Exciton-polarons in self-assembling helical aggregates: relating optical properties to supramolecular structure

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Chapter 1

General introduction

The goal of this chapter is to give background information for the rest of this thesis, to define the research goals and to give an outline of the thesis. We start by introducing the reader to the field of organic electronics, which studies the optoelectronic properties of π-conjugated molecules and polymers. Next, we introduce the reader into the field of supramolecular electronics. This rather new research field uses the concepts of supramolecular self-assembly for constructing functional nanomaterials with applications in optoelectronic devices. Optical spectroscopy is a very useful tool for studying supramolecular self-assembly and we introduce the concept of the exciton-polaron, which enables us to establish the relation between optical properties and supramolecular structure. Finally, we define the research goals and give an outline of the thesis.


1.1 Organic electronics

At the end of the 1970s, Alan MacDiarmid, Hideki Shirakawa and Alan Heeger discovered that certain polymers containing alternate single and double carbon bonds, so-called $\pi$-conjugated polymers, can conduct electrical current. This discovery, for which they were awarded the Nobel prize in Chemistry in 2000, has led to the birth of organic electronics. Within nearly three decades, this interdisciplinary research field at the intersection of Chemistry and Physics has developed from a proof-of-principle stage into a major research area that involves many academic and industrial research groups all over the world. Nowadays, organic semiconductors are a well-established class of functional materials and are highly promising candidates as active components in several optoelectronic devices such as organic field-effect transistors (OFETs), light-emitting diodes (OLEDs), photovoltaic cells and sensors. Important advantages of organic semiconducting materials over their inorganic counterparts are their almost limitless chemical tunability, their low weight, their relative low cost and the ease in which they can be processed. Many organic semiconductors can be processed from solution by using relatively cheap techniques like ink-jet printing or spin-coating, whereas ultra-clean high-vacuum conditions and high temperatures are required for inorganic semiconductors. Organic FETs, LEDs, photovoltaic cells and sensors pave the way for new applications, such as lighting systems, biomedical sensors, radio-frequency identification tags, electronic paper, and flexible displays and solar cells. The flexibility of the latter devices would be impossible by using more conventional materials like copper or silicon. As an example, Figure 1.1 shows a bendable polymer foil containing several electronic components and circuits. Furthermore, organic semiconducting materials may be used for spintronic applications as well. Organic semiconductors have much potential for spintronics because the spin relaxation time is much longer than in their inorganic counterparts, due to the much lower spin-orbit coupling in organic materials. This results in spin diffusion lengths of tens of nanometers, opening the possibility of spintronic applications. Although for some applications of organic optoelectronic devices there remain bottlenecks such as the relative low mobility of charges in organic materials compared to their inorganic counterparts and the short operating lifetime due to degradation, the first commercial products have already entered the market place.

The performance of devices like organic FETs, LEDs and solar cells depends largely on the charge-carrier mobility. Charges in these devices have to move between electrodes. Because the distance between electrodes is typically of the order of tens to hundreds of nanometers, the charge transport in these devices involves transfer of charges between many molecules. For efficient charge transport, charges should be able to move from molecule to molecule without getting trapped or scattered. Therefore, the charge transport is affected by many factors, for example the presence of impurities, disorder, molecular packing, temperature, charge-carrier density, pressure, electric field, and the size and molecular weight of the molecules. The highest charge-carrier mobilities are generally obtained for highly ordered crystals of $\pi$-conjugated oligomers with a well-defined structure. Some of the most widely investigated materials are molecular crystals of oloioacenes and oligothiophenes, of which the chemical structures are shown in Figure 1.2a. Oloioacenes are currently among the best organic semiconductors and the reported values of the charge-carrier mobility are as high as 2.4 cm$^2$V$^{-1}$s$^{-1}$ for...
tetracene,\(^{16}\) 20 cm\(^2\)V\(^{-1}\)s\(^{-1}\) for rubrene\(^{17}\) (a tetracene derivative), and 35 cm\(^2\)V\(^{-1}\)s\(^{-1}\) for pentacene.\(^{18}\) These charge-carrier mobilities are of the same order of magnitude, or even higher, than that in amorphous silicon, which is of the order of 1 cm\(^2\)V\(^{-1}\)s\(^{-1}\). Crucial for a high charge-carrier mobility in organic crystals is the purity of the material. Although organic crystals are inherently very pure, even trace amounts of impurities lower the charge-carrier mobility in OFETs significantly.\(^{18}\) Organic crystals of \(\pi\)-conjugated oligomers can be prepared by using vapor deposition techniques. However, these techniques are rather delicate and expensive, and for this reason organic crystals are not ideal candidates for large-scale production of electronics.

Organic semiconductors that can be processed from solution by relatively cheap techniques such as spin coating\(^ {19}\) and ink-jet printing\(^ {20}\) are \(\pi\)-conjugated polymers. Figure 1.2b shows the chemical structures of some of the most studied \(\pi\)-conjugated polymers, namely polyphenylenevinylene (PPVs), polyphenylenes (PPPs) and polythiophenes (PTs). Charge-carrier mobilities in these materials are in general several orders of magnitude lower in comparison to those in the organic crystals discussed above. The low mobility is mainly caused by the inherent structural disorder of these materials. On a microscopic scale, a picture of a thin film of \(\pi\)-conjugated polymers would look like cooked spaghetti. Coils, kinks and impurities disturb the \(\pi\)-conjugation of the polymer chains and each chain may therefore be considered to consist of a number of separated conjugated segments. This results in energetic disorder because the energies of the conjugated segments vary due to their different local arrangements and the
different length of each individual conjugated segment. In addition, structural disorder leads to poor electronic coupling between neighboring chains. Improvement of the structural ordering of the polymer chains would therefore lead to a vast improvement in the charge-carrier mobility. This is nicely demonstrated in FETs with poly-3-hexylthiophene (P3HT) as the active layer. The hexyl side chains on the polymer backbone can be positioned in either a regioregular or regiorandom pattern. Regioregular P3HT self-organizes into two-dimensional $\pi$-stacked lamellar structures, resulting in much higher charge-carrier mobilities ($0.01-0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) than in the more disordered regiorandom P3HT films ($\leq 10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$).

The optoelectronic properties of the organic semiconductors discussed above originate from the presence of $\pi$-conjugation. $\pi$-conjugation refers to the alternation of single ($\sigma$) and double ($\sigma + \pi$) bonds within the oligomer or polymer. Three of the four electrons in the outer shell of carbon occupy the $sp^2$ hybridized states. These states form the localized and very strong $\sigma$ bonds. The remaining nonhybridized $p_z$ states of neighboring carbon atoms overlap and form the so-called $\pi$-electron system, which in principle is delocalized over the entire molecule. Molecular orbitals that are filled ($\pi$-bonding orbitals) form the valence band and the filled orbital with the highest energy is called the Highest Occupied Molecular Orbital (HOMO). Vacant orbitals form the conduction band and the orbital with the lowest energy is called the Lowest Unoccupied Molecular Orbital (LUMO). The energy gap between the HOMO and LUMO level is typically a few eV and this relatively low energy is responsible for the semiconducting nature of organic materials.

The high charge carrier mobilities achieved in organic semiconductors and the easy processing techniques available hold high promise for engineering optoelectronic devices based on both polymers and oligomers. Both classes of semiconductors have their own advantages and disadvantages, with the easy processability of polymers and the high order in organic crystals of oligomers as their outstanding features. For many scientists it is a dream to take the design of
1.2 Supramolecular electronics

Nature utilizes non-covalent interactions to create complex functional nanostructures. For example, non-covalent interactions govern the self-assembly of DNA in its famous double-helix structure, stabilize the secondary and tertiary structures of proteins, or coalesce lipids to form cell membranes. Inspired by nature, scientists have started to apply the supramolecular design rules to create functional nanomaterials via programmed self-assembly. Supramolecular chemistry is the area in chemistry that uses non-covalent interactions to create complex molecular assemblies. Examples of non-covalent interactions are van der Waals forces, Coulomb forces, $\pi - \pi$ interactions, and hydrogen bonds. Non-covalent interactions, which are much weaker than covalent interactions, are highly reversible. Therefore, supramolecular assemblies are often formed under thermodynamic equilibrium, in which case the self-assembly process is driven by external control parameters, for example temperature and concentration. In recent years, enormous progress has been achieved in the engineering of functional nanomaterials using supramolecular self-assembly and this approach has resulted in supramolecular polymers with excellent mechanical properties, biologically active supramolecular nanostructures with applications in regenerative medicine, and aggregates that consist of $\pi$-conjugated molecular building blocks resulting in supramolecular electronics.

The central idea of supramolecular electronics is that specifically designed $\pi$-conjugated molecules self-assemble under suitable circumstances into ordered linear arrangements, such that the overlap of the $\pi$-orbitals allows for the transport of excitations (electrons, holes and excitons) along the stacking direction. One of the first demonstrations of a self-organizing system with conducting properties were discotic molecules of a triphenylene derivative. These discotic molecules have a disc-like planar aromatic core with aliphatic side chains attached to it. A helical columnar phase of the triphenylene derivatives was prepared by cooling the isotropic melt via the discotic liquid-crystal phase, in which the molecules are already organized with a high degree of order. The formation of the helical columnar phase is extremely sensitive to subtle structural changes in the triphenylene derivatives and the factors governing its formation are not understood completely yet. However, it has become clear that the sulphur atoms comprising the extended core are crucial for the helical phase formation. The room-temperature mobility of photoinduced charge carriers in the helical columnar phase was found to be of the order of 0.1 cm$^2$V$^{-1}$s$^{-1}$, which is higher than for any disordered $\pi$-conjugated polymer and comparable to that of amorphous silicon. An even higher charge-carrier mobility of 1 cm$^2$V$^{-1}$s$^{-1}$ was observed in the crystalline solid phase of hexabenzocoronene (HBC) derivatives, and a value as high as 0.5 cm$^2$V$^{-1}$s$^{-1}$ was found in the hexagonal columnar liquid crystalline phase. The lower
mobility in the columnar liquid crystalline phase is a result of the larger motional degree of freedom of the discotic molecules, which increases the structural disorder.

Hydrogen bonds can be used as secondary interactions to achieve higher structural order in supramolecular architectures because they are highly selective and directional. The double-helix structure of DNA is a beautiful example from nature, where the structure is formed by hydrogen bonds between the nucleobases in the opposite strands. Following nature’s example, nanometer-long, well-defined arrays of porphyrin molecules were constructed by anchoring porphyrin molecules to a helical poly-isocyanide backbone that is rigidified by hydrogen bonds. Functionalized monomeric units were designed such that they form dimers through quadruple hydrogen bonding between these units and solvophobic interactions induce stacking of these dimers into columnar polymeric architectures. Another beautiful example of using hydrogen bonding between the stacking molecules themselves are chiral stacks of \( \pi \)-conjugated \( p \)-phenylene-vinylene derivatives. These oligomers consist typically of \( n = 3, 4, \) or 5 \( p \)-phenylene-vinylene units (OPV\( n \)'s) with chiral side groups. The OPV\( n \)-backbone is capped on one end by a tridodecyloxybenzene and on the other end by an ureidotriazine unit that can engage in four hydrogen bonds with those of another oligomer. H-bonded pairs (dimers) form when OPV\( n \) molecules are dissolved in an apolar solvent at high temperature. Upon lowering the temperature, these dimers associate into small randomly ordered aggregates as a result of \( \pi-\pi \) and solvophobic interactions. Below a critical temperature, the randomly ordered assemblies attain a helical conformation, followed by a strong elongation upon further cooling. The helical structure gives the molecular nanowires a very high persistence length of the order of 100 nm. Figure 1.3 shows the molecular structure of OPV4 and a schematic representation of the self-assembly into long helical wires.

The helical OPV assemblies have been constructed with application as conducting nanowires.
in mind. Their charge-transport properties were investigated by depositing OPV helices on a substrate with electrodes separated by 200 nm. \(^{38}\) However, no current was measured through the helical wires. A possible explanation could be that the helical structure formed in solution is not preserved when the helical wires are transferred to the substrate. It was shown that the helices can be transferred from solution to a substrate while retaining a high degree of organization within the chiral fibers. \(^{39,40}\) However, it is possible that the organization within the assemblies differs from that in solution. Furthermore, it could well be that no conduction is measured because the charges have difficulties overcoming the injection barriers at the contacts. Therefore, pulse-radiolysis time-resolved microwave conductivity experiments have been performed on OPV helices. \(^{41}\) This technique can be used to measure charge-carrier mobilities in \(\pi\)-conjugated polymer chains or supramolecular aggregates in solution without the need to apply electrodes. For the helical OPV assemblies a charge-carrier mobility of only \(3 \cdot 10^{-3} \text{cm}^2\text{V}^{-1}\text{s}^{-1}\) was found for holes and \(9 \cdot 10^{-3} \text{cm}^2\text{V}^{-1}\text{s}^{-1}\) for electrons. \(^{41,42}\) The charge transport was calculated using a hopping model based on parameters from density-functional theory and it was concluded that the charge-carrier mobility in OPV helices can be improved by reducing the twist angle. \(^{41}\) Possible methods to achieve this are modifying the side chains such that the steric repulsion is reduced, or introducing additional functional groups that enable hydrogen bonding in the stacking direction, leading to even more ordered supramolecular aggregates. \(^{41,42}\)

The construction of complex supramolecular systems with a high degree of order requires good control of the self-assembly process. One of the challenges is the construction of monodisperse supramolecular assemblies. While the average size of the OPV helices can be controlled by the temperature or the concentration of oligomers, the size distribution of the helices is polydisperse. \(^{37}\) DNA-templated self-assembly is a very promising approach to control the length of nanowires because DNA strands have a well-defined length. \(^{43}\) Here, the bases of the DNA strand act as specific binding sites for the guest molecules. Furthermore, the specific sequence of these bases offers the opportunity to direct the exact position of various guest molecules, for example of electron donating and accepting molecules. DNA can also be used to construct even more complex nanostructures and its versatility is illustrated by the examples in Figure 1.4. Figure 1.4a shows 2D nanostructures formed by ‘DNA-origami’. Long, single-stranded DNA molecules are folded into two-dimensional shapes that are kept into the desired shape by DNA stapling. \(^{44}\) Figure 1.4b shows DNA that has self-assembled into 3D nanostructures. \(^{45}\) Recently, electron-beam lithography and dry oxidative etching were used to create DNA origami-shaped binding sites on a substrate. \(^{46}\) The approach of using DNA nanostructures as scaffolding may provide a way for precisely positioning active components at dimensions significantly smaller than possible with conventional semiconductor fabrication techniques.

