, since the \( T_e \) for S-OPV3 was found to be 316 K while the A-OPV4 showed a \( T_e \) of 330 K at the same concentration (\( c = 1 \times 10^{-4} \text{ M} \)). Mixing S-OPV3 and A-OPV4 in a 1:1 ratio (at a total concentration of \( 1 \times 10^{-4} \text{ M} \)) in the self-assembled state at room temperature did not reveal any chiral amplification and only the CD spectrum of pure S-OPV3 assemblies could be detected (see Figure 5.1a). The spectra did not change after standing for a couple of hours at room temperature (Figure 5.5a).
Circular dichroism to study the organization of achiral and chiral OPV mixed assemblies

Figure 5.5. a) CD spectra before annealing (a) and after annealing (b) in MCH (0-100 % S-OPV3 with 100-0% of A-OPV4, c = 1 × 10⁻⁴ M, T =293 K) c) The g⁰⁰-value at 500 nm (black) and 425 nm (gray) versus the incorporation of S-OPV3 before (squares, triangles) and after (circles) annealing and d) heating (squares) and cooling (circles) curve of a 1:1 mixture of S-OPV3 and A-OPV4 in MCH (c_total = 1 × 10⁻⁴ M, ∆T/∆t = 60 K/hr, λ = 455 nm). In (a) and (b), some spectra are omitted for clarity.

When changing the ratio between the two components at a constant total concentration, the CD effect appears only after 30 mol% of S-OPV3, indicating that at lower percentages the S-OPV3 molecules are in their molecularly dissolved state as hydrogen-bonded dimers. When the g⁰⁰-value at λ = 425 nm, a wavelength where both OPV3 and OPV4 absorb, is plotted against the molar percentage of S-OPV3 (Figure 5.5c, gray curve), a non-linear behaviour is observed indicating that both molecularly dissolved species and helical assemblies are present after 30 mol% of S-OPV3. These observations are in line with previous results obtained for a pure S-OPV3 solution and suggest that mixing between S-OPV3 and A-OPV4 is not occurring. This is supported by the absence of any CD effect at 500 nm (Figure 5.5c), where only the OPV4 chromophore absorbs (see Figure 5.1b) thus showing that the OPV4 assemblies do not have a preferred handedness. Previously, the self-assembly of A-OPV4 has been investigated using a chiral acid to bias the helical handedness of the fibers. There the cooling curve suggested that the large majority of molecules were present in the aggregated state and that at room temperature the A-OPV4 assemblies were not dynamic on the timescale of the experiment. Upon heating the non-amplified solution, it appeared that closer to the temperature of
elongation the assemblies became increasingly dynamic as was indicated by the presence of an induced CD effect at these higher temperatures. Combined, these results indicate that the S-OPV3 is not able to mix with A-OPV4 at room temperature, most likely due to the kinetic inertness of the A-OPV4 stacks, while at temperatures closer to the $T_e$, the kinetic inertness disappears (vide infra).

In order to create mixed assemblies the solutions containing varying amounts of S-OPV3 and A-OPV4 were heated to the molecularly dissolved state and subsequently cooled to room temperature. Interestingly, the CD spectrum is changed with respect to the non-annealed samples (Figure 5.5b versus Figure 5.5a). Until 30 mol% of S-OPV3 the shape and position of the CD effect is similar to an A-OPV4 solution where the helical handedness is biased by chiral acids.\textsuperscript{17} Already for the 1 mol% of S-OPV3 spectrum a helical OPV4 spectrum can be observed with CD spectroscopy. This shows that chiral amplification is not limited to molecules having only different (chiral) side-chains, but also for different chromophores having different side-chains. Remarkably, the CD spectra obtained for a solution containing a low percentage of S-OPV3 reveal that the S-OPV3 is present in A-OPV4 stacks, although at these concentrations S-OPV3 without A-OPV4 is in the molecularly dissolved state. At this point it should be noted that it is not clear if the S-OPV3 is present as hydrogen-bonded homodimers (S-OPV3 : S-OPV3) or as hydrogen-bonded heterodimers (S-OPV3 : A-OPV4) or both. For higher incorporation ratios (above 30 mol%) of S-OPV3 the CD spectrum starts to shift more towards that of pure S-OPV3 revealing also the formation of pure S-OPV3 helical aggregates. The CD spectra of the mixtures were simulated using a linear combination of the CD spectra belonging to pure S-OPV3 and S-OPV4 solutions. However, the difference in packing of chiral and achiral molecules hampered a good description of the measured spectra. This difference in packing was accounted for by performing the simulation of the CD spectrum with the 1 mol% S-OPV3 in 99 mol% A-OPV4 curve in combination with the pure (100 mol%) S-OPV3 spectrum. All the measured curves could be simulated by a linear combination of these two spectra. This already implies the presence of enriched clusters of S-OPV3 and A-OPV4 where some S-OPV3 has to be incorporated to be detected with CD spectroscopy. It is likely that also pure A-OPV4 clusters having a nonbiased helix handedness are present that cannot be detected with circular dichroism.

In order to further investigate the supramolecular organization in these mixed systems, the CD intensity (in $g_{abs}$-value) was evaluated at $\lambda = 500$ nm with respect to the molar percentage of S-OPV3 (Figure 5.5c). At $\lambda = 500$ nm only the ‘chiral’ OPV4 cluster is responsible for a CD effect thereby allowing the exclusive visualization of the chiral amplification.

Upon increasing the amount of S-OPV3, the CD effect at 500 nm reaches its maximum at 50 mol%. This increase in intensity is typical behaviour for the classical ‘Sergeant-Soldier’ chiral amplification studies as described in the beginning of this section. However, in contrast to the previous reports the increase levels off around 50 mol% of S-OPV3, after which the value even goes back to zero. Therefore, quite remarkably, the amplification of chirality becomes less for mixed assemblies having more than 50 mol% of S-OPV3. This can be explained by an increase in phase separation at higher incorporation ratios of S-OPV3, suggesting the formation of S-OPV3 rich and A-OPV4 rich clusters. Furthermore, the 50 mol% coincides with the point where S-OPV3 starts to assemble on its own (Figure 5.5c gray). Thus, the formation of these enriched clusters at high S-OPV3 content could be the result of a smaller difference in temperature of elongation of the two components. This could allow both components to nucleate it’s self-assembly within almost the same temperature range, ultimately
leading to an increased phase separation. In this way the values between 30 and 50 mol% S-OPV3 can be regarded as a transition phase where the nucleation of the S-OPV3 assembly becomes increasingly more dominant and phase separation becomes more pronounced.

To study the dynamics of the assemblies, the annealing process of a solution containing a 1:1 ratio of S-OPV3 with A-OPV4 that was mixed at room temperature, was heated to 363 K at 60 K/hr, and subsequently cooled down at the same rate (Figure 5.5d). Both the heating and cooling run were monitored by CD spectroscopy at $\lambda = 455$ nm, the CD maximum of the OPV4 assemblies. The non-annealed sample gives a CD intensity of -10 mdeg (Figure 5.5a), while the sample after annealing yields a value of ~ -30 mdeg (Figure 5.5b) at room temperature, as discussed above. Two distinct processes in the heating curve were observed. First a decrease in CD effect is observed which can be related to the disassembly of S-OPV3 assemblies. At $T \approx 314$ K the CD effect slightly increased, most likely a result of chiral amplification initiated by intimate mixing of A-OPV4 with S-OPV3 as a consequence of the enhanced dynamics of the A-OPV4 assemblies at this temperature. These enhanced dynamics at higher temperatures is consistent with previous reports on the binding of chiral acids to the ureidotriazine moiety to bias the helicity of the assemblies, which became only effective at elevated temperatures. The second effect is the subsequent reduction in CD effect in Figure 5.5c at higher temperatures which is related to the disassembly of the mixture of S-OPV3 and A-OPV4. Cooling this mixture from its molecularly dissolved state resulted in a significantly higher CD effect at $\lambda = 455$ nm than in the heating run for all temperatures below the $T_c$ of A-OPV4. The higher CD intensity is ascribed to chiral amplification of the A-OPV4 by S-OPV3 similar to the results discussed above. These observations show that the A-OPV4 assemblies are not dynamic at room temperature at this concentration. Since the S-OPV3 assemblies are closer to their $T_c$ at room temperature, it can be assumed that these are more dynamic than the A-OPV4 aggregates.

![Figure 5.6. a) CD spectra following the addition and cooling of S-OPV3 to A-OPV4 (ratio 1:1) at 293 K (black) and annealed 363 K (gray) measured at 273 K, and the spectrum of the mixture at 293 K (light gray) before cooling in MCH (c_total = 1 × 10^{-4} M, solutions were cooled at 60 K/hr, 2 mm cuvette). b) CD spectra of a 1:1 A-OPV4/S-OPV3 mixture or by addition at $T = 363$ K (gray), $T = 310$ K (light gray) and $T = 293$ K (black) (c = 1 × 10^{-4} M in 60:1 MCH/chloroform, $T = 273$ K, 2mm cuvette).]
In order to take the dynamic nature of the assemblies into account, a second preparation method was devised. Here, chiral $S$-OPV3 was added at a temperature relatively far below the $T_e$ of the already formed $A$-OPV4 assembly which was kinetically inert at this temperature. Since $S$-OPV3 was much closer to its $T_e$, the assemblies are likely to be more dynamic.

First pre-assembled MCH solutions of $S$-OPV3 and $A$-OPV4 having the same concentration were added at 293 K (Figure 5.6a) and subsequently cooled at 60 K/hr to 273 K to allow further assembly of $S$-OPV3. At these low temperatures the $A$-OPV4 assemblies are kinetically inert (vide supra). The spectrum at 293 K is similar in shape to that of the 1:1 ratio in Figure 5.5a and shows that chiral amplification is absent. The shape and the intensity of the spectrum obtained at 273 K is the same as at 293 K, indicating that the decrease in temperature does not result in further growth of the assembly and that the supramolecular structures do not mix. Upon heating this solution to the molecularly dissolved state at 363 K, intimate mixing is allowed and subsequent cooling results in chiral amplification of $A$-OPV4 by the $S$-OPV3 in a similar fashion as described above.

In the next experiment a concentrated $S$-OPV3 chloroform solution, where the chromophores are present in their hydrogen-bonded dimeric state, was injected into $A$-OPV4 MCH solution, after which the solution was cooled to 273 K. Three different injection temperatures were used being 293 K, 310 K and 363 K, where the first two are well below 314 K, the point where the $A$-OPV4 assemblies are still dynamic on the timescale of the experiment. Injection of a concentrated chloroform solution of $S$-OPV3 to an $A$-OPV4 solution in MCH at $T = 293$ K or at $T = 363$ K was followed by cooling the solutions at 60 K/hr to 273 K. For both injection temperatures, the CD spectra are similar to those obtained in pure MCH at $T = 273$ K while the components were mixed at 293 K and 363 K without the use of chloroform. This suggests that this amount of chloroform does not have any significant influence on the self-assembly (Figure 5.6b). Addition of $S$-OPV3 at 310 K also showed a CD effect in the OPV4 absorption region after cooling of the solution, which indicates mixing of the two components. When compared to the curve obtained after mixing at high temperature, the CD intensity at 500 nm is significantly lower suggesting the formation of more enriched clusters. Although, CD spectroscopy is able to give insight into the organization of mixed assemblies, it cannot distinguish between enriched clusters present in one single stack or as separate stacks.

### 5.4 Conclusion

Alignment of self-assembled objects of achiral molecules in dilute solutions by either a convective flow, shaking or stirring can create large apparent circular dichroic effects that can either be monosignate or bisignate in nature. The circular dichroic effect originates from phenomena at the macroscopic level in combination with imperfections in the apparatus. When performing, for example chiral amplification studies in self-assembled systems; one should discriminate between the chirality originating from the molecular, supramolecular or this macroscopic level. The presence of linear dichroism can be reduced as was observed for the supramolecular polymerization of OPV derivatives in methylcyclohexane, in which a linear dichroic signal was absent. Hence the observations from the CD studies performed in methylcyclohexane can be interpreted on a supramolecular level. Two preparation methods for obtaining mixed assemblies consisting of two components having unequal
Circular dichroism to study the organization of achiral and chiral OPV mixed assemblies

Oligomeric lengths have been analyzed for their influence on the internal organization of the components in the resulting assemblies. The first preparation method includes an annealing step in the molecularly dissolved state to allow full mixing of the components. The CD spectra of the cooled solutions showed the formation of enriched clusters of the separate components. Surprisingly the degree of chiral amplification became less when large amounts of sergeant (above 30 mol\%) were present. These results might give insight into how chiral amplification takes place in a classical ‘Sergeant-Soldier’ experiment. Injection of the second component from its molecularly dissolved state into a pre-assembled solution of the first component showed hardly any chiral amplification indicating that changing the injection temperature can influence the level of enrichment of the clusters. This shows that the organization of two components can be influenced when taking the dynamic nature of the self-assembled structures into account, eventually leading to clusters of pure compound. Overall this study has shown the use of circular dichroism to provide insight into the organization of multiple components in the assembled state, however, for the determination of the exact supramolecular organization CD spectroscopy should be combined with additional complementary techniques.

5.5 Experimental Section

**General methods.** All solvents were of AR quality except for MCH and dodecane (spectroscopic grade) and were purchased from Acros and Aldrich and were used without further purification. The synthesis is discussed elsewhere.\(^5,17,18\) Absorbance, LD and CD spectra were measured on a Jasco J-815 spectropolarimeter where the sensitivity, time constant and scan rate were chosen appropriately. Temperature-dependent measurements were performed with a PFD-425S/15 Peltier-type temperature controller with a temperature range of 263-383 K and adjustable temperature slope. Atomic Force Microscopy images were recorded under ambient conditions using a Digital Instrument Multimode Nanoscope IV operating in the tapping mode regime. Microfabricated silicon cantilever tips (NS) with a resonance frequency of approximately 300 kHz and a spring constant of about 50 Nm\(^{-1}\) were used. Shaking of the cuvette was performed by placing the right index finger on the cap of the cuvette and the thumb on the bottom and shaking the cuvette in its vertical direction. The A-OPV3 films were prepared by applying a couple of drops of a concentrated A-OPV3 (c = ~2 mM) solution in heptane on a glass plate and letting the solvent evaporate while the glass plate was held under an angle to induce flow. Clockwise and counter clockwise stirring was achieved with different stirrers. The first self-assembly protocol consisted of heating a solution to 363 K, after which the solutions were cooled at 60 K/hr either to 293 or 273 K. The second protocol was performed by injection of a concentrated chloroform solution of S-OPV3 into a pre-assembled solution of A-OPV4 in MCH, followed by cooling the solution at 60 K/hr to 273 K.

5.6 References and notes

Chapter 5


13 After quickly cooling the same solution by quenching in an ice bath, stirring showed a less intense bisignate CD effect similar in sign to the slowly cooled solution.


16 In dye-doped cholesteric LCs, usually monosignate CD effects arise. In this case, the LB component originates from the host liquid crystal, which usually does not show a pronounced wavelength dependence in the region where the dye absorbed, because the LDC is transparent in this region. See: Mason, S. F.; Peacock, R. D. J. *Chem. Soc. Chem. Commun.* 1973, 712-713.


The influence of reduced dynamics on the self-assembly of star shaped molecules

Abstract. The self-assembly of a chiral hexa(oligo(p-phenylene vinylene)) substituted benzene was studied in pure methylcyclohexane (MCH) and in a 4:1 mixture of MCH/toluene. Temperature-dependent CD and UV/Vis spectroscopy showed that the self-assembly follows a cooperative mechanism. In the solvent mixture a transition from one supramolecular state (A1) to a second supramolecular assembly (A2) was observed upon cooling to room temperature, this transition in MCH only occurred after 6 days standing at room temperature. The relative slow dynamics of the assemblies allowed the application of size exclusion chromatography (SEC) to address the characteristics of the supramolecular polymerization process in MCH and MCH/toluene mixture. In MCH the A1 aggregates could be resolved with SEC, while in the solvent mixture these aggregates were too dynamic to be measured and disassembled upon injection onto the SEC column. Remarkably, for the A2 state in the 4:1 mixture of MCH/toluene a constant monomer fraction of about 15 mol% in SEC could be determined, which was confirmed with $^1$H NMR spectroscopy. Strong hysteresis in the formation of A2 showed that the self-assembly process did not occur under thermodynamic control. The A1 – A2 transition was hampered in mixed assemblies containing both enantiomers of the chiral hexa(oligo(p-phenylene vinylene)) substituted benzenes. Due to the significant difference in kinetic stability of the A1 state in MCH and 4:1 MCH/toluene, the transition in these enantiomeric mixtures did not occur after 21 days observation in MCH and was achieved after 2 days in the solvent mixture. The kinetics of the transition of the mixtures in 4:1 MCH/toluene were studied by SEC and CD, revealing that the transition from A1 to A2 was faster for solutions having high content of one of the enantiomers. The transition was related to a tightening of the internal structure that was enabled by the formation of a certain length of enantiomerically pure material in the assembly. Thus a reduced dynamic nature leads to the formation of different types of supramolecular assemblies, of which the dynamics depend highly on the solvent and the organization of the molecules. Furthermore, the slow dynamics allowed the application of SEC to study the self-assembly and revealed an unusually high monomer content in the solvent mixture.
6.1 Introduction

Nanofibers represent an important class of one-dimensional nanostructures at the forefront of nano-sized electronics and sensing. The vast majority of reported self-assembled systems so far are composed of a single building block (see Chapter 1). The next step in this field is the formation of a p-n junction within a single fiber implying that the p-type and n-type material have a specific organization with respect to each other. In order to arrive at such a complex architecture, the dynamic nature of self-assembled structures should be reduced. However, the effect of the decreased dynamics on the self-assembly has been scarcely studied. To study this effect star shaped oligo(p-phenylene vinylene) (OPV) molecules (Scheme 6.1) were chosen, since previous reports showed that assemblies of S-Star could not be disassembled in heptane, thus revealing an impressive stability. Furthermore, due to the presence of six OPV oligomers in this molecule it is expected that the dynamics in the self-assembly is slow. When using methylcyclohexane (MCH) as solvent, the star shaped molecules could reach their molecularly dissolved state and temperature-dependent chiroptical studies showed that assembly was achieved via the cooperative mechanism upon cooling the solution.

An interesting aspect of the reduction of the dynamics in self-assembled systems is that other characterization techniques are likely to become available. For normal covalent polymer chemistry, size exclusion chromatography (SEC) is by far the best technique to simultaneously address the polymeric length and polydispersity as well as the monomer content. A reduction of the dynamics will enable the use of SEC to study the self-assembly processes as was reported by Aida and co-workers, where SEC was applied in combination with CD and UV/Vis for the elucidation of the assembly of a racemic hydrogen–bonded supramolecular polymer in chloroform. Besides reduced dynamics, the molecules should not interact with the packing material in SEC. For this reason the OPV ureidotriazine moieties as discussed in the previous Chapter could not be used. So far, the determination of the monomer content in the solution did not receive much attention. The presence of monomers can interfere with the assembly of a second component, thereby hampering its exact placement in the aggregate. The influence of reduced dynamics on the self-assembly process as well as the determination of the monomer content with SEC in alkane solvents will be discussed in this Chapter.