The foregoing discussion illustrates that supramolecular self-assembly is a very promising approach for constructing functional nanomaterials with optoelectronic applications. The applications for supramolecular assemblies based on \(\pi\)-conjugated molecules require a high degree of control over the position of molecules. In order to achieve this control, it is necessary to acquire a deeper insight in the self-assembly mechanisms of supramolecular systems. \(^{47}\) Optical spectroscopy is an extremely useful tool for monitoring the supramolecular self-assembly of \(\pi\)-conjugated molecules.
1.3 Monitoring supramolecular self-assembly using optical spectroscopy

There are several techniques available to demonstrate that molecules have aggregated into high-aspect-ratio wire-like structures. A technically simple manner is measuring the viscosity of the solution. Solutions that contain long, wire-like aggregates are much more viscous than solutions of non-wire-like structures. Furthermore, high-aspect-ratio assemblies will align under flow, making techniques like flow birefringence and flow linear dichroism spectroscopy very useful. The size and shape of the assemblies can be estimated by using scattering techniques. Examples include dynamic and static light scattering, small-angle X-ray scattering and small-angle neutron scattering. Although these techniques are very informative in ensuring that linear assemblies have formed in solution, they do not provide information of the supramolecular structure of the assemblies.

Optical spectroscopy has proven to be an extremely useful tool for obtaining information about the structure of proteins, DNA, liquid crystal phases and supramolecular assemblies. These systems have in common that they all consist of electronically coupled units, leading to delocalization of their photo-excitations (excitons, see next section). Delocalization affects the optical spectra and one may therefore attempt to extract the excitonic coupling strength between the units using optical spectroscopy. Since this coupling depends on the distance between units and their relative orientation, optical spectra contain information about the structure of the molecular system under investigation.

Circular dichroism (CD) measures the difference in absorption between left- and right-handed circularly polarized light and is particularly useful for studying molecular systems that involve chiral or non-chiral molecules that are assembled in a chiral and non-racemic manner. A chiral molecule lacks an internal plane of symmetry and cannot be superimposed on its mirror image. Most biological (macro)molecules are chiral and therefore CD spectroscopy is widely used to
Figure 1.5: (a) UV/vis absorption, (b) circular dichroism and (c) fluorescence spectra of OPV4 in dodecane solution (14 \( \mu \)M) at different temperatures (taken from ref 36).

study biological systems. For example, CD spectroscopy can be utilized to probe changes in the conformation of biological macromolecules and their interaction with other molecules. More recently, the application of CD spectroscopy has been extended to supramolecular chemistry in the study of the supramolecular self-assembly of chiral molecules.

Helical OPV aggregates are an instructive example of a system in which various spectroscopic techniques were used to unravel the supramolecular self-assembly mechanism.\textsuperscript{36,37} Figure 1.5 shows the UV/vis absorption, circular dichroism and fluorescence spectra of OPV4 in dodecane solution at different temperatures. The main signature of aggregation of the OPV dimers is the appearance of a shoulder on the low-energy side of the absorption spectra, while the transition into long helices leads to the emergence of a bisignate (change of sign within the absorption band) CD activity (Cotton effect) in the vicinity of the lowest molecular singlet transition, indicative of the formation of a left-handed helix.\textsuperscript{51} Further proof of aggregation are the changes in the fluorescence spectra with temperature. Upon lowering the temperature, the fluorescence decreases, shifts to the red and the spectral line shape changes drastically. The optical data were interpreted using a thermodynamic model for the self-assembly and it was concluded that OPV self-assembles via a cooperative supramolecular polymerization.\textsuperscript{37,56}

The main subject of this thesis is the relation between the optical properties of self-assembling helical aggregates and their supramolecular structure. Crucial for the understanding of the optical response of supramolecular aggregates is the concept of Frenkel excitons. A Frenkel exciton is a delocalized optical excitation and the delocalization is the main reason that the optical response of supramolecular aggregates deviates significantly from that of a single molecule. In addition, there is a strong coupling between optical excitations and molecular vibrations in many \( \pi \)-conjugated molecules, leading to the concept of exciton-polarons. These concepts are introduced in the next section.
1.4 Exciton-polarons in supramolecular aggregates

Frenkel excitons

Jelley\textsuperscript{57} and Scheibe\textsuperscript{58} were the first who recognized that aggregation of molecules strongly affects the optical response of a molecular system. They discovered independently that the absorption spectrum of a solution of pseudo-isocyanine (PIC) dyes changes dramatically upon increasing the concentration: the relatively broad absorption spectrum of PIC molecules disappears and is replaced by a much narrower, red-shifted absorption band. These changes in the absorption were attributed to aggregation of the PIC molecules. Aggregates that have a red-shifted absorption spectrum as compared to the monomer are usually referred to as J-aggregates (J from “Jelley”) and these aggregates can be superradiant at low temperatures.\textsuperscript{59} There are also aggregates that have a blue-shifted absorption. These aggregates are called H-aggregates (H from “hypsochromic”) and their fluorescence is quenched.\textsuperscript{60} See Figure 1.6.

The optical response of a supramolecular aggregate is noticeably different from that of a single molecule because intermolecular interactions result in the formation of Frenkel excitons.\textsuperscript{61} To explain the concept of Frenkel excitons, let us consider the absorption of light by a molecular aggregate consisting of \( N \) identical molecules. Due to absorption of a photon, one molecule in the aggregate becomes electronically excited. Without intermolecular interactions, the aggregate wave function would be a direct product of the excited state of this molecule and the ground states of all the other molecules. Since the excitation can occur on any molecule,
1.4 Exciton-polarons in supramolecular aggregates

This wave function is $N$-fold degenerate. Intermolecular interactions (excitonic coupling) lift this degeneracy and the excitation delocalizes over the aggregate, meaning that it is coherently shared by many molecules. As an illustration, for a sufficiently large ideal aggregate consisting of $N$ molecules with only nearest-neighbor coupling $J$ and periodic boundary conditions, the eigenstates of the Hamiltonian are given by

$$|k\rangle = \frac{1}{\sqrt{N}} \sum_{n=0}^{N} e^{i k n} |n\rangle, \quad k = 0, \pm \frac{2\pi}{N}, \pm \frac{4\pi}{N}, ..., \pm \pi$$  \hspace{1cm} (1.1)

with energies

$$E(k) = \epsilon_0 + 2J \cos(k).$$  \hspace{1cm} (1.2)

Here, the electronic state $|n\rangle$ denotes that the $n$-th molecule is electronically excited while all other molecules are in their electronic ground state, $\epsilon_0$ is the single-molecule excitation energy, and $N$ is even for the $k$-range shown in Figure 1.6. This figure shows the splitting of energy levels due to excitonic coupling, leading to an exciton bandwidth of $W = 4|J|$, with the exciton bandwidth defined as the energy difference between the highest-energy and lowest-energy exciton state.

A Frenkel exciton can also be viewed as a delocalized electronic excitation where the electron (occupied LUMO) and hole (unoccupied HOMO) are always positioned on the same molecule. There are also excitons that have an electron-hole separation that largely exceeds the size of a single atom or molecule. These so-called Wannier-Mott excitons typically occur in systems with strong binding forces between constituent atoms or molecules, such as in covalently bound semiconductors. These strong binding forces result in high hopping rates for the electron and hole, and due to the typically high dielectric constant in these materials, which decreases the Coulomb interaction, the electron and hole are separated by a relatively large distance while remaining bound. The electron and hole hopping rates are much lower in supramolecular aggregates, because the molecules are bound via the much weaker non-covalent interactions and because the dielectric constant is smaller. Therefore, the distance between the electron and hole does not exceed the intermolecular distance. Because excitons are electron-hole pairs, they carry no charge and do not contribute to electrical conduction. However, excitons do carry excitation energy and they are responsible for energy transport processes. Besides being of fundamental interest for the performance of promising commercial applications like organic light-emitting diodes and solar cells, energy transport processes by excitons play also an important role in biological systems. A fascinating example are the photosynthesis systems of bacteria and higher plants. These organisms have light-harvesting antennas that absorb sunlight and transport the excitation energy to the photosynthetic reaction center very efficiently.

The optical response of supramolecular aggregates differs considerably from that of a single excited molecule due to delocalization of Frenkel excitons. The relative strength of electronic transitions is proportional to the oscillator strength, which is the square of the transition dipole moment between two eigenstates. Because of the excitonic coupling between the constituent molecules and because the aggregate length is typically much smaller than the optical wavelength, the oscillator strength of all molecules is combined and divided over only a few eigenstates. These states are located at the bottom of the exciton band if the sign of the
Figure 1.7: Analogy of the motion of an exciton-polaron with a bowling ball on a mattress.

Excitonic coupling is negative, as in J-aggregates, whereas they lie at the top of the band in the case of H-aggregates, for which the couplings are positive. Figure 1.6 illustrates this for the case of ideal aggregates with periodic boundary conditions. The $|k = 0\rangle$ state combines the oscillator strength of all molecules of the aggregate because the phase of the wave function does not change along the aggregate. For the $|k = \pi\rangle$ state (and also all other states) the overall aggregate transition dipole moment is canceled out because the phase of $|k = \pi\rangle$ alternates from molecule to molecule. This explains the red- and blue-shift of the absorption spectrum relative to the monomer spectrum for J- and H-aggregates, respectively. At low temperature, emission occurs mainly from the lowest-energy exciton state in accordance with Kasha’s rule. J-aggregates may show superradiance, whereas the fluorescence of H-aggregates will be quenched because the transition from the lowest-energy exciton to the ground state is optically forbidden. Because of the antisymmetry of the $p_z$ orbitals of $\pi$-conjugated molecules with respect to the molecular plane, perfectly stacked molecules without twist angle form H-aggregates.

Exciton-polarons

Organic materials are ‘soft’, meaning that the presence of an electronic excitation induces a significant rearrangement of the nuclei in the participating molecules. The reorganization energy associated with this nuclear rearrangement is typically of the order of several tenths of an eV. Electronic excitations are thus dressed Frenkel excitons or exciton-polarons: a vibronically (electronically and vibrationally) excited central molecule that is surrounded by vibrationally excited molecules. The concept of exciton-polarons in organic materials is best illustrated by drawing an analogy with a bowling ball on a mattress, which is shown in Figure 1.7. Here, the bowling ball together with the spring in the mattress directly underneath the ball represents the
1.4 Exciton-polarons in supramolecular aggregates

vibronically excited molecule, while the neighboring springs represent the vibrationally excited molecules. The deformation field will accompany the bowling ball while it traverses the mattress. This situation is analogous to Frenkel excitons in organic materials, with the exception that excited molecules are elongated instead of compressed along the vibrational coordinate.

In many π-conjugated molecules, excitations couple strongly to a symmetric ring breathing/vinyl stretching mode with energy \( \omega_0 = 0.17 \text{ eV} \). The nuclear reorganization energy associated with this vibrational (phonon) mode is approximately 0.2 eV. In recent years, the impact of exciton-phonon coupling involving the \( \omega_0 = 0.17 \text{ eV} \) mode on the optical response has been studied via several theoretical approaches. A particularly successful approach has been the use of the multi-particle basis set originally introduced by Philpott. This basis set is very convenient for obtaining essentially exact absorption and emission spectral lineshapes using the Holstein Hamiltonian to account for the exciton-phonon coupling.

To understand the impact of exciton-phonon coupling on the optical spectra, we concentrate first on single, isolated molecules. Figure 1.8a shows the molecular ground state (\( S_0 \)) and excited state (\( S_1 \)) nuclear potentials corresponding to the \( \omega_0 = 0.17 \text{ eV} \) vibration. The nuclear potentials are approximated by harmonic wells for both the ground state and the excited state. These nuclear potentials are of identical curvature but shifted relative to each other as a result of the exciton-phonon coupling. The shift is quantified by the Huang-Rhys factor, \( \lambda^2 \). This dimensionless factor is a measure for the strength of the exciton-phonon coupling and is related to the nuclear reorganization energy, \( \lambda^2 \omega_0 \). For the \( \omega_0 = 0.17 \text{ eV} \) phonon mode, \( \lambda^2 \) is typically of the order of one. The absorption spectrum of the molecule is shown in Figure 1.8b and features a sequence of peaks. This sequence of peaks is called a vibronic progression and it is a result of strong exciton-phonon coupling. Each peak corresponds to an optical transition from the lowest vibrational level in the electronic ground state to one of the vibronic states. The intensities of the various vibronic transitions are determined by the Franck-Condon factors, which are the overlap integrals between two shifted states of the harmonic wells. An excitation that is created as a result of a photo-absorption process in the molecule has a finite lifetime. According to Kasha’s rule, this exciton will quickly relax to the lowest vibronic state before it eventually decays to one of the vibrational levels in the electronic ground state via a photo-emission process. The resulting emission spectrum is essentially the mirror image of the absorption spectrum, see Figure 1.8b.