6.2 Self-assembly of the pure compounds in MCH

The synthetic scheme of both S-Star and R-Star, having 24 stereocentres is depicted in Scheme 6.1. Although the synthesis and self-assembly of S-Star has been reported previously, the synthesis of the R-Star will be briefly discussed in this Chapter. The difference between the synthesis of the enantiomers is the enantiomeric purity of the starting 2-methyl-1-butanol (R-alcohol: ee = 97 %, S-alcohol: ee = 99.5 %). When assuming a statistical distribution of the chiral side-chains in the molecule, the calculation shows that for more than 99.4 % of the molecules R-Star will have at least 22 R-chiral side-chains, while S-Star has at least 23 S-chiral side-chains per molecule. The synthesis of the starting OPV3 aldehyde 2 will be described elsewhere. A Wittig-Horner coupling of aldehyde 2 with phosphonate 3 under basic conditions afforded 5 in 56 % yield. Subsequent Stille coupling with
commercially available bis(tributylstannyl)acetylene resulted in 7 after column chromatography. The use of an octacarbonyl cobalt catalyst in refluxing dioxane allowed the formation of the center benzene core by a cyclotrimerization of 7. MALDI-TOF analysis showed the presence of an impurity having a cyclopentadiene as the core of the molecular structure instead of the expected benzene.\(^{10,11}\) Intensive purification by recycling SEC allowed the removal of this side product from \textbf{R-Star}.\(^4\)

\textbf{Scheme 6.1.} The synthesis of \textbf{S-Star} and \textbf{R-Star}, the reader is referred to section 6.6 for further synthetic details. For the sake of clarity a correct balance in the dimerization and trimerization has been omitted.
It was previously shown that S-Star could not be molecularly dissolved in heptane, making the self-assembly mechanism difficult to ascertain.\textsuperscript{4} In order to reach the molecularly dissolved state and to avoid any undesirable contributions from linear dichroism artifacts (see Chapter 5), the self-assembly of R-Star and S-Star was investigated in detail in methlycyclohexane (abbreviated as MCH), where in this Chapter the results of the S-Star will be highlighted. Although there is a slight difference in enantiomeric purity (\textit{vide supra}), similar results have been obtained for S-Star and R-Star showing their enantiomeric relationship (Figure 6.1a). As was shown previously, at high temperatures in MCH the optical and chiroptical spectra exhibit the characteristic features of molecularly dissolved OPV molecules.\textsuperscript{4} Upon lowering the temperature at a controlled cooling rate a sharp non-sigmoidal increase of the CD intensity ($\lambda = 390 \text{ nm}$) at a specific temperature is observed (Figure 6.1a).\textsuperscript{4} A similar non-sigmoidal curve is seen by following the absorption intensity at the same wavelength (data not shown). This is a clear indication that these molecules self-assemble according to a cooperative supramolecular polymerization mechanism.\textsuperscript{12} The leveling of the CD cooling curve indicates that the degree of polymerization is nearly 100 \% at room temperature.\textsuperscript{4}

\textbf{Figure 6.1.} a) Temperature-dependent CD curve of S-Star (black squares) and R-Star (gray circles) with MCH as the solvent ($\lambda = 390 \text{ nm}$, $c = 2 \times 10^{-6} \text{ M}$, $\Delta T/\Delta t = -60 \text{ K/hr}$,) time-dependent CD (b) and UV/Vis (c) measurement ($c = 2 \times 10^{-6} \text{ M}$) and d) SEC curve of S-Star measured directly after cooling ($\lambda = 450 \text{ nm}$, $c = 2 \times 10^{-6} \text{ M}$) in MCH.

Remarkably when a MCH solution of S-Star was monitored with CD and UV/Vis over a period of 6 days at room temperature, changes in both CD (Figure 6.1b) and UV/Vis (Figure 6.1c) spectroscopy...
The influence of reduced dynamics on the self-assembly of star shaped molecules can be observed. Although changes in the UV/Vis are marginal, the CD spectra showed clear differences. The absence of light scattering and linear dichroism (data not shown) indicate that a different supramolecular arrangement in the aggregates is the likely cause of the change. As evident from the CD spectra for the two types of assemblies, one of the characteristic differences is the position of the zero-crossing that shifts to longer wavelengths with time. The first type of aggregate will be referred to as ‘A1’, while the second type is denoted as ‘A2’. The transition of A1 into A2 shows that A2 is the thermodynamically most stable aggregate at room temperature at this concentration.

The application of SEC is normally limited to the use of strong solvents for the packing material, like for example tetrahydrofuran, chloroform and toluene. However, alkanes are generally considered as an appropriate choice for the self-assembly of π-conjugated systems and hence these types of solvents are needed as eluent for the SEC. Alkane solvents are normally found to be a bad solvent for the packing material, and thus it is likely to hinder the swelling behaviour of the packing material and furthermore it can hinder the retention of the polymers through the column. Both effects limit the performance of the column. In order to investigate the possibility of using SEC as an analytical technique to study the assemblies, a freshly prepared $2 \times 10^{-6}$ M MCH solution of S-Star in the A1 state was injected onto a SEC column using MCH as eluent (Figure 6.1d). Interestingly, a single well-resolved peak was detected in the SEC trace that could be attributed to assembled molecules by online detection of a UV/Vis spectrum with a photodiode array UV/Vis detector. This result shows that the dynamics of the self-assemblies are such that SEC can be used as an analytical technique. The presence of monomers could not be observed indicating that the majority of the monomers are self-assembled, which is consistent with the CD spectroscopy data (Figure 6.1a). Furthermore, with the aid of fluorescence spectroscopy a previous study showed that the critical concentration was less than $1 \times 10^{-9}$ M, a concentration which is well below the detection limit of the photodiode array detector. The sharp onset of the aggregate peak indicates that the hydrodynamic volume is in the exclusion limit of this type of column (Polymer labs mixed B column, see section 6.6). For that reason, the apparent molecular weight (based on polystyrene standards) and polydispersity of the assemblies could not be determined. Furthermore, the SEC analysis discussed above was performed for a freshly prepared solution where the assemblies are present in the A1 state. To investigate the transition to the A2 state in closer detail with SEC, a column with larger pore size (mixed A column) was needed to allow for a better resolution of the aggregates. However, due to a difference in manufacturing of the packing material, the activity of the packing material was significantly higher in the new column; therefore MCH could not be used as eluent. The addition of 25 volume percentage of toluene to the MCH eluent circumvented this problem. Furthermore, toluene also allows self-assembly by cooling from high temperatures (~ 363 K) without loss of solvent. This inevitably means that the solvent for the self-assembly of the star compounds should also be altered to a 4:1 mixture of MCH/toluene.

6.3 Self-assembly in a solvent mixture

Before turning to the SEC analysis using the mixed A column and the 4:1 MCH/toluene mixture, the supramolecular polymerization of S-Star will first be addressed in this solvent mixture. The self-assembly process is monitored at a different wavelength than that used earlier in MCH ($\lambda = 450$ nm
instead of 390 nm), to produce a more pronounced difference in CD intensity between the different supramolecular states. Although the self-assembly of S-Star is discussed in detail; similar results have been obtained for R-Star showing that the components behave as enantiomers. Temperature-dependent CD (Figure 6.2a) and UV/Vis (data not shown) measurements showed a sharp non-sigmoidal change in intensity at a specific temperature ($T_e = 315$ K, $c = 5 \times 10^{-5}$ M) revealing the cooperative nature of the self-assembly. In order to show the influence of toluene on the temperature of elongation, a solution of S-Star in the solvent mixture should be compared to a solution in MCH at a similar concentration. For an $1 \times 10^{-6}$ M S-Star (data not shown) solution in 4:1 MCH/toluene the addition of toluene lowered the $T_e$ 26 K to 302 K when compared to a MCH solution ($T_e = 328$ K, $c = 2 \times 10^{-6}$ M, Figure 6.1a).

Figure 6.2. Temperature-dependent CD measurement monitored at $\lambda = 450$ nm both heating (circles) and cooling (squares) at 60 K/hr (a) and the full CD spectra (b) at $T = 293$ K (black) and $T = 308$ K (gray). Temperature-dependent CD curve ($\lambda = 450$ nm) of S-Star solution heated at 60 K/hr to 303 K (c) and 313 K (d) and subsequently cooled at 60 K/hr to 293 K. The full heating and cooling curves are displayed for clarity (gray), while the arrow indicates heating and cooling curves. ($c = 5 \times 10^{-5}$ M in 4:1 MCH/toluene)

Remarkably, at a temperature 7 K below the $T_e$ an inflection point, referred to as transition temperature $T_{tr}$, is observed in both the CD and UV/Vis cooling curve which is absent in the MCH cooling curve (Figure 6.1a). This indicates the presence of a second transition during the self-assembly process and its non-sigmoidal shape hints towards a second cooperative process. Interestingly, the CD spectrum at a temperature above $T_{tr}$ is characteristic for an A1 supramolecular arrangement that was
earlier found in a freshly prepared MCH solution, while at room temperature the CD spectrum resembles the A2 state that was observed for a six days old MCH sample (Figure 6.2b versus Figure 6.1b). In contrast to pure MCH, the transition from A1 to A2 occurs well before the cooling curve is saturated, indicating that the addition of toluene enhanced the rate of the transition. The transition temperature for a $5 \times 10^{-5}$ M solution of S-Star could be increased by reducing the cooling rate to 1 K/hr, while a lower transition temperature was observed for a faster cooled solution ($240$ K/hr, data not shown). A change in the cooling rate did not result in a different CD spectrum at $T = 293$ K showing that A2 aggregates are still formed. To study this intriguing transition the solution cooled at 60 K/hr was heated at the same rate from the assembled ($T = 293$ K) to the molecularly dissolved state ($T = 363$ K). A reduction of the CD intensity was observed at temperatures higher than $T_u$ (Figure 6.2a). To test the stability of the A2 state, a solution ($c = 5 \times 10^{-5}$ M) was heated to a temperature below (Figure 6.2c) and above (Figure 6.2d) $T_u$ and was kept at that temperature for an hour, after which the solution was cooled back to room temperature. At a temperature of 303 K, a temperature below $T_u$, there is no change in CD intensity during the hour annealing at 303 K (Figure 6.2c), however, at 313 K ($T > T_u$), the CD intensity drops to a similar value as observed in the initial cooling run (Figure 6.2d). This corresponds with the fact that in the heating curve there is only a drop in intensity at temperatures higher than $T_u$. Both observations indicate that the A2 aggregates are kinetically stable below the transition temperature. Decreasing the heating rate to 3 K/hr did not change the hysteresis (data not shown).

Figure 6.3. The concentration dependence (solutions cooled at 60 K/hr) of the zero crossing (a) and an AFM image (b) of $1 \times 1 \mu$m (height = 3 nm) on HOPG made via dropcasting a solution ($c = 5 \times 10^{-5}$ M S-Star) followed by evaporation of the solvent. For all measurements a 4:1 MCH/toluene solvent mixture has been used.

The concentration-dependent measurements show that at high concentration the A2 state is present while at low concentration the A1 state dominates at $T = 293$ K. The shape of the CD spectrum at $1 \times 10^{-6}$ M S-Star indicates that only the A1 state is present. By plotting the zero-crossing wavelength versus the concentration a transition concentration ($c_{tr}$) around $5 \times 10^{-6}$ M could be determined (Figure 6.3a), above which the majority of the assembly is in the A2 state and below $c_{tr}$ the A1 state is predominantly formed. An AFM image on HOPG of a dried dropcast solution of S-Star in the A2 state showed fiber-like assemblies similar to those observed in pure MCH (Figure 6.3b). The clustering of the fibers is likely caused by drying effects when preparing the sample.
As already mentioned SEC could be used to detect the aggregates in the MCH/toluene mixture. In sharp contrast to the results in MCH, a bimodal distribution in SEC for the solutions of S-Star was observed (Figure 6.4a). Similar to MCH, the online detection of a UV/Vis spectrum with a photodiode array detector allowed the first peak to be assigned to the supramolecular polymer, while, the second peak could be attributed to monomer. The increased pore size of the column allowed a more gradual onset of the aggregate peak showing that these assemblies could be resolved by using this type of column. Although some overlap between the two peaks is present, the resolution of the two peaks allowed the quantification of the monomer content. Repetitive injections of solutions having the same self-assembly protocol and concentration revealed that the intensity of the monomer peak could be reproduced; however, the position and shape of the peak corresponding to the aggregate changed in an irregular fashion. Furthermore, the retention times of both peaks are slightly affected by the concentration. These observations can be related to residual adsorption of star shaped molecules onto the column. This adsorption hampers the determination of the molecular weight and polydispersity of the aggregates. Furthermore, a small error in the integration of the peak area is likely to be introduced by these effects. Nevertheless, it allowed the monomer content to be determined for a self-assembled structure by using SEC.\(^{19}\) The quantification of the monomer content was achieved by calibrating the peak area of the monomers with a predetermined amount of monomers (see section 6.6 for the details). Subsequent integration of the peak area in the SEC trace allowed the calculation of the monomer content yielding a value of around 15 mol% at a concentration of \(c = 5 \times 10^{-5}\) M.

![Figure 6.4. a) SEC profile of three different concentrations of S-Star, after the supramolecular polymers have been formed (\(\Delta T/\Delta t = -60\) K/hr, 4:1 MCH/toluene) and b) monomer and A1 concentration as determined with SEC versus the total concentration of S-Star.](image)

Performing the SEC analysis for several different concentrations showed a significant difference between the A1 and A2 type of aggregates (Figure 6.4a). Although the CD spectra clearly show the presence of A1 assemblies at concentrations below \(c_t\), surprisingly, the peak of the supramolecular polymer could not be detected. Most likely, the dynamic nature of the A1 assemblies is too fast resulting in disassembly at an early stage of the SEC measurement. This instability hampered the determination of the monomer content and the values reported in Figure 6.4b are composed of monomers present after cooling and of monomers that were formed by the disassembly of the A1 aggregates. Based on \(^1\)H NMR, the first effect is likely to be the largest contributor to the observed...
The influence of reduced dynamics on the self-assembly of star shaped molecules

monomer content (*vide infra*). Remarkably the visualization of the A1 aggregates with SEC was possible in MCH (*vide supra*) revealing the drastic influence of toluene on the dynamic nature of the assemblies. Above $c_{tr}$ the aggregate peak could be detected in the solvent mixture revealing the reduced dynamics of the A2 aggregates. Quite remarkably at all concentrations above $c_{tr}$, at which the A2 aggregates are present, the monomer concentration is equal to approximately 15 mol% of initial monomer indicating that the degree of polymerization is independent of the concentration. As predicted by theoretical models, cooperative supramolecular polymerization processes have a constant monomer concentration (Chapter 1). However in the present case, the monomer concentration increased with the total concentration (Figure 6.4b). The deviation could be due to the fact that theoretical models are based on thermodynamically controlled reactions, while, for the star shaped molecules the self-assembly is not under thermodynamic control (*vide supra*).

![Figure 6.5](image)

**Figure 6.5.** a) Differential scanning calorimeter measurement of S-Star ($\Delta T/\Delta t = -60$ K/hr, $c = 1 \times 10^{-3}$ M, 4:1 MCH/toluene). b) Temperature dependence of the monomer fraction of S-Star (line is drawn to guide the eye). $^1$H NMR (500 MHz) of S-Star solution in a mixture of 4:1 MCH-d$_{14}$/toluene-d$_{8}$ ($c = 1 \times 10^{-3}$ M) at 293 K (c) and 343 K (d). The spectra are normalized to the signal of the internal standard at $\delta = 0.4$ ppm.

To confirm that the extraordinarily high monomer content in the 4:1 MCH/toluene solution was related to monomers still present after the self-assembly process of S-Star, $^1$H NMR spectroscopy was employed while using 1,4-bis(trimethylsilyl)benzene as an internal standard. For $^1$H NMR measurements, a high concentration ($c = 1 \times 10^{-3}$ M) is necessary to obtain a reasonable signal to noise. However, for this concentration optical techniques could not be used to determine at which temperature the molecules are molecularly dissolved. Instead, differential scanning calorimetry (DSC) proved helpful to determine the “starting point” of the supramolecular polymerization, which was
333 K at this concentration (Figure 6.5a). Furthermore, the asymmetry of the observed peak is additional evidence for the cooperative nature of the supramolecular polymerization.\textsuperscript{23}

The $^1\text{H}$ NMR spectra of S-Star in a 4:1 mixture of MCH-$d_{14}$/toluene-$d_8$ at 293 K (Figure 6.5c) and 343 K (Figure 6.5d) are both normalized to the intensity of the internal standard ($\delta = 0.4$ ppm). The integration of the singlet at $\delta = 6.9$ ppm\textsuperscript{24} and the multiplet at $\delta = 4.3 - 4.0$ ppm\textsuperscript{24} corresponding to protons of the S-Star were both taken to calculate the monomer fraction in solution. In order to confirm that these peaks were indeed related to monomer, diffusion ordered NMR spectroscopy was employed. The ratio between the diffusion coefficients of the peaks at 6.9 ppm and 0.4 ppm were independent of the temperature, indicating that the signal at 6.9 ppm corresponds to monomer and not to aggregates. Additional diffusing species could not be detected other than the signals belonging to the monomer, internal standard and solvents. Thus the resonances corresponding to the protons of both the A1 and A2 aggregates are likely to be too broad to be seen.\textsuperscript{25}

From Figures 6.5c and 6.5d it is clear that the intensity of the monomer peaks was greatly decreased at 293 K with respect to 343 K indicating a reduced monomer concentration at lower temperatures. The monomer content in the solution was determined at several different temperatures (Figure 6.5b). In analogy with the DSC trace the reduction in monomer concentration starts at 333 K. At the lowest temperature, $T = 293$ K, a monomer fraction of around 10 mol\% was determined which is in agreement with the SEC data. Combined with the concentration-dependent CD data (Figure 6.3a), this would suggest that at concentrations higher than $c_v$, monomers resulting from the disassembly of the A1 aggregates only marginally influence the monomer content (vide infra) determined with SEC and that it is mainly related to residual monomer in the solution.

The combined data showed that the star shaped OPV molecules are self-assembled in MCH and in a 4:1 MCH/toluene solution via the cooperative supramolecular polymerization mechanism. In both solvents a transition occurs from A1 aggregates to A2 type of assemblies. A transition between different supramolecular architectures has previously been reported for e.g. the thiophene derivatives discussed in Chapter 3, the merocyanine dyes described by Würthner\textsuperscript{26} and co-workers and the hexa-peri-hexabenzocoronenes (HBC) as investigated by Aida et al.\textsuperscript{27} However, in these cases the transition yielded a change in helicity for the septithiophene and merocyanine assemblies and a structural difference at the supramolecular level for the HBC aggregates. For the systems discussed in this Chapter, the difference is likely to be related to a slightly different internal organization of the star shaped molecules in the assemblies. In MCH the dynamics of A1 is such that the aggregates could be resolved by SEC. The addition of toluene significantly increased the dynamics of A1 which most likely hampered the detection of this type of aggregate with SEC. The enhanced dynamics could allow for a reorganization of the internal structure of the assembly that already occurs during the polymerization in the solvent mixture, while it only occurs after 6 days annealing at room temperature in pure MCH. The significant enhancement of the thermodynamic stability of A2 with respect to A1 could relate the transition to a tightening of the internal structure of the assemblies, which will be the subject of the next section.

The decreased dynamic nature of the aggregates can hinder the formation of the thermodynamically most favorable state and thus multiple self-assembled structures can be formed. Furthermore, the present study revealed a significant amount of monomers being present after the self-assembly process in the MCH/toluene mixture. The exact reason for this high content is still
The influence of reduced dynamics on the self-assembly of star shaped molecules

unclear; however, it is evident that the addition of a good solvent facilitated the presence of these monomers. Together with the enhanced dynamic nature of the A1 state in the solvent mixture, the drastic influence of the solvent on the self-assembly process is demonstrated. Since the determination of the monomer content is a subject that has not attracted much attention in the past, it poses the question if this high monomer content is limited to this specific example or is a more general phenomenon.

6.4 The transition from A1 to A2 in mixed systems

In order to investigate if the origin of the transition can be related to a tightening of the internal structure, the two enantiomers R-Star and S-Star (Scheme 6.1) were mixed. It can be anticipated that the 24 opposite stereocentres present in the wrong enantiomer can hinder a tighter packing of the molecules as proposed for the A2 state thereby hampering the A1 – A2 transition. Furthermore for the A1 state, the mixing of both enantiomers enabled the use of the ‘Majority-Rules’ effect (see Chapter 5) as a probe to study the organization and dynamics of the self-assemblies. The self-assembly of these mixed systems is investigated in detail, first in MCH and secondly in the 4:1 MCH/toluene mixture.

Figure 6.6. a) CD intensity at $\lambda = 390 \text{ nm}$ versus the incorporation ratio of S-Star into R-Star in mol% S-Star. b) CD spectrum of 100 mol% of R-Star in MCH measured directly after cooling, 2 days and 21 days after cooling. CD spectra before cooling and directly, 2 days and 21 days after cooling for 75 mol% R-Star (c) and 60 mol% R-Star (d). ($c = 2 \times 10^{-4} \text{ M in MCH}, \Delta T/\Delta t = -60 \text{ K/hr}$)
Freshly prepared MCH solutions of S-Star and R-Star, where the assemblies were present in the A1 state (vide supra), were mixed at room temperature and the resulting CD spectra corresponded to a summation of the CD spectra of the pure solutions (data not shown). The enantiomers were allowed to be fully mixed in MCH by heating the solutions to a temperature corresponding to the molecularly dissolved state and subsequently cooled to form mixed assemblies. The CD effects after cooling corresponded again to the A1 aggregated state. When plotting the CD intensity at $\lambda = 390$ nm against the incorporation of S-Star (Figure 6.6a) a non-linear relation was observed that indicates chiral amplification via the ‘Majority-Rules’ principle.\textsuperscript{28} After leaving the solution for 21 days at room temperature the CD spectra still showed A1 type assemblies, while the pure components already showed A2 aggregates after 6 days (Figure 6.1b), and therefore also after 21 days (Figure 6.6b). This suggests that the A1 - A2 transition is hindered in the mixed state.