In a recent review about the impact of molecular aggregation on the spectral lineshapes, it is shown that aggregation leads to a distortion of the vibronic progression in the absorption and emission spectra of J- and H-aggregates. This distortion can be utilized to extract important information about the molecular packing, the exciton bandwidth, the nature of the disorder, and the exciton coherence length. Figure 1.9a shows the energy level diagrams for ideal H- and J-aggregates in the weak excitonic coupling regime and Figure 1.9b shows the corresponding absorption and emission spectra, demonstrating the distortion in the vibronic progression. In the weak coupling regime, the excitons are organized in well-separated vibronic bands, making this regime very appropriate to illustrate the essential physics of exciton-polarons in H- and J-aggregates.

Note that strictly speaking the emission spectrum is only a mirror image of the absorption spectrum if the cubic frequency dependence of the emission rate is ignored.
Figure 1.8: a. Harmonic wells for the molecular electronic ground state ($S_0$) and excited state ($S_1$) nuclear potentials corresponding to the $\omega_0 = 0.17$ eV vibration. Absorption of a photon results in a transition from the lowest vibrational level in the ground state potential to one of the vibrational levels in the excited state potential. The excitation quickly relaxes to the lowest vibronic state (Kasha’s rule) from which emission takes place. b. Schematic absorption (blue line) and emission (red line) spectrum of a single molecule. The intensities of the various $0-n$ and $n-0$ transitions are given by the Franck-Condon factors, $\lambda^2 ne^{-\lambda^2/n!}$, with $\lambda^2$ the Huang-Rhys factor.

J-aggregates. Only transitions to the $|k = 0\rangle$ states are optically allowed from the vibrationless ground state. For H- (J-)aggregates, the $|k = 0\rangle$ exciton in the $\nu$-th vibronic band, $|A_{\nu+1}\rangle$, lies at the top (bottom) of the band. Excitonic coupling causes interband coupling between the $|k = 0\rangle$ states of different bands, leading to a redistribution of the oscillator strength. For H- (J-)aggregates, this results in a decreasing (increasing) intensity of the 0-0 absorption peak, as demonstrated in Figure 1.9b. The decrease of the 0-0 absorption peak in H-aggregates has been utilized to determine the packing arrangement in carotenoid aggregates, to monitor the self-assembly of perylene diimide aggregates, and to extract the exciton bandwidth and the average conjugation lengths in P3HT $\pi$-stacks.

Emission occurs from the lowest-energy exciton state $|em\rangle$, where $em$ stands for emission. In H-aggregates with Frenkel excitons without exciton-phonon coupling the transition from this state to the ground state is optically forbidden. If exciton-phonon coupling is present, the transition can terminate on the electronic ground state with $n$ vibrational phonons, leading to 0-$n$ emission. Of these transitions only the 0-0 transition is forbidden, see Figure 1.9. This transition violates the familiar selection rule $\Delta k = 0$ for optical transitions since the band-bottom exciton has $k = \pi$, while the ground state carries no momentum. The 0-$n$ transitions with $n > 0$ leading to sideband emissions are able to maintain momentum conservation by

$^\dagger$The photon momentum is negligible because the optical wavelength is much larger than the aggregate dimensions.
Figure 1.9: a. Exciton-polaron energy level diagrams for ideal H- and J-aggregates in the weak excitonic coupling regime, in which the exciton states are organized in well-separated vibronic bands. Only transitions to the \(|k = 0\rangle\) states are optically allowed from the vibrationless ground state. For H- (J-) aggregates, the \(|k = 0\rangle\) exciton state in the \(\nu\)-th vibronic band, \(|A_{\nu+1}\rangle\), lies at the top (bottom) of the band. The emission occurs from the lowest-energy exciton state \(|em\rangle\). For ideal H-aggregates, the transition from \(|em\rangle\) to the vibrationless ground state is optically forbidden. b. Absorption (blue lines) and emission (red lines) spectra for H- and J-aggregates with labeling of the various peaks, showing that the peak intensities have changed dramatically in comparison to the single-molecule spectra. To calculate the spectra, the Huang-Rhys factor is set to \(\lambda^2 = 1.0\), the nearest-neighbor coupling to \(|J| = 0.12\omega_0\), and the homogeneous line width to \(\sigma_H = 0.33\omega_0\), with \(\omega_0\) the energy of the vibrational mode.
terminating on the electronic ground states with one or more vibrational phonons, where these phonons carry the excess momentum. In J-aggregates, the 0-0 emission is not only allowed but also strongly enhanced compared to that of a single molecule, leading to superradiance. The 0-0 emission in J-aggregates is so strong because the oscillator strength of each of the $N$ molecules is concentrated in this transition.

Energetic disorder has a localizing effect on excitons, reducing the number of molecules over which the exciton is delocalized below $N$. This results in a decrease of the 0-0 intensity in J-aggregates with increasing disorder. On the other hand, energetic disorder breaks the symmetry, allowing the 0-0 emission in H-aggregates. The intensity of the 0-0 emission peak relative to the sideband emissions depends on the amount of disorder and on the correlation of this disorder. This intensity can be used as a probe for the nature of the disorder and the related exciton coherence size.

### 1.5 Exciton-polarons in helical OPV assemblies

The helical OPV assemblies introduced above will receive special attention in this thesis, as we will use these supramolecular aggregates as a model system in our theoretical analysis of the optical properties of self-assembling helical aggregates. There are two reasons for using this supramolecular system.

Firstly, these helical assemblies have received considerable attention in recent years and have been studied by experimentalists with numerous spectroscopic techniques, where the helicity makes it possible to obtain valuable information using polarized light. For example, time-resolved spectroscopy studies on OPV helices show fast diffusion of excitons along the helices, leading transfer of excitons to traps and to luminescence depolarisation. Femtosecond transient absorption spectroscopy was used to demonstrate that exciton bimolecular annihilation dynamics in OPV aggregates is dominated by a combination of exciton diffusion over nearest-neighbor length-scales and long-range resonance energy transfer. The effect of ‘impurities’ can be studied in a controlled way by mixing in oligomers with a different number of phenylene-vinylene units. When a small fraction of OPV4 is added to OPV3, fast diffusion of excitons to the OPV4 impurities is observed. The influence of intermolecular ordering was investigated by comparing the optical properties of OPV helices with different packing geometries. It was found that exciton transfer dynamics and depolarization occur on a much shorter timescale in helically ordered stacks as compared to disordered stacks due to the much higher intermolecular excitonic coupling.

The second reason is that the well-defined architecture of the OPV helices makes them ideal candidates for testing theoretical models of exciton dynamics. It was found that the experimental time-dependent polarization anisotropy could only be reproduced theoretically if one assumes exciton delocalization among chromophores in the acceptor state and localization to a single chromophore after geometric relaxation in the donor state. The experimental absorption, fluorescence and circular dichroism spectral lineshapes of the helical OPV assemblies were successfully reproduced by employing a Holstein Hamiltonian with spatially correlated disorder. This Hamiltonian takes into account the coupling of the exciton to a symmetric
1.5 Exciton-polarons in helical OPV assemblies

Exciton-polarons in helical OPV assemblies can be described by using the two-particle basis set that was originally introduced by Philpott. The two fundamental excitation types of this basis set are depicted schematically in Figure 1.10. A one-particle excitation, $|n, \tilde{\nu} \rangle$, consists of a vibronically (both electronically and vibrationally) excited chromophore at site $n$ that contains $\tilde{\nu}$ vibrational quanta in the shifted excited-state (denoted by the $\sim$ on top of the $\nu$) nuclear potential. All other chromophores comprising the aggregate remain electronically and vibrationally unexcited. A vibronic/vibrational pair excitation is a two-particle state and is denoted by $|n, \tilde{\nu}; n', \nu \rangle$. In addition to a vibronic excitation at site $n$, this state has a vibrational excitation at site $n'$ that contains $\nu'$ vibrational quanta in the ground-state nuclear potential. Two-particle states are necessary for describing the spatial extension of the vibrational distortion field that surrounds the central vibronic excitation. Likewise one can define three- and higher

Figure 1.10: Examples of the fundamental excitations in helical OPV assemblies: a vibronic excitation and a vibronic/vibrational pair. The vibronic excitation represents a one-particle state $|n, \tilde{\nu} = 2 \rangle$ and the vibronic/vibrational pair represents a two-particle state $|n, \tilde{\nu} = 2; n + 1, \nu = 1 \rangle$.

ring breathing/vinyl stretching mode with energy 0.17 eV ($\sim$1400 cm$^{-1}$) that is responsible for the clear vibronic progression in the fluorescence spectra of OPV (see Figure 1.5c). Optical excitations in OPV assemblies are thus vibrationally dressed, so they are exciton-polarons. It was found that energetic disorder and exciton-phonon coupling act synergistically in delocalizing the exciton-polaron over only a few molecules.
particle states.

Within the two-particle approximation, the $\alpha$-th eigenstate of the aggregate Hamiltonian $H$, which we will specify further below, is expanded as

$$\left| \psi^{(\alpha)} \right\rangle = \sum_{n, \tilde{\nu}} c_{n, \tilde{\nu}}^{(\alpha)} \left| n, \tilde{\nu} \right\rangle + \sum_{n, \tilde{\nu}, n', \nu'} c_{n, \tilde{\nu}, n', \nu'}^{(\alpha)} \left| n, \tilde{\nu}; n', \nu' \right\rangle. \quad (1.3)$$

This expansion is highly accurate for the intermediate coupling regime that is appropriate for the OPV helices. In this regime the vibrational energy $\omega_0$, the nuclear relaxation energy $\lambda^2 \omega_0$ and the free exciton bandwidth $W$ are all comparable in magnitude. Contributions from three-particle states have a negligible effect on the aggregate absorption and emission. The two-particle approximation leads to an enormous reduction of the basis set size and allows us to obtain an essentially exact solution to the optical response of exciton-polarons for relatively large aggregates.

We can evaluate the wave function coefficients $c_{n, \tilde{\nu}}^{(\alpha)}$ and $c_{n, \tilde{\nu}, n', \nu'}^{(\alpha)}$ in eq 1.3 by diagonalizing the aggregate Hamiltonian $H$. The diagonal elements of this Hamiltonian consist of the energies of the localized one- and two-particle states. If we use units in which $\hbar = 1$, we find $\omega_{0-0} + D + \Delta_n + \tilde{\nu} \omega_0$ for the one-particle state $\left| n, \tilde{\nu} \right\rangle$, and $\omega_{0-0} + D + \Delta_n + (\tilde{\nu} + \nu') \omega_0$ for the two-particle state $\left| n, \tilde{\nu}; n', \nu' \right\rangle$. Here, $\omega_{0-0}$ is the gas-phase 0–0 transition energy corresponding to the lowest optically allowed transition and $D$ is the gas-to–crystal shift that arises from the difference between Coulomb interactions in the excited state and Coulomb interactions in the ground state. To distinguish these interactions from the resonant interactions that cause excitation transfer, they are often referred to as non-resonant interactions. The randomly assigned transition energy offsets $\Delta_n$ account for fluctuations in transition energies along the aggregates.

Excitonic coupling has a delocalizing effect on excitations and the localized one- and two-particles states shown in Figure 1.10 are therefore no longer eigenstates when excitonic coupling is activated. The complete aggregate Hamiltonian $H$ can be written as

$$H = H_0 + H_{\text{ex}}, \quad (1.4)$$

with

$$H_{\text{ex}} = \sum_{n,m} J_{nm} \left| n \right\rangle\left\langle m \right| \quad (1.5)$$

Here, $H_0$ is the diagonal part of $H$ containing the energies of the one- and two-particle states. The off-diagonal elements of $H$ are determined by the excitonic Hamiltonian $H_{\text{ex}}$, which is expressed in a basis of purely electronic states $\left| n \right\rangle$, where $J_{nm}$ represents the excitonic coupling between the $n$-th and the $m$-th chromophore. This purely excitonic Hamiltonian intermixes all one- and two-particle states and the matrix elements of $H_{\text{ex}}$ necessarily involve the vibrational overlap integrals (Franck-Condon factors), which depend on the Huang-Rhys factor. To conclude this section we point out that the Hamiltonian obtained is exactly equivalent to the Holstein Hamiltonian when the latter is represented in the two-particle basis set. The Holstein Hamiltonian plays a central role in this thesis and will be discussed more extensively in chapter 4 and further.
1.6 Aim and outline of this thesis

The aim of the work described in this thesis is to acquire a better understanding of the optical properties of self-assembling aggregates by confronting fundamental and phenomenological modeling with experimental data. This requires a good insight in the underlying physics of exciton-polarons in supramolecular assemblies and the relation between their optical response and supramolecular structure. Here, we will give an outline of this thesis and we will specify the topics of each chapter. An outline of a statistical mechanical theory for helical self-assembly will be presented first in chapter 2, and we will apply this theory to the helical self-assembly of OPV4 aggregates.

As we have discussed in section 1.3, optical spectroscopy is a very useful tool for monitoring the supramolecular self-assembly of π-conjugated molecules. In order to provide the interpretation of measured spectroscopic data with a firm theoretical basis, we present in chapter 3 a theory that combines the helical aggregation theory with a quantum-mechanical model for the optical excitations. The combined theory enables us to calculate photoluminescence spectra at different stages in the helical self-assembly and the theoretical predictions are compared to the measured fluorescence spectra of OPV4 molecules at different temperatures.

The optical spectra of helical OPV aggregates are characterized by a clear vibronic progression due to strong coupling of excitons to a high-energy intramolecular vibration. In chapter 4 we study the photoluminescence from helical OPV aggregates using the disordered Holstein Hamiltonian. This Hamiltonian includes excitonic coupling, exciton-phonon coupling and spatially correlated disorder in the chromophore transition energies. We study the dependence of the Stokes shift, the emission line widths and the ratio of the 0–0 to 0–1 emission peaks on the aggregate size and disorder, and we will explain how the ratio of the 0–0 to 0–1 emission peaks may provide information about the coherence size of the emitting exciton. Furthermore, we will show that the exciton diffusion length may be estimated by analyzing the Stokes shift in the optical spectra.