\textbf{Figure 6.7.} a) CD spectra ($T = 293$ K) before annealing (a) and after annealing (b); some curves are omitted for clarity. c) The $g_{ab}$-value at $\lambda = 450$ nm before annealing (squares) after annealing (circles) and after 2 days at 293 K (stars) versus the mol% of S-Star. d) CD cooling curves for low incorporations of S-Star (0-8 mol%) in R-Star, while being cooled at 60 K/hr and monitored at $\lambda = 450$ nm. (constant concentration of $c = 5 \times 10^{-5}$ M, 4:1 MCH/toluene, while changing the ratio of the enantiomers)

For the 4:1 MCH/toluene solvent mixture, the addition of the solutions of R-Star and S-Star at room temperature, where the compounds are in the A2 self-assembled state, resulted in the same CD spectra as the summation of the CD spectra that corresponded to the pure compounds (Figure 6.7a).
Furthermore, the SEC measurements showed that for all mixtures 15 mol% of monomer was present before annealing (data not shown) similar to the pure compounds. The solutions were annealed by heating to 363 K, where the molecules are molecularly dissolved, and subsequently cooled at 60 K/hr to the self-assembled state. Remarkably, CD spectra taken directly after cooling showed the formation of A1 aggregates for the mixed samples, revealing that the transition observed for the pure compounds was absent (Figure 6.7b). This indicates that the enantiomers are not orthogonally assembled but are mixed. Although the CD intensity for an A1 state for the pure compounds could not be measured, a very small degree of non-linearity is observed for the mixtures similar to the results in MCH indicating some chiral amplification (Figure 6.7c, circles).

It was confirmed that the transition from A1 to A2, normally observed for the pure compounds (vide supra), did not occur in the mixtures when monitoring the cooling process by CD and UV/Vis spectroscopy. Upon lowering the incorporation of S-Star in R-Star assemblies both CD and UV/Vis spectroscopy revealed that for the mixtures containing less than 6 mol% of S-Star, the transition starts to appear in the cooling curve at 303 K (Figure 6.7d). The transition temperature shifts to higher temperatures ($T_{tr} = 305$ K for 1 mol%) upon further decreasing the S-Star content to 1 mol%. This suggests that a certain length of enantiomerically pure compound is necessary to facilitate the transition from A1 to A2. The temperature of elongation determined from the temperature-dependent CD and UV/Vis measurements was higher for the pure compounds than the racemic mixture (data not shown) indicating that the formation of the mixed assemblies is less favorable with increasing amount of the other enantiomer.

The SEC analysis of the mixed assemblies did not show any contribution from aggregates, which indicates again that the A1 state in MCH/toluene cannot be observed as aggregates by SEC. Furthermore, it shows that A2 assemblies are not present in solution. Besides the absence of an aggregate peak in the SEC, the monomer peak corresponds to ~100 mol% of monomer. To quantify the degree of aggregation in the A1 state $^1$H NMR was employed. As shown earlier directly after controlled cooling of a concentrated solution of 10 mol% S-Star in R-Star ($c = 1 \times 10^{-3}$ M, 4:1 MCH-d$_4$/toluene-d$_8$) at 60 K/hr from the molecularly dissolved state to the assembled state, the CD spectrum shows the formation of A1 aggregates while the SEC exclusively reveals monomers. In contrast, the $^1$H NMR yields 10 mol% of monomer which is the same as observed for the pure compounds (vide supra). This confirms that the A1 aggregates are too dynamic to be analyzed by SEC. Furthermore, the difference between the 10 mol% of monomer determined with $^1$H NMR and the monomer content obtained for the mixtures by SEC can be related to molecules that were originally present in the A1 state.
Figure 6.8. a) CD spectrum of a 10 mol% S-Star solution followed in time at room temperature for 96 hrs where the time elapse is shown by the arrows. b) Monomer fraction versus the annealing time at room temperature for three solutions having varying amounts of S-Star. (c = 5 × 10^{-5} M, 4:1 MCH/toluene)

The kinetics of the transition was followed with CD and SEC. Upon annealing the solutions at room temperature, CD spectroscopy revealed the transition of A1 to A2 occurring in time (Figure 6.8a). In contrast to the A1 state, in the A2 state no chiral amplification could be observed (Figure 6.7c, stars). Since the CD spectra are similar to a linear combination of the pure components, this suggests that that intimate mixing between the two components is not occurring in the A2 state indicating phase separation. With CD spectroscopy, the presence of A1 and A2 aggregates could not be quantified; however, the SEC experiments proved useful to study the transition. For three solutions having varying amount of S-Star (10, 30 and 50 mol% S-Star in R-Star) the monomer fraction is equal to 100 mol% directly after cooling (Figure 6.8b), while it drops to 25 mol% after standing at room temperature for 48 hrs and to 10 mol% after 11 days (determined with SEC and ¹H NMR, c = 1 × 10^{-3} M, 10 mol% S-Star/90 mol% R-Star, data not shown). The rate at which this decrease occurs is higher for the 10 mol% S-Star solution, than for the solutions containing a larger amount of S-Star. This shows that the transition from A1 to A2 is faster for the more enantiomerically pure samples, suggesting that clusters of pure component are facilitating the transition. In MCH, the slower dynamics hamper this rearrangement and hence the rate of the transition is significantly reduced. The enhanced dynamics of the A1 state in the solvent mixture most likely allows the mixed assemblies to rearrange their internal structures in order to phase separate the enantiomers into enantiomerically pure clusters that can subsequently undergo the transition to A2.

Table 6.1. An overview of the type of aggregate obtained for the pure and mixed systems and the influence of the self-assembly protocol as discussed for both solvents

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<td>Pure</td>
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<td>Pure</td>
<td>Mixed</td>
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<td>After cooling</td>
<td>A1</td>
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<td>A2</td>
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<td>1 day at T = 293 K</td>
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The combined results showed that the presence of a specific self-assembled structure depends highly on the solvent, the self-assembly protocol and the enantiomeric purity (Table 6.1). The solvent also has an influence on the dynamic nature of the aggregates, where the addition of good solvent enhanced the dynamics thereby facilitating the A1 – A2 transition. The presence of two different types of aggregates could be the result of the reduced dynamics that prevents the immediate formation of the thermodynamic most stable state.

6.5 Conclusion

The synthesis and characterization of R-Star and S-Star has been reported and the self-assembly has been investigated in detail in MCH and in a 4:1 mixture of MCH/toluene. In both solvents, the self-assembly is achieved via the cooperative supramolecular polymerization mechanism and revealed the transition of one type of aggregate (A1) to a second, a more thermodynamic stable type of assembly (A2). Furthermore, in both solvents the slow dynamics of the assemblies allowed the application of SEC to study the characteristics of the self-assembly. Although the A1 state could be detected with SEC using MCH as the eluent, the addition of toluene increased the dynamics of the assemblies to such an extent that A1 disassembled upon injection onto the SEC column. Furthermore, the increased dynamic nature in this solvent mixture allowed the transition from A1 to A2 to occur more rapidly. A high monomer content of 15 mol\% was determined by SEC and confirmed by $^1$H NMR techniques in the solvent mixture. However, in pure MCH, the monomer content, being less than $1 \times 10^{-9}$ M, could not be detected. This shows that the addition of toluene has a significant influence on the monomer content. By mixing the two enantiomers, a small degree of chiral amplification was observed in the A1 state in both solvents. Upon standing at room temperature the A2 state in MCH could not be formed in 21 days, however, in the solvent mixture formation of A2 was nearly complete after 2 days. Here, the slight chiral amplification observed in the A1 state was completely absent in the A2 state. The combined results indicate that the transition from A1 to A2 leads to a tightening of the internal structure that is facilitated by the formation of an enantiomerically pure phase. For the mixtures, these phases can be in a single stack held together by a region where the components are mixed, or the phases are present as single but separate stacks.

The results show that the reduction of the dynamics leads to the presence of multiple types of assemblies, in this case two being the A1 and A2 self-assembled states, that have different properties. A transition between these aggregates is possible and the kinetics depend on the enantiomeric content and the choice of the solvent. The mole fraction of monomer in the solution was determined and was found too be remarkably high and concentration independent (above $c_0$) in the solvent mixture. For MCH the presence of monomer could not be detected. The question arises if this high monomer content is an exception or that this phenomenon is more widespread, especially when mixed solvents are used to achieve aggregation.
6.6 Experimental Section

General methods. All solvents were of AR quality. Other reagents used were purchased from Acros and Aldrich and were used without further purification. MCH was of spectroscopic grade. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. and were used without purification. Toluene was dried over sodium and benzophenone, while dioxane was dried over moliesieves. $^1$H NMR and $^{13}$C NMR spectra were recorded on a 400 MHz NMR (Varian Mercury, 400 MHz for $^1$H NMR and 100 MHz for $^{13}$C NMR) or a 500 MHz NMR (Varian Unity Inova, 500 MHz for $^1$H NMR). The chemical shifts in deuterated chloroform were reported against trimethylsilane (TMS) standard. HPLC-grade chloroform was purchased from Biosolve. UV/Vis, CD and LD spectra were measured on a Jasco J-815 spectropolarimeter where the sensitivity, time constant and scan rate were chosen appropriately. Temperature-dependent CD, LD and UV/Vis measurements were performed with a PFD-425S/15 Peltier-type temperature controller with a temperature range of 263-383 K and adjustable temperature slope on the J-815. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a PerSeptive Biosystems Voyager-DE PRO spectrometer. To check the purity of the star shaped molecules gel permeation chromatography was performed on a Shimadzu LC10-AT using two PL Gel 3 µm 100 Å (length per column 300 mm, diameter 7.5 mm) column, a Shimadzu Photodiodearray SPD-M10Avp detector from 250-700 nm and chloroform as eluent with a flow rate of 1 mL/min ($T = 293$ K). For the SEC in MCH a Mixed B column was used having 10 µm particles, 300 × 7.5 mm, molecular weight range 500 – 10,000,000 (based on PS standards), while for both a flowrate of 1 mL/min was used. The columns were purchased from Polymer Labs. The peak area of the monomers was calibrated by averaging the peak area of 20 injections (100 µL) of a $1 \times 10^{-7} M$ solution of $^{5}$-Star in a 4:1 MCH/toluene mixture that was passed through only tubing instead of the column. The MCH was purchased from Aldrich (GC quality; 99%) and toluene was purchased at Biosolve (AR quality). Recycling size exclusion chromatography was performed on a modified Shimadzu LC10-AT using 1 Jaigel 2.5 H (600 × 20 mm) + 1 Jaigel 2 H (600 × 20 mm) column, a Shimadzu SPD-10Avp UV/Vis detector at 450 nm and 510 nm and chloroform as eluent with a flow rate of 3.5 mL/min ($T = 293$ K). Atomic Force Microscopy images were recorded under ambient conditions using a Digital Instrument Multimode Nanoscope IV operating in the tapping mode regime. Microfabricated silicon cantilever tips (NS) with a resonance frequency of approximately 300 kHz and a spring constant of about 50 N m$^{-1}$ were used. AFM samples were prepared by dropcasting the solutions on graphite.

Synthesis and characterization.

R-OPV4-Bromide (5). Potassium tert-butoxide (0.26 g, 2.3 mmol, 2.25 eq) is added to a solution of 3 (0.47 g, 1.5 mmol, 1.5 eq) in dry N,N-dimethylformamide (DMF, 5 mL) and stirred under an inert atmosphere at room temperature for 15 min. Compound 2 (1.24 g, 1.0 mmol, 1.0 eq) is dissolved in a mixture of tetrahydrofuran (THF, 15 mL) and DMF (5 mL) and subsequently added to the reaction mixture in a dropwise manner after which the solution was stirred for 2 hours. The reaction mixture was poured into 150 mL 6N HCl/ice mixture and the yellow precipitate was dissolved in 75 mL of dichloromethane (DCM). The combined organic layers were washed with a saturated KCl, dried with MgSO$_4$ and evaporated under vacuum. The crude mixture was purified by column chromatography (SiO$_2$, DCM/pentane 1:1) yielding 1.31 g (94 % yield) of yellow 4 as a solid material. $^1$H NMR (CDCl$_3$, 400 MHz): δ (ppm) 7.6-7.4 (m, 9H, ArC=CH, ArH); 7.2-7.1 (m, 4H, ArCH=CH, ArH); 7.05 (d, J = 16 Hz, 1H, ArCH=CH); 6.72 (s, 2H, ArH); 4.05-3.9 (m, 14H, OCH$_2$); 1.98 (m, 6H, OCH$_2$CH$_2$(CH$_3$)CH$_2$); 1.7-1.5 (m, 8H, OCH$_2$CH(CH$_3$)CH$_2$); 1.3 (m, 54H, OCH$_2$CH$_2$(CH$_3$)CH$_2$); 1.15-0.95 (m, 33H, CH$_3$). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ (ppm) 153.30; 151.40; 151.20; 151.14; 150.99; 138.07; 133.10; 135.97; 133.30; 131.81; 131.78; 128.63; 128.05; 128.02; 127.98; 127.91; 127.38; 127.32; 126.90; 126.18; 124.33; 122.85; 122.50; 121.60; 120.99; 110.93; 110.42; 109.84; 109.51; 105.08; 74.48; 74.41; 74.19; 73.99; 73.58; 69.10; 35.23; 35.22; 35.16; 35.02; 32.01; 30.44; 29.85; 29.82; 29.80; 29.75; 29.70; 29.52; 29.48; 29.45; 26.49; 26.46; 26.42; 26.21; 22.77; 16.93; 16.90; 16.84; 14.19; 11.61; 11.57; 11.46. MALDI-TOF MS (calc MW = 1360.93; C$_{86}$H$_{135}$O$_{7}$Br): 1360.69 [M$^+$]. IR ν (cm$^{-1}$): 2958; 2900; 2854; 1730; 1579; 1502; 1465; 1384; 1340; 1260; 1202; 1115; 1072; 1041; 1009; 965; 856; 806; 723.

Bis(R-OPV4)acetylene (7). Dry and oxygen free toluene (9.5 mL) was added to 5 (0.68 g, 0.50 mmol, 2.05 eq), after which the solution was purged with argon for 10 min. Pd(PPh$_3$)$_3$ (31 mg, 0.026 mmol, 0.11 eq), was added, followed by the dropwise addition of bis(trimethylsilyl)acetylene. The reaction mixture was refluxed for 16 hrs followed by cooling the solution and evaporating of the solvent. The crude mixture was extensively purified.
using column chromatography (SiO\textsubscript{2}; THF as eluent), biobeads column chromatography (SX1 on THF) and recycling SEC (CHCl\textsubscript{3} as eluent) eventually yielding 170 mg (61 %) of 7 as a red powder after precipitation in cold methanol. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): δ (ppm) 7.60-7.45 (m, 14H, ArC=CH, ArH); 7.45-7.30 (m, 12H, ArC=CH, ArH); 7.20-6.90 (m, 60H, ArC=CH, ArH); 6.72 (s, 12H, ArH); 4.05-3.95 (m, 36H, OCH\textsubscript{3}) (CDCl\textsubscript{3}, 100 MHz): δ (ppm) 153.30; 151.20; 151.10; 150.97; 140.37; 139.95; 138.18; 134.84; 133.30; 131.92; 128.77; 127.55; 127.26; 126.89; 126.75; 125.21; 122.57; 122.43; 110.74; 110.46; 109.86; 109.50; 105.11; 74.43; 74.19; 74.10; 73.57; 35.20; 35.16; 35.13; 34.88; 32.01; 31.98; 30.41; 29.82; 29.79; 29.76; 29.73; 29.67; 29.49; 29.46; 29.42; 26.46; 26.43; 26.20; 26.18; 22.75; 16.92; 16.90; 16.87; 16.82; 14.16; 11.54; 11.52; 11.33. MALDI-TOF MS (calc MW = 2584.1; C\textsubscript{14}H\textsubscript{23}O\textsubscript{5}N): 2584.41 [M\textsuperscript{+}].

**Hexa(R-OPV4)-benzene (R-Star).** Dry and oxygen free 1,4-dioxane (3.0 mL) was added to 7 (230 mg, 88.9 µmol) and the suspension was kept at 100 °C under an argon atmosphere for 7 hours after which it was cooled to room temperature. Evaporation of the solvent in vacuo allowed the crude mixture to be intensively purified by column chromatography (SiO\textsubscript{2}, 5 % of methanol in THF as eluent), biobeads column chromatography (SX1 on THF) and recycling SEC (CHCl\textsubscript{3} as eluent) eventually yielding 169 mg (73 %) of 7 as a yellow solid. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): δ (ppm) 7.55-7.45 (m, 12H, ArCH\textsubscript{2}CH=CH, ArH); 7.45-7.30 (m, 12H, ArCH=CH, ArH); 7.20-6.90 (m, 60H, ArCH=CH, ArH); 6.72 (s, 12H, ArH); 4.05-3.95 (m, 36H, OCH\textsubscript{3}) (CDCl\textsubscript{3}, 100 MHz): δ (ppm) 153.26; 151.44; 151.17; 151.12; 150.99; 138.17; 138.02; 133.25; 131.90; 128.61; 127.97; 127.92; 127.38; 126.37; 124.47; 122.87; 122.52; 122.01; 110.92; 110.44; 109.90; 109.38; 105.97; 90.66; 74.49; 74.42; 74.20; 74.06; 73.56; 69.10; 35.16; 35.11; 34.99; 31.96; 30.37; 29.78; 29.73; 29.68; 29.64; 29.46; 29.41; 29.39; 26.41; 26.15; 22.71; 16.90; 14.13; 11.55; 11.50; 11.41.

MALDI-TOF MS (calc MW = 7758.2; C\textsubscript{127}H\textsubscript{148}O\textsubscript{13}N\textsubscript{14}): 7758.30 [M\textsuperscript{+}]. IR ν (cm\textsuperscript{-1}): 3058; 2957; 2920; 2852; 1627; 1578; 1504; 1465; 1421; 1387; 1340; 1244; 1200; 1153; 1117; 1044; 1009; 963; 914; 851; 815; 769; 718; 694.

### 6.7 References and notes

16. Due to limited solubility, the monomer content could not be verified by for example \textsuperscript{1}H NMR spectroscopy.
17. A decrease in size of the assemblies by lowering the concentration will hamper the use of CD and UV/Vis as detection techniques, while an increase in temperature will significantly influence the interaction with the column and will enhance the dynamics of the self-assembly.
For 9:1 mixture of MCH/toluene the absorption on the column was still too high, while the 7:3 MCH/toluene ratio did not allow the system to be assembled at room temperature at a concentration where reliable temperature-dependent CD and UV/Vis measurements could be performed.

The difference in packing material can also result in the observed monomer content; however, $^1$H NMR experiments confirmed the SEC results.

Dynamic and static light scattering data showed scattering profiles of which the shape was independent of temperature and concentration (below $T_\text{tr}$ and above $c_\text{tr}$, data not shown). The light-scattering results suggest that the self-assembly yields a specific length of polymer after which the elongation process is significantly decreased in rate. It is tempting to relate this specific length to the transition of A1 to A2.

All the SEC measurements were performed immediately after the solution was cooled to room temperature.

For the assignments of the resonances to specific protons the reader is referred to section 6.6.

Dosy NMR spectroscopy confirmed that the integrated proton signals at $\delta = 6.9$ and $\delta = 4.0 – 4.3$ ppm were corresponding to protons in the monomer of the star shaped molecules.
Epilogue

Since the introduction of supramolecular chemistry by Cram, Lehn and Pederson impressive progress has been achieved to understand the aggregation of molecules. Especially self-assembly of molecules for example by hydrogen bonding and π-π interactions has reached a high level of understanding (see Chapter 1). However, to arrive at complex architectures with distinct functional properties, a perfect organization of multiple components in the aggregates needs to be achieved. For example, applications like p-n junctions for use in supramolecular electronics and photocatalysts similar to the photosynthetic unit found in Nature can be considered when using well-defined multicomponent systems (Figure 1).