Due to strong coupling of excitons to high-energy intramolecular vibrations, excitations in helical OPV aggregates are vibrationally dressed, so they are exciton-polarons. In chapter 5 we develop a theory that describes the dynamics of exciton-polarons in helical OPV4 aggregates. With our theory we examine the polarization anisotropy decay in OPV4 aggregates and we study the migration of exciton-polarons along the helical assemblies by evaluating their mean square displacement. Furthermore, we study the changes in the emission spectra due to relaxation of high-energy exciton-polarons to lower-lying excited states.

Circular Dichroism (CD) is a particularly useful tool for studying chiral molecular systems and stems entirely from the excitonic coupling between chiral molecules. In chapter 6 we will show that CD is extremely sensitive to long-range excitonic interactions between chromophores in helical assemblies and that this high sensitivity is retained even in the presence of extreme energetic disorder and strong interaction with vibrations, when excitons are mainly localized on individual molecules. In addition, we will demonstrate that excitonic couplings can be extracted directly from experimental CD spectra without having information about the energetic disorder and vibrational interactions.

Insight in the self-assembly mechanism of supramolecular polymers may be obtained by
fitting the experimental CD data with an appropriate thermodynamic model. Two assumptions are commonly made to relate a thermodynamic model with the experimental CD data, namely that the magnitude of the CD response of helical assemblies scales linearly with their length and that it scales linearly with the mean helicity of an aggregate. In chapter 7 we assess these assumptions and we examine the consequences of our findings for the interpretation of CD data of supramolecular polymers that self-assemble via an isodesmic polymerization, of assemblies that exhibit a helical transition in the limit of a high degree of polymerization, and of the helical OPV4 assemblies. Finally, in chapter 8 we give the main conclusions drawn from the research described in this thesis and we propose directions for future studies.

References


Chapter 2

Helical self-assembly of supramolecular aggregates

In this chapter we give a brief outline of a statistical mechanical theory for helical self-assembly. This theory is a combination of the standard theory of linear self-assembly and a theory for the helix-coil transition. We will apply the helical aggregation theory to the helical self-assembly of OPV4 aggregates and we find quantitative agreement with the experimental circular dichroism intensities.
2.1 Introduction

Linear self-assembly is the formation of chain-like aggregates in which the monomeric building blocks are held together by non-covalent interactions. Examples of non-covalent interactions are van der Waals forces, Coulomb forces, Hydrogen bonds, and $\pi-\pi$ interactions. The latter interactions are important in $\pi$-conjugated materials. They consist of the sum of an attractive $\pi-\sigma$ and a repulsive $\pi-\pi$ electrostatic interaction that determines the geometry of the structure, and van der Waals forces that lead to an overall attractive interaction. Non-covalent interactions, which are much weaker than covalent interactions, are highly reversible and therefore supramolecular aggregates are often formed under thermodynamic equilibrium. The equilibrium nature of the supramolecular aggregates makes it possible to control their properties (like the mean aggregate size) by external conditions, for example by changing the temperature or the monomer concentration.

Many linear assemblies exhibit a helical structure or, as in the case of some biopolymers, undergo a transition between the entropically favored random-coil state to a more ordered helical state due to a change in external conditions, for example concentration or temperature. The theoretical description of helical self-assembly has been subject of intense study in our group.\textsuperscript{1–5} Van der Schoot and collaborators devised a theory for helix-coil transitions in solutions of self-assembled polymers.\textsuperscript{1} In this theory, the standard theory of linear self-assembly is combined with a simple two-state model for the helicity of the bonds between the molecules in the aggregates, which is based on the Zimm-Bragg theory for the helical transition in conventional polymers.\textsuperscript{6} The Zimm-Bragg theory can be mapped onto the well-known Ising model. Later, the theory was extended by van Gestel to allow for a more accurate description of the helix-coil transition by explicitly including deviations from the long-chain limit.\textsuperscript{2–4} The theoretical modeling was successfully applied to interpret the experimental data of chiral discotic molecules.\textsuperscript{2,3}

In this chapter we will outline the theory of helical self-assembly. We will first discuss the theory of isodesmic self-assembly and subsequently we will combine this theory with the Ising model for the helix-coil transition. We only discuss the main ingredients of the theory. For a more thorough discussion of isodesmic and helical self-assembly we refer to the Ph.D. thesis of van Gestel\textsuperscript{4} and the review of van der Schoot.\textsuperscript{5} We conclude this chapter by applying the helical aggregation theory to the self-assembly of helical OPV4 aggregates.

2.2 Isodesmic self-assembly

The isodesmic (after the Greek ‘isos’, meaning equal, and ‘desmos’, meaning bond) self-assembly of monomers in dilute solution into aggregates is characterized by the reversible formation of a single non-covalent bond that is identical in all steps of the self-assembly process. In the simplest possible model, the free energy of a single aggregate consisting of $N$ monomers is given by the free energy associated with the formation of a bond, $E$, multiplied by the number of bonds, $N - 1$. The summed free energy of all linear aggregates together is balanced against an ideal entropy of mixing. For a dilute solution of non-interacting self-assembled
linear aggregates this leads to the following Helmholtz free-energy density,

$$F = \sum_{N=1}^{\infty} \rho(N) [\ln \rho(N) - 1 + E(N - 1)], \quad (2.1)$$

where the free-energy density $F$ and the free energy $E$ (like all energies in this chapter, unless stated otherwise) are expressed in units of the thermal energy $k_B T$, with $k_B$ Boltzmann’s constant and $T$ the absolute temperature. In eq 2.1, $\rho(N)$ is the dimensionless number density of aggregates with length $N$. The first two terms in eq 2.1 represent an ideal entropy of mixing and the third term corresponds to the free energy change upon aggregation, with the former promoting the generation of many small aggregates and the latter favoring the formation of a few long aggregates. In equilibrium, the free-energy density $F$ is optimized by the size distribution $\rho(N)$. Setting $\frac{\partial F}{\partial \rho(N)} = 0$ while imposing conservation of mass,

$$\phi = \sum_{N=1}^{\infty} N \rho(N), \quad (2.2)$$

gives

$$\rho(N) = e^{-E(N-1)+\mu N}. \quad (2.3)$$

Here, $\phi$ is the volume fraction of the dissolved material and $\mu < 0$ is a Lagrange multiplier that can be interpreted as the dimensionless chemical potential of the solute molecules. Equation 2.3 indeed minimizes the free energy because $\frac{\partial^2 F}{\partial \rho(N)^2} > 0$. The chemical potential in eq 2.3 can be eliminated by using conservation of mass. This leads to the equilibrium size distribution

$$\rho(N) = \left(1 - \frac{1}{\langle N \rangle_n} \right)^N e^{-E}, \quad (2.4)$$

with the number-averaged (denoted by the subscript $n$) mean aggregate size $\langle N \rangle_n$ given by

$$\langle N \rangle_n = \frac{\sum_{N=1}^{\infty} N \rho(N)}{\sum_{N=1}^{\infty} \rho(N)} = \frac{1}{2} \frac{1}{2} \sqrt{1 + 4 \phi e^{-E}}. \quad (2.5)$$

For $\phi e^{-E} \ll 1$, the mean aggregate size scales with $1 + \phi e^{-E}$, whereas for $\phi e^{-E} \gg 1$ it scales with $\sqrt{\phi e^{-E}}$.

The fraction of material in the aggregated state, $\eta$, is related to the mean aggregate size, $\langle N \rangle_n$, through the identity

$$\eta \equiv 1 - \rho(1) \phi^{-1} = 1 - \langle N \rangle_n^{-2}. \quad (2.6)$$

This quantity can be measured by means of spectroscopic techniques, see for example ref 7. Characteristic of isodesmic self-assembly is that the transition from the monomer-dominated regime to the aggregate-dominated regime is gradual. We somewhat arbitrarily define that this transition occurs when $\eta = \frac{1}{2}$, that is, when half of the dissolved material is in the aggregated state. At a fixed concentration, information about the thermodynamics of the self-assembly process can be obtained by probing the temperature dependence of $\eta$, since

$$\langle N \rangle_n \simeq \frac{1}{2} \frac{1}{2} \sqrt{1 + \hat{\gamma} \exp \left(\frac{h_p(T - T_p)}{k_B T_p^2}\right)}. \quad (2.7)$$
Figure 2.1: The fraction of aggregated material $\eta$ as a function of the dimensionless quantity $-h_p(T - T_p)/k_B T_p^2$, with $h_p$ the net enthalpy of the formation of a single bond, $T_p$ the polymerization temperature and $k_B$ Boltzmann’s constant. Note that $h_p$ is always smaller than zero. Inset: mean aggregate size as a function of $-h_p(T - T_p)/k_B T_p^2$.

This equation is obtained by making the temperature dependence of the free energy associated with the formation of a bond $E$ explicit through a first-order Taylor expansion around a polymerization temperature $T_p$ at which $\eta = \frac{1}{2}$ for the given concentration of the material. The free energy associated with the formation of a bond at $T = T_p$, $E_p$, is fixed by the condition $4e^{-E_p} = \gamma$, with $\gamma \equiv 4(2 - \sqrt{2}) \approx 2.34$ a numerical constant. This value follows naturally from eq 2.6 and eq 2.7, since $\eta = \frac{1}{2}$ at $T = T_p$. The quantity $h_p$ in eq 2.7 is the enthalpy of the formation of a single bond at $T = T_p$. Here, we have used an enthalpy instead of an energy in order to relate to experimentally accessible quantities. Figure 2.1 shows the fraction of aggregated material $\eta$ as a function of the dimensionless quantity $-h_p(T - T_p)/k_B T_p^2$. Typical for isodesmic self-assembly is the 'S'-shape of the curve. The inset shows the mean aggregate size. Note that $\langle N \rangle_n = \sqrt{2}$ if $\eta = \frac{1}{2}$, so at the polymerization transition the solution still consists mainly of monomers and dimers.

### 2.3 Helical self-assembly

To account for the helix-coil transition in linear aggregates, a free energy term associated with the helical transition should be included in eq 2.1 prior to minimization. This can be done by expressing the free energy $f$ of a single aggregate that can undergo a helical transition in its canonical partition function $Q(N)$, since $f = -\ln Q(N)$ in the canonical ensemble. The single-aggregate partition function $Q(N)$ contains information about the conformational state of the
aggregate. A conformational state is specified by the state of the bonds between neighboring molecules within an aggregate. In the high-energy/low-entropy bonded state two neighboring molecules are locked in a helical arrangement, where the helical sense is fixed by the chiral nature of the molecules involved. In the low-energy/high-entropy bonded state the molecules do not have fixed orientations relative to each other. For simplicity we will refer to the former as the helical bond, and to the latter as the non-helical bond. The Helmholtz free-energy density $F$ is now given by

$$F = \sum_{N=1}^{\infty} \rho(N) \left[ \ln \rho(N) - 1 - \ln Q(N) \right], \quad (2.8)$$

which is minimized by the equilibrium size distribution

$$\rho(N) = Q(N) e^{\mu N}. \quad (2.9)$$

Equation 2.9 indeed minimizes the Helmholtz free energy since $\partial^2 F / \partial \rho(N)^2 > 0$ irrespective of the functional form of $Q(N) > 0$. Because $\rho(N) \propto Q(N)$, the size distribution must depend sensitively on the configurational state of the linear aggregates.

The single-aggregate partition function $Q(N)$ is calculated by applying a model that can be mapped onto the well-known one-dimensional Ising model. The Ising model is a two-state lattice model and in this case the state represents the type of bond, helical or non-helical. In the model we do not explicitly consider any contributions from flexing, stretching, or writhing of the assemblies, nor of their interaction with the solvent. These contributions should be extensive in the length of the assemblies and may be absorbed in the free-energy scales that we present now. We denote the free energy that is associated with the formation of a non-helical bond by $M < 0$ and the free-energy difference between a helical and a non-helical bond by $P$. A helical bond is more favorable than a non-helical one if $P < 0$ while for $P > 0$ the opposite is true. Because conformational frustration occurs if a molecule is involved in two types of bonding with its direct neighbors, a free energy penalty $R \geq 0$ is introduced for those molecules. This free-energy penalty can be viewed as a parameter for the cooperativity of the self-assembly.