![Figure 1. Schematic picture of a p-n junction (a) and a photocatalyst (b) converting $A \rightarrow B$ while energy and electron transfer processes tunnels the absorbed energy to the photocatalysts as indicated by the arrows.](image-url)

Crucial for the fabrication of such systems is the ability to exactly place the components at specified positions or in controlled clusters of building blocks and the stability of the organization in time. Since the spontaneous formation of highly ordered structures from multiple components in their monomeric state is unlikely to occur, a more stepwise approach is probably necessary to direct the assembly of multiple components towards a desired organization. However, an important consequence of devising such a multi-step non-covalent synthetic route for complex supramolecular assemblies is that the product of each synthetic step should be kinetically stable, implying the use of systems that display controlled dynamics. Furthermore, similar to the synthesis of small molecules and polymers the progress and outcome of each reaction needs to be monitored and should have a high yield.
In the self-assembly of $\pi$-conjugated molecules, the coassembly of the different components is assumed to occur in a random fashion. However, by simply considering the mixing of two different components that can be present in their assembled state, as monomers or as both, already four possibilities can be envisioned (Figure 2). These four organizations are a fully phase separated system, blocks, randomly distributed and an alternating sequence. Since the latter two possibilities show a high degree of mixing, they are likely to be formed when the dynamics of the self-assembled structures are high and the interaction between the different components is strong. However, within the same self-assembled structure a multiplicity of these possibilities can exist. For example, in the case of block copolymers the two blocks can be separated by a region of a more randomly distributed organization instead of a strict separation between the components as depicted in Figure 2. However, in order to simplify the following discussion, only these four cases will be considered.

**Figure 2.** Schematic picture of the four possibilities for a two components system to be organized depending on the dynamics and self-assembly protocol

Two of the four possibilities allow the control over the position of the components in a self-assembled structure, namely the alternating sequence and the block copolymer. The alternating sequence is a special case and is almost exclusively determined by having a much stronger interaction of component A with B than the interaction of A with another molecule of A. Furthermore, a significant amount of mixing is necessary, therefore the dynamic nature of the assemblies should not be slow. A reduction of the dynamics, while the interaction between A and B is still the most favorable one, will allow the synthesis of block copolymers. The formation of these structures can be seen as a first step to create supramolecular assemblies where the position of the different components is predetermined.

Covalently preparing such structures is a possibility; however, the synthesis of relatively small foldameric architectures with pendant chromophores can take close to 30 steps when starting from commercially available materials. Therefore, for the design and synthesis of complex structures a supramolecular approach seems more viable.

As mentioned in the beginning of this epilogue, for the specific organization of the different components to be kinetically stable, the components should have controlled dynamics in the self-assembled state. However, the presence of a reduced dynamic nature implies that multiple supramolecular organizations can be obtained due to the slow conversion between the states. Depending on the properties of the different self-assembled structures the presence of multiple states can hamper or benefit the formation of supramolecular block copolymers. For example, by choosing a specific solvent for the self-assembly, properties like $T_c$, length, monomer content and dynamic nature
of the supramolecular assemblies can be controlled. Additionally the degree of mixing between the
different components can be influenced by the solvent. Thus, an optimization of the reaction
conditions used for the self-assembly will eventually allow the synthesis of supramolecular block
copolymers or even more complex architectures, which was recently reported for the self-assembly of
covalent block copolymers by the groups of Manners and Winnik (Chapter 5).

Cooperative supramolecular polymerizations are characterized by having a nucleation event that
precedes the formation of elongated polymers. This nucleation can either be a homogeneous or
heterogeneous process. For the latter, seeds of foreign molecules can be used to initiate the self-
assembly process. This opens up the possibility of forming supramolecular block copolymers by a
sequential additional of monomers, as was attempted in Chapter 5. Furthermore, the development of
a more elaborate toolbox of self-assembly protocols, like the use of kinetically controlled or dissipative
conditions, could further enhance the control of different components in supramolecular architectures.

The exact determination of the internal structure of the self-assemblies is still a challenge for the
supramolecular chemist. Circular dichroism can be used to monitor the coassembly of multiple
components. While giving valuable insights, the precise internal organization of the two components
cannot be determined with this technique alone. Additional techniques like SEC and AFM are
generally used to determine the organization of covalent polymers, however, the results discussed in
this thesis (only for SEC, the AFM study has not been discussed) did not yield an increased insight
into the supramolecular organization. The resolution in SEC was not sufficient to visualize the
different assemblies, while in the AFM, drying and surface effects hampered the visualization of
single fibers. The application of small angle X-ray scattering, magnetic field alignment and linear
birefringence lead to the elucidation of the internal structure of a self-assembled system. However, the
drawback of these techniques is that a high concentration of the molecules is necessary, which is not
always attainable for self-assembled structures. In synthetic organic and polymer chemistry, the
reaction products are analyzed with a variety of complementary techniques. Therefore, for the exact
determination of the internal organization of self-assembled structures additional techniques are
necessary that are complementary to the chiroptical and optical techniques discussed in the previous
Chapters.

At first sight the properties of self-assembled systems as revealed in this thesis seem to be a
drawback for the formation of complex architectures. However, the dynamic nature that is dependent
on temperature, concentration and solvent shows that it is crucial to optimize the reaction conditions
for achieving the formation of complex supramolecular systems. Furthermore, making use of the
ability to nucleate the self-assembly process either in a homogenous or heterogeneous fashion opens
up unprecedented synthetic pathways. The synthetic pathways encountered in Nature employ
external influences, for example the use of templated assembly and chaperone proteins, to direct the
self-assembly towards a specific organization. By applying the lessons learned in the past on synthetic
chemistry (both organic and polymer chemistry) and the knowledge about the self-assembly
pathways found in Nature, the development of synthetic supramolecular chemistry can be
significantly boosted to a level where complex systems can be synthesized.
Insights into the self-assembly of \(\pi\)-conjugated systems

Summary

In Chapter 1 supramolecular polymerization of small molecules is introduced and exemplified. The self-assembly of these single component systems, for example by hydrogen bonding and \(\pi-\pi\) interactions, has reached a high level of understanding. However, for the fabrication of complex architectures with specific properties, a perfect organization of multiple components in the aggregates needs to be achieved. In order to arrive at such complex architectures more insight into the specificities of the self-assembly of \(\pi\)-conjugated systems is a necessity, which is the subject of this thesis.

A covalent strategy for the spatial organization of \(\pi\)-conjugated components by placement on a foldameric scaffold is discussed in Chapter 2. Although the synthesis of these foldamers was successful, the 30 synthetic steps make the synthesis of a specific foldamer a lengthy process while only achieving relatively small structures. It was found that placing the chromophores in a defined three dimensional environment hampered a uniform description of the charge transfer characteristics within the current theoretical models. Furthermore, the level of complexity in these synthetic systems pales in comparison with the examples found in Nature.

A more promising approach could be the self-assembly of molecules. Supramolecular polymerization via the cooperative mechanism is generally observed for the examples discussed in this thesis. Cooperative mechanisms have a nucleation event preceding the formation of the self-assembled structures. The evidence presented in Chapter 3 showed that the nucleation of oligothiophenes can be either homogeneous or heterogeneous in nature, depending on sample purity. Especially when the supramolecular interactions are counterbalancing each other, heterogeneous nucleation is likely to be present. By changing the self-assembly protocol, e.g. altering the cooling rate and method, the outcome of the self-assembly was remarkably different. This showed that the oligothiophenes were able to self-assemble into multiple different structures thereby displaying the presence of a complex energy landscape in analogy to polymorphism in the crystallization of molecules and to protein folding.

At higher concentration the internal structure of the oligothiophene assemblies was resolved by using a combination of small angle X-ray scattering and linear birefringence on magnetically aligned assemblies as discussed in Chapter 4. Optical and chiroptical studies showed that the cooperative nature of the self-assembly at this higher concentration was maintained. Cylindrical assemblies were observed, where the thiophene molecules were radially organized and \(\pi-\pi\) stacking was in a tangential direction.

Chapter 5 discusses the use of circular dichroism (CD) spectroscopy to monitor the coassembly of multiple components. For the achiral oligo(\(p\)-phenylene vinylene) ureidotriazine systems, artificial CD effects are observed for the self-assembled structures in dodecane that are a result of unwanted linear dichroic (LD) effects as a consequence of flow induced alignment in the cuvette. These LD artifacts interfere with the CD measurements. By using methylcyclohexane (MCH) the LD effects are absent.
and the observed CD effects can be considered as a result of exciton coupling between the chromophores. The influence of two preparation methods on the organization of mixed assemblies consisting of achiral and chiral OPV derivatives with different oligomeric length is studied with CD spectroscopy in MCH. The first preparation method allows the molecules to be fully mixed at high temperature, while subsequent cooling shows chiral amplification of the achiral longer oligomer by the shorter chiral oligomer. The study indicates the formation of enriched clusters of one of the two components either within one stack, or as separate stacks. The second method is based on the addition of the shorter oligomer at a temperature, where the assemblies of the achiral oligomer are already present and kinetically inert. In this case the chiral amplification is reduced, indicating the formation of more enriched clusters of compounds. However, to arrive at an unambiguous assignment of the internal structure of the assemblies, the CD data should be combined with complementary techniques.

In Chapter 6 the influence of reduced dynamics on the self-assembly of π-conjugated star shaped molecules is discussed. Two different types of aggregates, A1 and A2, are distinguished for the self-assembly in MCH, where a transition from A1 to A2 occurs, thereby showing the increased thermodynamic stability of the A2 aggregate. The addition of a good solvent enhances the rate of the transition. SEC in these alkane solvents shows that the A1 state in the solvent mixture (4:1 MCH/toluene) was far more dynamic than in pure MCH. Furthermore, it reveals an unusually high monomer content of 15 mol% in the solvent mixture, which is confirmed by 1H NMR. As expected, in pure MCH the monomer content is much lower and for that reason it could not be detected.

In order to investigate the origin of the A1–A2 transition, the two enantiomers are mixed and chiral amplification in the form of the ‘Majority-Rules’ effect is shown to occur in MCH, while it is only weakly present in the solvent mixture. The presence of the other enantiomer significantly slows down the kinetics of the transition from A1 to A2, where the transition only occurred in the solvent mixture. Quite remarkably, chiral amplification is absent in the A2 state in the solvent mixture. The combined results suggest that the A1–A2 transition is related to a tightening of the internal structure, where the transition is facilitated by the presence of an enantiomerically pure cluster.