Accordingly, the dimensionless Hamiltonian $H$ for an aggregate of $N > 2$ chain units is given by

$$H = -\frac{1}{2} R \sum_{i=1}^{N-2} (s_is_{i+1} - 1) + \frac{1}{2} P \sum_{i=1}^{N-1} (s_i + 1) + (N - 1) M, \quad (2.10)$$

with $s_i = -1$ if the bond following the $i$-th monomer unit is non-helical and $s_i = +1$ if it is helical. For $N = 1$ there are no bonds and we put $H \equiv 0$ (and thus $Q(1)=1$), while for $N = 2$ and $N = 3$ the Hamiltonian depends on the boundary conditions we impose on the first and last bond, $s_1$ and $s_{N-1}$. For instance, for free boundary conditions, $H(2) = \frac{1}{2} P(s_1 + 1) + M$ and $H(3) = \frac{1}{2} P(s_1 + 1) + \frac{1}{2} P(s_2 + 1) - \frac{1}{2} R(s_1s_2 - 1) + 2M$. The single-aggregate partition function $Q(N)$ is given by

$$Q(N) = \sum_{\{s\}} e^{-H}, \quad (2.11)$$

where the summation over $\{s\} \equiv \{s_1, \ldots, s_{N-1}\}$ involves all possible conformations. This conformational sum can be evaluated straightforwardly by employing the transfer-matrix method.\(^8\)
The evaluation has been carried out explicitly in ref 4 and for \( N > 2 \) the result is

\[
Q(N) = [x\lambda_1^{N-2} + y\lambda_2^{N-2}] e^{-M(N-1)},
\]

(2.12)

where

\[
\lambda_{1,2} = \frac{1}{2}[1 + s \pm \sqrt{(1-s)^2 + 4\sigma_C s}] \quad (2.13)
\]

as well as the quantities \( x \) and \( y \) are functions of the so-called Zimm-Bragg parameters \( s = \exp(-P) \) and \( \sigma_C = \exp(-2R) \). The precise form of \( x \) and \( y \), and that of the partition function of the dimers \( Q(2) \), depends on the boundary conditions that are imposed on the first and last bond. At first sight one would presume free boundary conditions, but this cannot be reconciled with the non-isodesmic character of the helical self-assembly of many aggregates, including OPV4 helices. Since in the next section we want to apply the helical aggregation theory to OPV4 helices, we use boundary conditions where the first bond is non-helical and the last one is free. This asymmetric boundary condition is consistent with the chiral nature of the monomer units and allows for non-isodesmic, nucleated self-assembly. For these boundary conditions, the quantities \( x \) and \( y \) are given by

\[
x = \frac{\lambda_1 - s + s\sqrt{\sigma_C}}{\lambda_1 - \lambda_2},
\]

(2.14)

\[
y = \frac{s - \lambda_2 - s\sqrt{\sigma_C}}{\lambda_1 - \lambda_2},
\]

and \( Q(2) = \exp(-M) \). Expressions for \( x \) and \( y \) for other boundary conditions can be found in ref 3. The eigenvalue \( \lambda_1 \) is always larger than \( \lambda_2 \), and the larger eigenvalue will therefore dominate the partition function \( Q(N) \) when the mean aggregate size, \( \langle N \rangle_n = \phi / \sum_{N=1}^{\infty} \rho(N) \), is much larger than unity.

Once the partition function is known, standard methods from statistical mechanics allow for the calculation of quantities like the mean aggregate size, the fraction of material in the aggregated state, and the mean fraction of helical bonds. To calculate these quantities in terms of the concentration of the dissolved material instead of the chemical potential \( \mu \), we insert eq 2.11 and 2.9 into eq 2.2, and carry out the sum. The result is a polynomial of degree six in the fugacity \( z \equiv \exp(\mu - M) \). We solve this equation numerically as a function of the system parameters \( M, P, R, \) and \( \phi \). Only one of the six solutions is physically relevant. The fugacity \( z \) is non-negative and real, since \( \mu \) and \( M \) are real numbers. Furthermore, in order for the sum in eq 2.2 to converge, \( z\lambda_1 \) has to be smaller than unity for all \( s \). This implies that \( z < 1 \), since \( \lambda_1 \geq 1 \). These considerations leave only one physically relevant solution for \( z \) in all cases studied.

Besides the average aggregate size, the assemblies are also characterized by the mean helicity, a quantity that can be observed using circular dichroism (CD) spectroscopy. Following ref 3, the weight-averaged fraction of helical bonds is given by

\[
\langle \theta \rangle_w = -\frac{1}{\phi} \sum_{N=3}^{\infty} \rho(N) \frac{N}{N-2} \frac{\partial \ln Q(N)}{\partial P}.
\]

(2.15)

The partial derivative in this expression counts the number of helical bonds in an aggregate of length \( N \). For boundary conditions where the first bond is non-helical and the last one is free
the maximum number of helical bonds in a single aggregate is \( N - 2 \) (monomers and dimers do not contribute to the mean helicity). Equation 2.15 counts thus the total number of helical bonds and compares it to the maximum attainable number of helical bonds in the system. In the long-chain limit, where \( \langle N \rangle_n \gg 1 \), this expression reduces to

\[
\langle \theta \rangle_w = \frac{1}{2} + \frac{s - 1}{2\sqrt{(s - 1)^2 + 4\sigma_C s}},
\]

showing that in the limit of \( \langle N \rangle_n \gg 1 \), the mean fraction of helical bonds does not depend on specific details of the aggregate ends and the mean aggregate size.

Circular dichroism spectroscopy is a commonly used tool for probing the mean helicity of a system experimentally. The helical aggregation theory can be used to interpret the CD data by utilizing eq 2.15. For that purpose, it is assumed that the magnitude of the CD spectrum scales linearly with the aggregate length as well as with the number of helical bonds. In chapter 6 and 7 we will revert to these assumptions.

To conclude this section we note that the helical aggregation theory indicates the existence of two regimes: one in which the helical transition and the polymerization transition are separated, and another in which they coincide.\(^3\)–\(^5\) In the next section we will apply the helical aggregation theory to interpret the optical data of self-assembling OPV4 aggregates and we will see that this supramolecular system can be classified as belonging to the latter regime.

### 2.4 Application to self-assembling OPV4 aggregates

Various optical techniques were used in refs 7 and 9 to monitor the helical self-assembly of OPV4. The optical data were interpreted by Jonkheijm et al.\(^9\) using the nucleation-growth model,\(^9\) which we will discuss briefly below. Their analysis suggests that initially small randomly ordered aggregates form via isodesmic polymerization. Once a critical size is attained, these nuclei transform into small helical assemblies, after which strong elongation occurs.\(^9\) In this section we will apply the helical aggregation theory to interpret the optical data of OPV4. By fitting the optical data we obtain valuable information about the size distribution of the aggregates in solution and about their conformational states. We will utilize this information in chapters 3 and 7, in which we will combine the helical aggregation theory with a quantum-mechanical model for the optical excitations to study the temperature-dependent photoluminescence (chapter 3) and circular dichroism (chapter 7).

Within the nucleation-growth model, monomers are either highly active for polymerization or inactive. The inactive state is in thermal equilibrium with the highly active state of the monomers and the equilibrium constant associated with the reaction from the inactive to the active state is denoted by \( K_a \). Only monomers in the active state are able to polymerize into helical stacks whereas the inactive material remains monomeric. We denote the equilibrium constant associated with the polymerization by \( K_e \). The number-averaged mean aggregate size
of the helical assemblies, $\langle N \rangle_n$, then obeys the following algebraic equality\textsuperscript{5,9}

$$K_e = \exp \left( -\frac{h_e}{k_B T_e^2} (T - T_e) \right)$$

$$= 1 - \frac{1}{\langle N \rangle_n - 1} + K_a \langle N \rangle_n (\langle N \rangle_n - 1).$$

(2.17)

Here, $T_e$ is the temperature where elongation sets in and $h_e$ is the enthalpy of the formation of a helical bond in the elongation process. Here an enthalpy is used instead of an energy in order to make a link with experimentally accessible quantities. In the helical polymerized regime $T < T_e$, the fraction of molecules in helical aggregates is approximately given by\textsuperscript{5,9}

$$\eta \approx 1 - \exp \left( -\frac{h_e}{k_B T_e^2} (T - T_e) \right).$$

(2.18)

Unlike the helical aggregation theory, the nucleation-growth model assumes beforehand that the assemblies formed are always perfectly helical and that the helical transition coincides with the polymerization transition.

Figure 2.2 shows the normalized CD intensities at a wavelength $\lambda = 466$ nm measured for a monomer concentration of $1.1 \cdot 10^{-5}$ M, corresponding to a molar fraction $\phi = 2.5 \cdot 10^{-6}$. The red dotted line represents the theoretical fit using the nucleation-growth model with parameters\textsuperscript{*} $h_e = -80$ kJ·mol$^{-1}$ and $K_a = 0.46 \cdot 10^{-4}$. It was found in ref 9 that the experimental CD data deviate from the predictions of the nucleation-growth model at low temperatures, which was attributed to clustering of the assemblies. Therefore, we choose to fit the theoretical predictions to the experimental data only around the helical transition temperature and normalize the experimental data accordingly.

The blue solid line in Figure 2.2 corresponds to the theoretical prediction obtained with the helical aggregation theory. To obtain this result, we had to relate the theoretical parameters $M$ and $P$ to experimentally accessible quantities. In doing so we followed ref 1 and made the temperature dependence of these parameters explicit through a first-order Taylor expansion around two reference temperatures $T_*^0$ and $T_*^\infty$, defined below:

$$M(T) \approx M(T_*^0) + (1 - \frac{T}{T_*^0}) \frac{h_n}{k_B T_*^0},$$

(2.19)

and

$$P(T) \approx (1 - \frac{T}{T_*^\infty}) \frac{h_h}{k_B T_*^\infty}.$$  

(2.20)

Here, $M(T_*^0) \equiv \ln \phi/(2 - \sqrt{2})$ is the binding free energy associated with the non-helical bond at the polymerization transition temperature $T_*^0$ where half of the monomer units would have assembled if there were no helical transition. This free energy depends on the overall mole fraction $\phi$ of the molecular building blocks. Finally, the quantities $h_n$ and $h_h$ represent the (now dimension-bearing) enthalpy of the formation of a non-helical bond and the enthalpy

---

*Note that in ref 9 the value $h_e = -56$ kJ·mol$^{-1}$ was used to fit the experimental data. However, we could not reproduce the curves presented there with this value.*
Figure 2.2: Symbols: experimental CD intensity at $\lambda = 466$ nm as a function of temperature for OPV4 molecules in dodecane solution (11 $\mu$M). Solid blue line: calculated mean fraction of helical bonds versus temperature, as predicted by the helical aggregation theory, with parameters as given in Table 2.1. Dotted red line: calculated fraction of molecules in helical aggregates as predicted by the nucleation-growth model with parameters $h = -80$ kJ·mol$^{-1}$ and $K_a = 0.46 \cdot 10^{-4}$. Inset: mean aggregate size $\langle N \rangle$ versus temperature, as predicted by the helical aggregation theory.

So, even if we presume the free-energy penalty $R$ to be temperature independent, the helical aggregation model has five free parameters that (ideally) need to be fixed independently from each other: $h_h$, $h$, $T_0$*, $T_{\infty}^*$ and $R$.* This is, of course, no trivial matter. For the chiral discotic molecules described in ref 3 this proved possible because of the large body of experimental data available for a range of temperatures and concentrations. For OPV4 we do have at our disposal sufficient data to fix all model parameters, but unfortunately not to the extent that all parameters can be determined independently.

In principle, we can determine the enthalpy of the formation of a non-helical bond and the polymerization transition temperature by fitting the fraction of monomeric building blocks in the aggregated state $\eta \equiv 1 - \rho(1)\phi^{-1}$ to a normalized UV/vis absorption intensity at the wavelength $\lambda = 490$ nm, measured at a concentration of $1.1 \cdot 10^{-5}$ M, corresponding to a molar fraction $\phi = 2.5 \cdot 10^{-6}$. However, this results in an enthalpy for the non-helical bond formation that is

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*This wavelength corresponds to the lowest molecular singlet transition in OPV4 and a shoulder develops in the absorption spectra at this wavelength upon aggregation, see Figure 1.5.
far too high to reproduce the normalized CD intensity. The absorption spectra do presumably not only change as a result of aggregation, but also due to planarization of the OPV4 molecules. The enthalpy obtained from the absorption intensities is therefore not associated exclusively to the polymerization and we have estimated only the polymerization transition temperature $T^0_\infty$ from the experimental UV/vis absorption intensities.

The remaining parameters, viz. the enthalpy of the formation of a non-helical bond $h_n$, the enthalpy of the formation of a helical bond $h_h$, the helical transition temperature $T^\infty_\infty$, and the parameter $R$, we estimated by comparing normalized CD intensities at $\lambda = 466$ nm, obtained at the same concentration, to the theoretical weight-averaged fraction of helical bonds (eq 2.15). We are thus in the non-ideal situation that we need to estimate four parameters from one theoretical fit. However, we were still able to make a fair estimate, since the parameters are responsible for different features of the theoretical curve. The helical transition temperature determines almost exclusively at which temperature the transition to helices occurs, while the sharpness of this transition is determined by the parameter $R$. After a steep initial rise, the experimental data gradually reach a saturation value. This gradual approach of the saturation point is determined by the bond enthalpies. Table 2.1 shows the values that have been used to reproduce the normalized CD intensities at $\lambda = 466$ nm. For these values agreement between theory and the spectroscopic data is quantitative, see Figure 2.2. The deviation at low temperatures is again attributed to clustering.\(^9\) We note that the differences with the nucleation-growth model are minor, so that we may conclude that for this system the application of the nucleation-growth model is sufficient. The inset of Figure 2.2 exhibits the mean aggregation size as a function of temperature, showing that the polymerization transition and the helical transition coincide. We use the values in Table 2.1 in the next chapter, where we combine the helical aggregation theory with a quantum-mechanical model to calculate temperature-dependent photoluminescence spectra.

Summarizing, we conclude from our analysis that upon lowering the temperature, H-bonded pairs of OPV4 molecules associate into small randomly ordered aggregates via an isodesmic pathway. Below a critical temperature, the randomly ordered assemblies attain a helical conformation, followed by a strong elongation upon further cooling. This picture of the self-assembly agrees with that of Jonkheijm et al., who interpreted the optical data with the nucleation-growth model.


References


Chapter 3

Photoluminescence spectra of self-assembling helical supramolecular aggregates

The reversible assembly of helical supramolecular polymers of chiral molecular building blocks is known to be governed by the interplay between mass action and the competition between weakly and strongly bound states of these building blocks. The highly co-operative transition from free monomers at high temperatures to long helical aggregates at low temperatures can be monitored by photoluminescence spectroscopy, which probes the energetically lowest-lying optical excitations in the assemblies. In order to provide the interpretation of measured spectroscopic data with a firm theoretical basis, we present a comprehensive model that combines the helical aggregation theory of the previous chapter with a quantum-mechanical theory for the optical excitations. This quantum-mechanical theory not only accounts for the conformational properties of the assemblies but also describes the impact of correlated energetic disorder stemming from deformations of the chromophores and the interaction of the chromophores with solvent molecules. The theoretical predictions are compared to measured fluorescence spectra of chiral oligo(p-phenylene-vinylene) molecules in the solvent dodecane. We find that the predictions qualitatively describe the red-shift of the main fluorescence peak and its decreasing intensity upon aggregation.

3.1 Introduction

Supramolecular self-assembly has proven to be a very useful tool for constructing well-organized nanomaterials with widespread applications. Examples include nanotube architectures formed by self-assembly of amphiphilic molecules with applications in bionanotechnology, molecules that form responsive gels through self-organization in three-dimensional networks of fibers, and supramolecular polymeric (wire-like) assemblies of \( \pi \)-conjugated systems. With regard to the latter, self-assembly provides a way to combine the advantages of easy solution-processing, one-dimensional structural order, and rigidity. The central tenet is that in selective solvents and under suitable conditions specifically tailored \( \pi \)-conjugated molecules self-assemble into helical fibers, such that the overlap of the regularly positioned \( \pi \)-orbitals allows for the transport of excitations (electrons, holes and excitons) along the stacking direction. These nanowires hold potential for applications in electronic devices in the 5-100 nm size range.

Recently, helical supramolecular assemblies have been studied that consist of chiral oligo(p-phenylene-vinylene) derivatives functionalized with an ureidotriazine unit (OPV). We have introduced these molecules in the previous chapters and the molecular structure of OPV4 is shown in Figure 1.3. The functional unit enables an OPV molecule to engage in four hydrogen bonds with another OPV molecule. If dissolved in an apolar solvent at high temperatures, the OPV molecules form dimers as a result of the quadruple hydrogen bonding. Upon lowering the temperature, these H-bonded pairs associate into linear aggregates due to the \( \pi-\pi \) interactions of the phenylene-vinylene backbones. The formation and growth of these aggregates, which attain a helical conformation below some critical temperature, can be monitored by spectroscopic techniques, in particular ultraviolet and visible (UV/vis) absorption, fluorescence and fluorescence decay as well as circular dichroism (CD) measurements.

The self-assembly of OPVs is not only hierarchical but also highly cooperative, see Figure 1.3. Indeed, at high temperatures (or very low concentrations) the OPVs form H-bonded pairs, which on cooling down (or increasing the concentration) first self-organize into short, imperfectly ordered stacks of which the growth is characterized by isodesmic self-assembly. The transformation of these irregularly stacked assemblies into highly ordered (helical) ones occurs at a well-defined temperature. It is this transformation that is so cooperative because from this temperature down the short ordered helical stacks experience a strong elongation, resulting in long helical assemblies. The combination of supramolecular polymerization and a conformational transition reminiscent of, but not quite identical to, the helix-coil transition in biopolymers, has been studied theoretically and the predictions agree well with CD and UV absorption measurements on OPVs dissolved in alkanes. By combining theory and experiment, Jonkheijm and collaborators discovered that the solvent plays a crucial role in the ordering transition of the assemblies.

Although spectroscopy is routinely used to study cooperativity in self-assembly, there is no firm theoretical basis for linking measured absorption or fluorescence intensities to the fraction of molecules in assemblies or to some average aggregation number. Indeed, results seem to depend (if only fairly weakly so) on the choice of spectroscopic technique, the wavelength, the normalization of the intensity, and so on. In other words, the interpretation of spectroscopic data by their fitting to statistical mechanical models cannot yet be considered an exact science,
because these models alone cannot account properly for absorption and fluorescence intensities.

Several studies have been made to come to a quantum-mechanical description of the prob-
lem in hand.\textsuperscript{12–14} Spano and collaborators, for example, recently reported on a study of excitons
in helical OPV aggregates in dodecane solution at $T = 278$ K.\textsuperscript{14} They calculated circularly
polarized absorption and emission spectra using a Holstein Hamiltonian with spatially corre-
lated disorder in the transition energies\textsuperscript{†} of the stacked chromophores, taking into account
phenomenologically the impact of coupling of low-frequency phonons to the excitons and the
presence of solvent. By comparison to experimental spectra they were able to characterize the
excited state and they found that disorder and exciton-phonon coupling act synergistically in
localizing the vibrationally dressed exciton over only a few molecules.

Although quite advanced, the quantum-mechanical model of Spano and co-workers ignores
any influence of mass action and conformational transitions, and their results are applicable
only at temperatures $T$ around 278 K, far below the helical transition temperature. In that
temperature region almost all OPV molecules are in the aggregated state and the aggregates
are very long. Moreover, the aggregates are then almost perfectly helical and conformational
transitions do not play a role.

At higher temperatures one should take into account the fact that there is a broad distri-
bution of aggregate sizes and that the conformational state of a single aggregate is not fixed,
because on approach of the helical transition temperature strong fluctuations in the helical
order of the assemblies do occur. Both effects potentially affect the absorption and photolu-
minescence spectra. In fact, Figure 3.1 shows measured photoluminescence spectra taken at
different temperatures,\textsuperscript{5} together with the calculated (number-averaged) mean aggregate size
as a function of temperature (see chapter 2). Upon lowering the temperature, the main pho-
toluminescence peak red-shifts and the intensity of the spectrum decreases. It is quite natural
to presume that these significant changes in the photoluminescence spectra observed with a
lowering of the temperature must somehow be related to the concomitant increase in mean
aggregate size. Hence, a theory of photoluminescence spectra of supramolecular wires should
at least in principle account for the temperature (and concentration) dependence of both the
size distribution and the conformational state of the assemblies.

Here, we indeed go one step further by taking into account the influence of mass action and
conformational transitions to obtain an understanding of photoluminescence spectra in relation
to supramolecular polymerization. We present a quantum-mechanical model that describes the
delocalization of the excitons on the aggregates and combine that with a theory that describes
their helical self-assembly. To our knowledge, we are the first to follow such an approach and
the combined model is a first step in providing measured fluorescence intensities with a firm
theoretical basis. As temperature-dependent fluorescence measurements are used to monitor all
aspects of the self-assembly, unlike CD measurements that provide only information about the
helicity of the assemblies, a full understanding of how helical self-assembly affects fluorescence
spectra could lead to a deeper insight in it. Note that in principle our combined quantum
and statistical mechanical approach can be used to obtain temperature-dependent absorption

\textsuperscript{†}The transition energy is the energy needed for exciting a chromophore from its electronic ground state to
its first optically allowed excited state.
Photoluminescence spectra of self-assembling helical supramolecular aggregates

Figure 3.1: Photoluminescence spectra of OPV4 in dodecane solution for different temperatures (taken from ref 5). Inset: calculated (number-averaged) mean aggregate length, given as the number of stacked OPV dimers, as a function of temperature (see chapter 2).

spectra and CD spectra as well.

In this chapter we apply the helical aggregation theory\textsuperscript{8–11} that was presented in the previous chapter to calculate the size distribution of the aggregates and the distribution of their conformations as a function of temperature (and concentration). For every aggregate of given length and conformation, we calculate within a tight-binding model the energy of the energetically lowest-lying optical excitation, presumed to be the state from which radiative decay to the ground state takes place. The disorder in the on-site energies stemming from deformations within the chromophores and their interaction with the solvent molecules is taken into account phenomenologically in the same way as done by Spano \textit{et al.}\textsuperscript{14} By averaging over the distributions of aggregate lengths and conformations, and by accounting for optical matrix elements that take into account the transition intensities, we finally obtain the luminescence spectrum as a function of temperature (and concentration).

In what follows, we will show that by accounting for the influence of mass action and conformational transitions, the red-shift of the main photoluminescence peak can be understood qualitatively. We shall see that by comparing theory and experiment we can estimate the mean exciton diffusion length, the average distance that excitons overcome before decaying radiatively, and we will show that our model predicts the decrease in intensity of the spectrum upon lowering the temperature reasonably well.

The remainder of this chapter is set up as follows. First, in section 3.2 we present a very brief outline of the helical aggregation theory. For details we refer to the previous chapter and to the work of van Gestel and van der Schoot.\textsuperscript{8–11} In section 3.3 we discuss our tight-binding theory for describing the excitons on a single molecular aggregate of given length. Next, in section 3.4 we describe how photoluminescence spectra are calculated by combining the two
3.2 Helical self-assembly

In the previous chapter we have presented the helical aggregation theory. Being a combination of equilibrium polymerization theory and a model for the helix-coil transition, the helical aggregation theory enables us to calculate the size distribution of aggregates, \( \rho(N) \), as a function of temperature. In addition, the model provides information about the conformational states of individual aggregates as a function of temperature via the single-aggregate partition function \( Q(N) \). A conformational state is specified by the state of the bonds between neighboring molecules within an aggregate. In the high-energy/low-entropy bonded state two neighboring molecules are locked in a helical arrangement, where the helical sense is fixed by the chiral nature of the molecules involved. The molecules do not have fixed orientations relative to each other if the bond is in the low-energy/high-entropy state. For simplicity we refer to the former as the helical bond, and to the latter as the non-helical bond.

We concluded the previous chapter by applying the helical aggregation theory to the case of OPV4. The model parameters were estimated by comparing the normalized CD intensities at \( \lambda = 466 \text{ nm} \) to the theoretical weight-averaged fraction of helical bonds.\(^9\) Table 2.1 shows the values used in our calculations for OPV4. For these values the agreement between theory and the spectroscopic data is quantitative, except at very low temperatures where OPV helices are thought to form bundles.\(^7\) With the values of Table 2.1 at hand, we are in the position to predict the density of aggregates of length \( N \) using eq 2.9. Furthermore, these values allow us to predict the probability that an aggregate of a certain length attains some conformational state, since this probability is proportional to \( e^{-H} \), with \( H \) the Ising-like Hamiltonian given by eq 2.10. We need both the density distribution and the configurational statistics of the aggregates as input in our quantum-mechanical calculations outlined in the next two sections.

3.3 Tight-binding model for OPV photophysics

We model the OPV assemblies as linear chains consisting of \( N \) two-level chromophores with radially oriented transition dipoles. Each oligomer pair is thus considered as a single chromophore with an electronic ground state \( |g\rangle \) and an energetically lowest-lying excited state \( |e\rangle \). The energy needed for exciting a chromophore from its ground state to its first optically allowed excited state is the so-called transition energy. We describe the delocalization of the exciton on the aggregate within a tight-binding approximation, with the exciton Hamiltonian,

\[
H = \sum_{n=1}^{N}(\epsilon_0 + \Delta_n)|n\rangle\langle n| + \sum_{n=1}^{N-1} V_{n,n+1} \{ |n+1\rangle\langle n| + |n\rangle\langle n+1| \},
\]

representing the contribution of the chromophore transition energies and the transfer of excitons from one chromophore to the next. In eq 3.1, \( |n\rangle \) denotes an electronic state in which the \( n \)-th
Photoluminescence spectra of self-assembling helical supramolecular aggregates

The chromophore is electronically excited while all the other chromophores remain in the electronic ground state, $|n\rangle \equiv |e_n\rangle \prod_{m\neq n} |g_m\rangle$. This means that we consider low excitation densities, i.e., each aggregate contains at most one exciton. We expect this assumption to hold true due to the low laser intensity and density used in experiment.\textsuperscript{15,16} The optical spectra of OPV show a clear vibronic progression due to coupling of the exciton to a high-energy vibrational mode (see chapter 1 and ref 14). In our simplified tight-binding model we neglect this exciton-phonon coupling, meaning that we concentrate only on the 0–0 peak in the photoluminescence spectra (implying no phonons in either the electronic ground state or the excited state).

Because of thermally induced deformations within each chromophore, e.g., by bending and twisting, statistical conformations of the polymeric side groups, and the presence of some degree of randomness in the direct environment of each chromophore on account of the presence of solvent, the chromophore transition energies fluctuate around an average energy $\epsilon_0$. As in ref 14, we assume that the chromophore transition energies are exponentially correlated and $l_0$ is the spatial correlation length in dimensionless units of the distance between two bound chromophores. There is no spatial correlation in the case of $l_0 = 0$ and all transition energies are identical in the limit where $l_0 \rightarrow \infty$.

The energies of the exciton states depend on the conformational state of the aggregate via the effective (see below) transfer integral $V_{n,n+1}$ between two neighboring chromophores, since we expect the transfer integral of a helical bond to deviate from that of a non-helical bond. Two chromophores are much more loosely bound in the non-helical bonded state than they are in the helical state. In that case they presumably are able to rotate freely with respect to each other. Therefore we expect the transfer integral of two loosely bound chromophores to be much smaller than in the more strongly bound helical state, and for simplicity we set it equal to zero. Experimental investigations of the transfer rate of excitons along supramolecular OPV aggregates for two different packing geometries seem to support this assumption. Indeed, the transfer of excitons is highly efficient in well-defined helical stacks, whereas a slow transfer of excitons along the stacks is observed in disordered assemblies.\textsuperscript{17} The slow exciton transfer in disordered assemblies was attributed to the much weaker excitonic coupling.

Our tight-binding model neglects exciton-phonon coupling. In the case of weak excitonic coupling, exciton-phonon coupling is known to renormalize the exciton bandwidth with a factor $e^{-\lambda^2}$, where $\lambda^2$ is the Huang-Rhys factor. By approximation, we can take into account the influence of exciton-phonon coupling on the 0–0 emission by using an effective transfer integral $V_{n,n+1} = e^{-\lambda^2}J_{n,n+1}$, where $J_{n,n+1}$ is the transfer integral without exciton-phonon coupling.
3.4 Calculation of temperature-dependent photoluminescence spectra

Figure 3.2: Schematic representation of the procedure for calculating the photoluminescence spectra by combining the helical aggregation theory with the tight-binding model. The meaning of the different symbols is explained in the main text.

We now possess all the ingredients to calculate the photoluminescence at any stage in the self-assembly. The helical aggregation theory provides information about the size distribution and the conformational state of the aggregates as a function of temperature, while the tight-binding model enables us to calculate the energies of exciton states from which radiative decay takes place for any aggregate of given length and conformational state. In the next section we outline how we combine the helical aggregation theory with the tight-binding model for calculating temperature-dependent photoluminescence spectra.