In general the research described in this thesis reveals some important parameters that determine the self-assembly process and its outcome. Reflection on these parameters and their implication on the design and synthesis of complex multicomponent supramolecular architectures is given in an epilogue to this thesis.
Samenvatting

Inzichten in de zelfassemblage van \( \pi \)-geconjugeerde systemen

Samenvatting

In Hoofdstuk 1 wordt de supramoleculaire polymerisatie van kleine moleculen geïntroduceerd. De moleculaire zelfassemblage van systemen bestaande uit één soort bouwsteen door bijvoorbeeld waterstof bruggen en \( \pi \)-\( \pi \) stapeling is redelijk goed begrepen. Voor de vorming van complexe zelfgeassembleerde structuren met specifieke eigenschappen moeten verschillende soorten bouwstenen op een perfecte wijze in hetzelfde aggregaat worden georganiseerd. Door deze verhoogde complexiteit is veel meer inzicht nodig in de moleculaire zelfassemblage van kleine moleculen. In dit proefschrift worden moleculen gebruikt die door een afwisseling van enkele en dubbele bindingen in de moleculaire structuur een kleurstof zijn. Naast het vergemakkelijken van de detectie van de zelfassemblage is de alternenderende structuur verantwoordelijk voor de optoelectronische eigenschappen van deze moleculen. De introductie van deze eigenschappen in complexe zelfgeassembleerde structuren creëert de noodzaak voor het verschaffen van meer inzicht in de assemblage van deze \( \pi \)-geconjugeerde moleculen. Het doel van dit proefschrift is dan ook het uitzoeken van de parameters die invloed hebben op de assemblage van \( \pi \)-geconjugeerde systemen.

In Hoofdstuk 2 wordt een covalente strategie besproken om \( \pi \)-geconjugeerde bouwstenen te organiseren door plaatsing op een gevouwen structuur. Hoewel de synthese van deze structuren succesvol is verlopen, maakt de 30 synthetische stappen de vorming van deze relatief kleine structuren een langdurig proces. De drie-dimensionale organisatie van de kleurstoffen met behulp van deze gevouwen structuur zorgt ervoor dat de trend in de ladingsoverdracht processen niet met de huidige theorieën kan worden beschreven.

Een meer belovende aanpak is dan de zelfassemblage van moleculen. De systemen die in dit proefschrift worden besproken assembleren over het algemeen via het zogenaamde coöperatieve mechanisme. Dit mechanisme heeft een nucleatie die voorafgaat aan de groei van de zelfgeassembleerde structuur. In Hoofdstuk 3 wordt bewijs geleverd dat de nucleatie zowel homogeen als heterogeen kan zijn. Vooral wanneer de supramoleculaire interacties elkaar tegen werken is er een grote kans op het optreden van heterogene nucleatie. Door een verandering in de aggregatie condities, ofwel een verandering in de koelsnelheid en de koelmethode, kunnen verschillende zelfgeassembleerde structuren worden gevormd. Dit resultaat geeft aan dat een complex energielandschap aanwezig is voor de zelfassemblage van oligothiofenen. Complex energielandschappen zijn eerder waargenomen voor de kristallisatie van moleculen, ook wel polymorfisme genoemd, en voor de vouwing van eiwitten. Echter in de zelfassemblage is dit fenomeen onderbelicht en de studie in Hoofdstuk 3 geeft een duidelijke waarschuwing voor het ontwerp van complexe structuren, zodra heterogene nucleatie een belangrijke rol kan spelen.

In Hoofdstuk 4 wordt de interne structuur van oligothiofeen assemblages in geconcentreerde oplossingen opgehelderd met behulp van kleine hoek röntgen verstrooing en dubbelbreking aan magnetisch uitgelijnde aggregaten. De optische en chiroptische studies tonen aan dat de zelfassemblage ook bij hoge concentraties coöperatief verloopt. Onder de gebruikte aggregatie
omstandigheden vormen de oligothiofenen cilindrische aggregaten, waarbij de thiofeen moleculen radieel zijn georganiseerd en π-π stapeling tangentiële plaatsvindt.

Hoofdstuk 5 behandelt circulair dichroïsme (CD) spectroscopie als techniek om de coassemblage van twee verschillende soorten bouwstenen te bestuderen. Een artificieel CD effect is waargenomen voor aggregaten bestaande uit achirale oligo(p-fenyleen vinyleen) ureidotriazine bouwstenen aanwezig in een oplossing van dodecaan. Deze CD effecten worden veroorzaakt door ongewenste linear dichroïsche (LD) effecten veroorzaakt door de uitleiding van de aggregaties als gevolg van een convectieve stroming in de cuvette. Deze LD artefacten interfereren met de CD metingen. Door het gebruik van methylcyclohexaan (MCH) kan het LD effect tot een absoluut minimum worden beperkt, waardoor interpretatie van de waargenomen CD effecten met behulp van exciton koppeling mogelijk wordt. Met behulp van CD spectroscopie is de invloed van twee bereidingsmethoden op de organisatie van verschillende bouwstenen in gemengde aggregaten bepaald. De aggregaten worden opgebouwd uit achirale en chirale OPV derivaten met een verschillende oligomeer lengte. In de eerste bereidingsmethode worden de moleculen volledig gemengd door de coassemblage te laten beginnen bij een hoge temperatuur (moleculair opgeloste toestand). Het afkoelen van de oplossing resulteert in chirale amplificatie van de achirale oligomeer door de chirale oligomeer. Deze studie suggereert de vorming van clusters die zijn verrijkt in een van de twee bouwstenen. Het is onduidelijk of de verschillende clusters in één aggregaat of in gescheiden aggregaten voorkomen. De tweede bereidingsmethode is gebaseerd op het toevoegen van de chirale oligomeer aan een oplossing van achirale verbindingen bij een temperatuur waarbij de achirale oligomeer al kinetische stabiele aggregaten heeft gevormd. Toevoeging van de chirale verbinding resulteert in minder chirale amplificatie. Dit duidt op de vorming van clusters die sterker zijn verrijkt in een van de bouwstenen. Om tot een eenduidige bepaling van de interne structuur te komen, dient CD spectroscopie met complementaire technieken te worden gecombineerd.

In Hoofdstuk 6 wordt de invloed van gereduceerde dynamica op de zelfassemblage van sterkachtige π-geconjugeerde moleculen besproken. In MCH zijn twee verschillende aggregaten, A1 en A2, waargenomen, waarbij in de tijd een overgang van de A1 naar de A2 toestand mogelijk is. Dit toont aan dat de A2 toestand thermodynamisch stabiel is. De overgang van A1 naar A2 wordt versneld door toevoeging van een goed oplosmiddel zoals toluëen. Gel Permeatie Chromatografie (GPC) in alkanen geeft aan dat A1 aggregaten dynamischer zijn in het oplosmiddel mengsel (4:1 MCH/toluëen) dan in zuiver MCH. Een opmerkelijk hoog monomeer gehalte van 15 mol% is bepaald voor de assemblage in het oplosmiddel mengsel. Dit gehalte is bevestigd met 1H NMR. Zoals verwacht, is het monomeer gehalte in zuiver MCH te laag om met GPC te detecteren. De oorsprong van de A1–A2 overgang is onderzocht door het mengen van de enantiomeer. Hoewel chirale amplificatie is waargenomen in MCH, is het effect slechts zwakjes aanwezig in het oplosmiddel mengsel. De overgang van de A1 naar de A2 toestand wordt vertraagd door het innemen van het andere enantiomeer in het aggregaat, waarbij de overgang alleen in het oplosmiddel mengsel plaatsvindt. Opmerkelijk genoeg vindt er geen chiral amplificatie plaats in de A2 toestand. Concluderend kan de A1–A2 overgang worden gerelateerd aan een verstarring van de interne structuur, waarbij de vorming van enantiomeer zuivere clusters de overgang mogelijk maakt.

De resultaten beschreven in dit proefschrift onthullen verschillende belangrijke parameters die de route van de zelfassemblage en de eigenschappen van het uiteindelijke product beïnvloeden.
Curriculum Vitae


Martin Wolffs was born on December 15th 1981 in Zeven (Germany). After finishing secondary school at the Zwijsen College in Veghel he started in 2000 the study Chemical Engineering at the Eindhoven University of Technology. In 2003 he obtained his bachelor degree cum laude and continued his masters in Molecular Engineering, which he finished cum laude in 2005. His undergraduate work was performed in the group of Prof. Dr. E. W. Meijer and was nominee for the KIVI Niria award and laureated with the Mignot award in 2006. Starting from 2005 he performed his Ph. D. research in the group of Prof. Dr. E. W. Meijer and Dr. A. P. H. J. Schenning, where a short stay in the group of Dr. I. Huc in Bordeaux enabled him to study the synthesis and characterization of foldameric structures. The most important results of his graduate research are discussed in this thesis.
List of Publications

Investigation of factors influencing the chemoenzymatic synthesis of block copolymers

Sequential energy and electron transfer in aggregates of tetrakis[oligo(p-phenylene vinylene)]
porphyrins and C₆₀ in water

Influence of supramolecular organization on energy transfer properties in chiral oligo(p-phenylene vinylene)
porphyrin assemblies

Wolffs, M.; George, S. J.; Tomović, Ž.; Meskers, S. C. J.; Schenning, A. P. H. J.; Meijer, E. W.
Macroscopic origin of circular dichroism effects by alignment of self-assembled fibers in solution

Wolffs, M.; Korevaar, P. A.; Jonkheijm, P.; Henze, O.; Feast, W. J.; Schenning, A. P. H. J.; Meijer, E. W.
The role of heterogeneous nucleation in the self-assembly of oligothiophenes

C₃-symmetrical self-assembled structures investigated by vibrational circular dichroism
*Chirality* **2008**, *20*, 1016-1022.

Schenning, A. P. H. J.; Meijer, E. W.
Visualization of various supramolecular assemblies of oligo(p-phenylene vinylene)-melamine and
perylene bisimide

Schenning, A. P. H. J.; Christianen, P. C. M.
Molecular organization of cylindrical sexithiophene aggregates measured by X-ray scattering and magnetic alignment
Meijer, E. W.; Schenning, A. P. H. J.
Side-chain degradation of ultrapure π-conjugated oligomers: implications for organic electronics

Wolffs, M.; Bovee, R. A. A.; Lou, X.; van Dongen, J. L. J.; Tomović, Ž.; Schenning, A. P. H. J.;
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Self-assembly of chiral star-shaped oligo(p-phenylene vinylene) substituted hexaarylbenzenes
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Helical aromatic oligoamide foldamers as organizational scaffolds for photoinduced charge transfer

de Greef, T. F. A.; Smulders, M. M. J.; Wolffs, M.; Schenning, A. P. H. J.; Sijbesma, R. P.; Meijer, E. W.
Supramolecular polymerizations
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