3.4 Calculation of temperature-dependent photoluminescence spectra

Figure 3.2 exhibits a schematic representation of the procedure that we follow to calculate temperature-dependent photoluminescence spectra. The assembly model provides us with the size distribution of aggregates in solution, \( \rho(N) \), and the single-aggregate partition function, \( Q(N) \). We use \( \rho(N) \) to define a probability distribution \( P(N) \), which is discussed in more details below. This distribution determines how much the photoluminescence from aggregates with length \( N \) contributes to the total photoluminescence spectrum. Next, we take a large number of aggregates according to the distribution \( P(N) \) and for each aggregate we generate an energetic disorder configuration. To obtain the photoluminescence spectrum of each aggregate,
we employ the tight-binding model to calculate the photoluminescence from each configurational state and we average over all configurational states by utilizing $Q(N)$. In the following we will give a more detailed discussion of our procedure for calculating temperature-dependent photoluminescence spectra.

Let us first concentrate on how we calculate the photoluminescence spectrum of a single aggregate of a given length $N$. In our photoluminescence gedanken experiment we presume that, due to the low laser intensity used, at most one chromophore absorbs a high-energy photon, leading to one high-energy exciton on the aggregate. We assume that this exciton relaxes rapidly to the energetically lowest-lying state of the aggregate and then decays radiatively to the ground state. This relaxation is possible due to Förster transfer\(^1\) of the exciton along the aggregate, which is accompanied by the excitation of low-energy phonons. Experiments on aggregates of OPV3 (containing only one dialkoxybenzene unit) with a small amount of OPV4 mixed in demonstrate how efficient this process is: almost all photoluminescence comes from the OPV4 molecules, which have an energetically lower-lying excited state than the OPV3 molecules.\(^1\)\(^9\) The assumption that radiative decay takes place from the energetically lowest-lying excited state breaks down if the aggregates become very long. In that case, radiative decay occurs before the exciton has found the lowest-lying excited state on the aggregate. To account for the finite lifetime of the excitons, we use an effective maximum aggregate length for calculating the lowest-lying excited state.

We denote the energetically lowest-lying excited state of the aggregate by $\Psi_{N,i} \equiv \sum_n c_{i,n} |n\rangle$. This state has an energy $E_i$, where the subscript $i$ refers to a particular conformational state of the aggregate. The coefficients $c_{i,n}$ and the energy $E_i$ are found by diagonalization of the Hamiltonian in eq 3.1. In order to obtain the photoluminescence spectrum $S_N(E)$ of a single aggregate with length $N$, we average over all conformational states of an aggregate with length $N$,

$$S_N(E) = \langle I_{N,i} \delta(E - E_i) \rangle,$$

(3.4)

with $I_{N,i}$ being the intensity of the photoluminescence of an aggregate with length $N$ and conformation $i$, and $\langle \cdots \rangle$ indicating the averaging over all conformational states.

In order to determine $I_{N,i}$, we need to take into account non-radiative processes and other possible non-fluorescent decay channels such as intersystem crossing, which leads to phosphorescence. For simplicity we assume that the rate of non-fluorescent decay processes, $k_{nf}$, is independent of the aggregate length and its conformational state. The rate of fluorescent decay, $k_{f,N,i}$, is proportional to the oscillator strength, which is the square of the transition dipole moment between the lowest-lying excited state and the electronic ground state,

$$k_{f,N,i} = \frac{\tilde{k}_f}{\mu_0^2} |\langle \Psi_{N,i}| \tilde{M} \prod_n |g_n\rangle|^2 e^{-\lambda^2}.$$

(3.5)

Here, the Franck-Condon factor $e^{-\lambda^2}$ takes into account the influence of the exciton-phonon coupling on the 0–0 transition, $\tilde{k}_f$ is a constant, assumed to be independent of the aggregate length, and $\tilde{M}$ represents the transition dipole moment operator of the aggregate, which is
3.4 Calculation of temperature-dependent photoluminescence spectra

given by

$$\vec{M} = \sum_{n=1}^{N} \vec{\mu}_n.$$  

(3.6)

Taking the z-axis along the stacking direction, the transition dipole moment operator \(\vec{\mu}_n\) at site \(n\) is defined as

$$\vec{\mu}_n = \mu_0 \left( \cos(\varphi_n) \hat{e}_x - \sin(\varphi_n) \hat{e}_y \right) \left( |n\rangle \langle g_n| + |g_n\rangle \langle n| \right),$$  

(3.7)

where \(\mu_0\) is the transition dipole moment of a single chromophore, \(\varphi_n\) the angle between the \(x\)-axis and the long axis of the oligomer at site \(n\), along which the dipole moment of OPV is oriented, and \(\hat{e}_x\) and \(\hat{e}_y\) are unit vectors in the \(x\)- and \(y\)-direction. Accordingly, the intensity of the photoluminescence of an aggregate of length \(N\) and conformation \(i\) becomes

$$I_{N,i} = \frac{k_{f,N,i}}{k_{f,i} + k_{nf}} = \frac{|\langle \psi_{N,i} | \vec{M} \prod_n |g_n\rangle |^2 e^{-\lambda^2/\mu_0^2} / \mu_0^2}{|\langle \psi_{N,i} | \vec{M} \prod_n |g_n\rangle |^2 e^{-\lambda^2/\mu_0^2} + k_{nf}/k_f}. \quad (3.8)$$

The ratio \(k_{nf}/k_f\) can be estimated from the experimental spectra.

We have to carry out an additional averaging over all aggregate lengths \(N\) in order to obtain the total photoluminescence spectrum. Each chromophore in an aggregate can absorb a photon and therefore the absorption cross section of an aggregate is proportional to its length. This means that each spectrum of aggregates of length \(N\) should be weighed by the probability distribution

$$P(N) = N \rho(N) / \sum_{N=1}^{\infty} N \rho(N). \quad (3.9)$$

Hence, the total photoluminescence spectrum is then obtained as

$$S(E) = \sum_{N=1}^{\infty} P(N) S_N(E). \quad (3.10)$$

In the numerical evaluation of the sum in eq 3.10 we have introduced a cutoff \(N_{\text{max}}\) that is fixed by \(P(N_{\text{max}})/\max(P(N)) \approx 0.001\). For OPV, this leads to cut-off values between \(N_{\text{max}} = 7\) at \(T = 353\) K and \(N_{\text{max}} \approx 1.4 \cdot 10^4\) at \(T = 273\) K. In addition, we need to take into account energetic disorder. For that purpose, we take a large number (up to about \(10^6\)) of aggregate lengths \(N\) according to the distribution \(P(N)\) of eq 3.9, and for each aggregate we generate an disorder configuration for the chromophore transition energies by using the joint Gaussian distribution in eq 3.2. We then carry out the conformational averaging in eq 3.4 for each aggregate by a Monte-Carlo procedure based on single spin-flip sampling. Starting from a random configuration, an equilibration time of 40\(N\) Monte-Carlo steps proved sufficient for all temperatures studied. After equilibration data are gathered for 100 configurations, with 20\(N\) Monte-Carlo steps between these configurations. With this procedure we obtain a spectrum for each temperature with an accuracy of about 2% around the peak position.
3.5 Results and comparison with experiment

In this section we apply our combined model to calculate the temperature-dependent photoluminescence spectra of self-assembling OPV4 aggregates. For that purpose we have to estimate several parameters in our combined theory from the experimental photoluminescence spectra. In the following we will first estimate the average chromophore transition energy and the disorder strength from the highest-temperature spectrum. Next, we estimate the ratio \( k_{nf}/k_f \) and the effective maximum aggregate length from the lowest-temperature spectrum. With these parameters we are able to calculate the temperature-dependent photoluminescence spectra and we will compare our results to the experimental spectra. Since our model neglects exciton-phonon coupling, which is responsible for the sideband emission, we concentrate in particular on the red-shift of the main photoluminescence peak and its decreasing intensity.

Figure 3.3 shows the experimental photoluminescence spectra (black solid curves, taken from ref 5) together with the theoretical spectra (red dashed curves and blue dash-dotted curves) for OPV4 in the solvent dodecane, obtained with the parameters taken from Table 2.1. The theoretical spectra are normalized such that the peak height of the theoretical spectrum at \( T = 353 \) K equals that of the corresponding experimental spectrum. To obtain the theoretical curves, we put in a theoretical estimate for the transfer integrals. The transfer integral \( J_{n,n+1} \) for OPV4 was calculated in ref 20 for two superimposed chromophores and found to have a value of 57 and 46 meV for twist angles of 6° and 12°, respectively. Here, we take the median angle 9° and accordingly insert \( J_{n,n+1} = 50 \) meV for the transfer integral if the bond between two neighboring chromophores is helical. The effective transfer integral is then given by \( V_{n,n+1} = e^{-\lambda^2} J_{n,n+1} \). Following ref 14 we have used \( \lambda^2 = 1.2 \) for the Huang-Rhys factor. As discussed in section 3.3, we expect that the transfer integral is much smaller if the bond is non-helical and for simplicity we set it equal to zero.

To determine the experimental 0–0 peak positions, we take into account the peak positions of the sideband emission as well by carrying out a four-Gaussian fitting procedure to the experimental spectra. The average chromophore transition energy \( \epsilon_0 \) and the width of the energy distribution \( \sigma \) are then determined by the Gaussian corresponding to the 0–0 peak of the emission spectrum at \( T = 353 \) K, a temperature at which the solution consists mainly of single oligomer pairs. The optimal values we find are \( \epsilon_0 = 2.48 \) eV and \( \sigma = 77 \) meV. The latter value is quite close to the value of 85 meV obtained in ref 14 deep into the helical polymerized regime. This suggests that the disorder in the chromophore transition energies cannot be associated with the conformational properties of the assemblies, a point we discuss further in the next section. Furthermore, Spano and collaborators found that in the aggregated state the chromophore transition energies are spatially correlated. They estimated the spatial correlation length from the ratio of the 0–0 and 0–1 emission intensities, and found \( l_0 = 4.5 \). In our calculations we have used the same correlation length.

Due to their finite lifetime, excitons on very long aggregates cannot always reach the lowest-lying excited state before radiative decay takes place. In fact, calculations on exciton diffusion along OPV4 helices predict a root-mean-squared displacement of the exciton of about 20–25 nm, corresponding to 53 to 67 stacked oligomer pairs, in the first 100 ps after excitation. Time-resolved photoluminescence experiments indicate that more than 50% of the excitons
Figure 3.3: Experimental photoluminescence spectra (black solid curves) and theoretical spectra (red dashed curves and blue dash-dotted curves, corresponding to effective maximum aggregate lengths of 60 and 13, respectively) of OPV4 aggregates at different temperatures. The spectra are normalized such that the peak height of the theoretical spectrum at $T = 353$ K equals that of the corresponding experimental spectrum. The vertical dotted line indicates the position of the experimental 0-0 peak. Note that the graphs have different y scales.
Photoluminescence spectra of self-assembling helical supramolecular aggregates

Figure 3.4: (a) Position of the 0–0 emission peak versus temperature. (b) Relative integrated intensity versus temperature. The vertical dotted line indicates the helical transition temperature as observed in the CD measurements of ref 7.

decays during this time, suggesting that excitons on very long aggregates experience an effective maximum aggregate length. For that reason, we use an effective maximum aggregate length of 60 and assume that the energetically lowest-lying excited state in aggregates of this length corresponds to the one reached by an exciton on all longer aggregates.

To take into account non-fluorescent decay processes we have estimated the ratio \( k_{nf} / \tilde{k}_f \) in eq 3.8. We have determined numerically that the oscillator strength of an aggregate containing 60 chromophores is on average equal to \( 0.24 \mu_0^2 \). Because the average aggregate length at temperatures below 273 K is much larger than 60, we find from eq 3.8 that the intensity of the photoluminescence at these low temperatures is proportional to \( 0.24e^{-1.2}/(0.24e^{-1.2} + k_{nf}/\tilde{k}_f) \) for \( \lambda^2 = 1.2 \). At \( T = 353 \) K the solution contains almost exclusively single oligomer pairs. The oscillator strength of a single oligomer pair is equal to \( \mu_0^2 \), so that the intensity of photoluminescence at \( T = 353 \) K is proportional to \( e^{-1.2}/(e^{-1.2} + k_{nf}/\tilde{k}_f) \). Since the integrated experimental fluorescence intensity for \( T \leq 273 \) K is about 26% of the integrated intensity at \( T = 353 \) K (see Figure 3.1), we estimate that \( k_{nf} \approx 2.4\tilde{k}_f \), and we will use this value in our calculations for an effective maximum aggregate of length of 60.

We now concentrate on the behavior of the 0–0 peak as a function of temperature. Experimentally, it red-shifts and reduces in intensity with decreasing temperature, as can be seen in Figures 3.1 and 3.3. Figure 3.4a shows the position of the 0–0 emission peak as a function of temperature. The theoretically predicted red-shift of the spectra, the red curve in Figure 3.4a, follows the experimental red-shift reasonable well at high temperatures. To calculate these spectra we have used a correlation length of \( \lambda_0 = 4.5 \). In preliminary calculations we have observed that smaller correlation lengths lead to a clear overestimation of the red-shifts at these high temperatures. On the other hand, we have observed that the calculated spectra...
do not change upon increasing the correlation length if $l_0 \geq 4$ and we have thus chosen to use the same correlation length as in ref 14. The theoretically predicted red-shift starts to deviate substantially from the experimental results below $T = 333$ K. Figure 3.3 shows that the spectra at $T = 293$ K and lower, where the mean aggregate size is much larger than the effective maximum aggregate length, exhibit a theoretical red-shift that is about 0.06 eV too large.

The theoretical red-shift matches the experimental red-shift at $T = 293$ K and lower if an effective maximum aggregate length of 17 is used, as shown by the blue curves in Figures 3.3 and 3.4a. Again, to take into account non-fluorescent decay processes, we have estimated the ratio $k_{nf}/\tilde{k}_f$. On average, the oscillator strength of an aggregate consisting of 17 chromophores is equal to $0.22\mu_0^2$, resulting in $k_{nf} \approx 1.2\tilde{k}_f$. As we pointed out in the previous section, the effective maximum aggregate length of 17 can be interpreted as an estimate for the average exciton diffusion length.

Figure 3.4b shows that our theoretical predictions for the integrated intensity of the 0–0 peak as a function of temperature follow the experimental results reasonably well. Below $T = 323$ K the decrease in intensity becomes very substantial, which we attribute to the formation of helical aggregates. If perfect cofacial stacking would occur without energetic disorder, the aggregates would be so-called ideal H-aggregates and the 0–0 emission would be strictly forbidden by symmetry. The presence of helicity and disorder leads to a symmetry breaking, causing a weakly allowed 0–0 emission. Our theory predicts that the onset of the decrease occurs at lower temperatures than measured. In the next section, we discuss possible explanations for this discrepancy.

3.6 Discussion and conclusions

In this chapter we have combined a statistical-mechanical theory for the self-assembly of quasi one-dimensional helical aggregates in solution with a quantum-mechanical tight-binding model for describing excitons on the aggregates. This approach allows us to calculate photoluminescence spectra in systems of supramolecular aggregates that not only adjust their size distribution to the ambient conditions but in addition undergo a helix-coil type conformational transition. The self-assembly of this class of supramolecular polymers can be highly co-operative and non-isodesmic.

We have applied the theory to OPV4 aggregates, which are thought to belong to this class of supramolecular polymers. The theory is able to qualitatively describe the initial red-shift of the 0–0 (zero phonon) peak in the photoluminescence spectrum with decreasing temperature, see Figure 3.3 and 3.4a. However, the theoretical red-shift is substantially larger than the experimental one at further decrease of the temperature. Below a temperature of $T = 293$ K the theory overestimates the red-shift by about 0.06 eV if an effective maximum aggregate length of 60 is used to account for the average exciton diffusion length. The decrease in intensity of the spectrum upon lowering the temperature is reasonably predicted by the theory, albeit that it occurs at a too low temperature (see Figure 3.4b). Furthermore, Figures 3.4a and 3.4b exhibit different behavior: the theoretical red-shift starts to deviate from experiment below the
Photoluminescence spectra of self-assembling helical supramolecular aggregates

helical transition temperature, whereas the disagreement between theory and experiment for the integrated intensity is most substantial above the helical transition temperature.

The theoretical red-shift roughly equals the experimentally observed red-shift at \( T = 293 \) K and below if an effective maximum aggregate length of 17 oligomer pairs is used. This length is relatively short, which is probably due to the fact that we consider the oligomer pairs to be single chromophores. However, due to energetic disorder, the transition energies of two chromophores comprising the oligomer pair are not necessarily equal. Therefore, our estimate of 2.48 eV for the average chromophore transition energy could be too low. A higher value of the average chromophore transition energy results in a higher effective maximum aggregate length. Indeed, Spano and et al. reproduced the line shape of the photoluminescence and absorption spectra at low temperature (\( T = 278 \) K) by employing the disordered Holstein Hamiltonian with an average chromophore transition energy that is 50 meV higher than ours and an aggregate consisting of 20 oligomer pairs. The latter is not sufficiently long for reproducing the experimental red-shift. Furthermore, the oligomer pairs are actually (very small) J-aggregates due to the small negative transfer integral between the two chromophores\(^{14}\) and their emission intensity is therefore much higher than that of the long helices, which are H-aggregates. The oligomer pairs dominate thus the emission spectra until most of them are in the aggregated state, possibly explaining why the theoretical red-shift starts to deviate from experiment below the helical transition temperature.

The integrated intensity of the spectrum as predicted by our theory drops at a temperature somewhat below the temperature at which the experimental integrated intensity drops. This may be due to our assumption that the transfer integral between non-helical bonds is zero, forcing the exciton to remain localized on a single chromophore. A non-zero but still small transfer integral could lead to some delocalization of the exciton, which may lead to a decrease of the fluorescence. This results then in a reduction of the spectra at temperatures above \( T = 325 \) K, where the aggregates are mainly randomly ordered stacks. Moreover, transfer of excitons along the aggregates to quenching sites may occur by Förster transfer even without such a transfer integral.

In our theoretical description we took a value of \( \sigma = 77 \) meV for the width of the energetic disorder distribution. This value was extracted from the spectrum of single OPV pairs (\( T = 353 \) K spectrum). One may wonder if this value also applies to aggregates. Remarkably, this value is very close to the value \( \sigma = 85 \) meV obtained by Spano and collaborators for their fit to all-helical aggregates.\(^{14}\) This indicates that the disorder in the chromophore transition energies for the aggregates is the same as for the single pairs, suggesting that the origin of the disorder is not associated with any property of the aggregated state. We put forward that this can only be explained by presuming that the fluctuations in the chromophore transition energies are caused by low-frequency phonons within the chromophore or/and by the interaction of the chromophores with the solvent molecules. Note that in the aggregated state the side chains of the OPVs are strongly sterically hindered, so one would expect to see a decrease in \( \sigma \) upon aggregation.

Finally, an obvious improvement of the quantum-mechanical part of the theory would be the inclusion of coupling of the exciton to the high-energy vibrational mode (exciton-phonon coupling) that causes a clear vibronic progression in the emission and absorption spectra of OPV. Inclusion of exciton-phonon would give the entire spectrum instead of only the 0–0 emission
line. However, it would also complicate our calculations significantly. Our methodology requires sampling over the lowest-lying excited states of many aggregates of different lengths, disorder configurations, and conformational states. This sampling is feasible with a tight-binding Hamiltonian, but inclusion of exciton-phonon coupling leads to a much more complicated Hamiltonian that requires a very large basis set, resulting in excessively long sampling times. In the next chapter we will include exciton-phonon coupling in our quantum-mechanical model, but we will restrict ourselves to the low temperature limit, where the mean aggregate length is very long and the aggregates are almost perfectly helical. The sampling over different aggregate lengths and conformational states is then avoided and explicit calculations are feasible.

References


Photoluminescence spectra of self-assembling helical supramolecular aggregates


Chapter 4

Optical spectra and Stokes shift in double-stranded helical assemblies

We study the photoluminescence from helical OPV4 aggregates using a model that includes excitonic coupling, exciton-phonon coupling, and spatially correlated disorder in the chromophore transition energies. The helical aggregates consist of stacked dimers of OPV4 chromophores. We model these helical stacks as double-stranded aggregates, allowing us to investigate the effect of correlated disorder within the dimers on emission. We study the dependence of the Stokes shift, the emission line widths and the ratio of the 0–0 to 0–1 emission peaks on the aggregate size and disorder. Our findings show that this peak ratio is quite insensitive to the aggregate size if this size exceeds the coherence length of the emitting exciton. This makes this ratio a reliable probe for both disorder and the coherence length of the emitting exciton. We find only a weak dependence of this peak ratio on the degree of correlation between the transition energies within each dimer, whereas such correlation has a large effect on the aggregate-size dependent Stokes shift. By comparison with experiment, we estimate the coherence length of the emitting exciton to be only one lattice spacing along the stacking direction. From our analysis of the Stokes shift we conclude that the exciton diffusion length is in the range 6-13 nm.*

4.1 Introduction

Organicπ-conjugated systems are highly promising candidates as active components in optoelectronic devices such as light-emitting diodes, field-effect transistors, and solar cells. An essential ingredient for designing and optimizing these devices is a good understanding of the intricate nature of charge and energy transport in these systems. Ideal systems for studying one-dimensional energy and charge transport in organic materials are self-assembled OPV helices. These helical aggregates have received considerable attention lately and have been investigated with numerous spectroscopic techniques. In particular, ultraviolet and visible (UV/vis) absorption, fluorescence and fluorescence decay, as well as circular dichroism and circularly polarized luminescence spectroscopy studies have been performed on these aggregates.

The OPV molecules studied in refs 4 and 5 have already been introduced in the previous chapters. Figure 1.3 shows the molecular structure of OPV4 and a schematic representation of the self-assembly into helical assemblies. The main signatures of the helical aggregation are the appearance of a shoulder on the low-energy side of the absorption spectra and the emergence of bisignate circular dichroism activity in the vicinity of the lowest molecular singlet transition. The fluorescence spectra of OPV are characterized by a clear vibronic progression due to a symmetric ring breathing/vinyl stretching mode with energy $\omega_0 = 0.172$ eV ($\sim 1400$ cm$^{-1}$). Upon aggregation, the fluorescence spectra red-shift and the 0–0 emission intensity decreases relative to the side-band emission.

In the previous chapter, we combined a helical aggregation theory with a tight-binding model, enabling us to describe the red-shift of the fluorescence spectra upon aggregation (decreasing temperature) qualitatively. The helical aggregation theory is a statistical-mechanical model that accounts for the temperature-dependent growth of the helical assemblies and their conformational transition. We used a quantum-mechanical tight-binding model for describing the delocalization of the excitons. This model does not take into account the coupling of the exciton to the above-mentioned high-energy vibrational mode. Therefore, our model could describe only the red-shift of the 0–0 emission upon aggregation but not the decreasing 0–0 intensity relative to the side-band intensities.

An explanation of the reduced 0–0 emission intensity at low temperature ($T = 278$ K) was given in ref 10. At this low temperature, the aggregates are long and almost perfectly helical. A helical aggregate was modeled as a stack of chromophoric units, with each unit representing an H-bonded pair. The coupling of each chromophore to the high-energy vibrational mode was accounted for using a Holstein-type Hamiltonian. It was shown that excitonic coupling causes the reduction of the 0–0 emission intensity with respect to the side-band intensities. The most extreme case is that of ideal H-aggregates, in which chromophores are perfectly cofacially stacked with no disorder. The 0–0 emission is then strictly forbidden due to symmetry, leading to a complete suppression of the 0–0 emission peak. The presence of helicity and disorder leads to a breaking of this symmetry, allowing the 0–0 emission. Because the 0–0 emission is very sensitive to disorder, in contrast to the side-band emissions, the ratio of the 0–0 and 0–1 peak intensities, $S_R$, is a reliable probe for disorder. A Gaussian distribution with spatial correlation was used in ref 10 to model the disorder in the chromophore transition energies.
4.1 Introduction

After the standard deviation $\sigma$ of this Gaussian distribution was determined from an analysis of the experimental absorption spectrum, the spatial correlation length $l_0$ was extracted from the measured ratio $S_R$ and was found to be $l_0 \approx 4.5$ chromophoric units\(^1\). Although with an aggregate length of 20 chromophoric units (dimers) the calculated spectra reproduced the measured value of $S_R$ and the line widths, the calculated Stokes shift (the difference in energy between the 0–0 peaks in the absorption and emission spectrum) was smaller than the measured value by about 50 meV.

In this chapter we will study the emission spectrum in more detail, in particular with respect to the Stokes shift, which was not reproduced in ref 10. A larger Stokes shift in the calculation can be obtained with a larger aggregate size, because in a larger aggregate the probability that emission takes place from a low-energetic state is enhanced. We utilize sparse-matrix techniques and a restricted two-particle basis set to accurately explore much larger aggregates than were possible in ref 10, and to model the helices as double-stranded aggregates, in contrast to the (effective) single-stranded aggregates considered in ref 10. The single-stranded model assumes that the transition energies of the two chromophores forming the H-bonded pair are equal, although there is no a priori reason to assume that this is the case. In the present work we will study the dependence of the Stokes shift, the line width and the ratio $S_R$ on the aggregate size and on disorder. The double-stranded model enables us to not only to study the effect of intrastrand correlation, but also the effect of interstrand correlation on the emission spectrum and Stokes shift. We will argue that from our analysis of the Stokes shift we can estimate the exciton diffusion length in OPV4 helices. Furthermore, the emission line shapes obtained with both the single-stranded model and the double-stranded model do not reproduce all details of the experimental emission spectrum, but we will show how two emission line shapes can be superimposed to obtain excellent agreement with the experimental emission spectrum of OPV4 in dodecane ($T = 278$ K) reported in ref 10.

Because the exciton localizes with increasing disorder, $S_R$ serves not only as a probe for the correlation of disorder,\(^{14}\) but also for the degree of coherence of the exciton.\(^{7,10,15}\) In what follows, we divide the exciton coherence function introduced in ref 10 into intra- and interstrand contributions and show how both are related to the 0–0 emission intensity and $S_R$. We further show how the $L$-independence of $S_R^{10,14,15}$ can be traced back to an independence of the exciton coherence size on $L$, where $L$ is the number of H-bonded pairs comprising the helical aggregate.

The remainder of this chapter is organized as follows. In section 4.2 we present an overview of our model. We discuss the properties of the 0–0 and 0–1 emission in section 4.3. To establish a relationship between the 0–0 emission and the degree of coherence of the exciton, we introduce the exciton coherence function in section 4.4. The dependence of the Stokes shift on the aggregate length is analyzed in section 4.5. A comparison to experiment is made in section 4.6, and we conclude in section 4.7 with a summary, the main conclusions, and an outlook.

\(^1\)The value of $l_0 = 4.5$ arrived at in ref 10 was actually the best compromise for reproducing both the measured value of $S_R$ and the measured vibronic line widths.
4.2 Model for helical OPV4 aggregates

A schematic representation of the helical OPV4 aggregates is shown in Figure 1.3. Each rung of the helix is formed by an H-bonded pair of molecules. The intermolecular distance and angle between two consecutive H-bonded pairs (dimers) along the stacks is 0.375 nm and about 14°, respectively.\textsuperscript{5,10} Each chromophore (OPV molecule) within an aggregate is taken to be a two-level system with an electronic ground state \( |g\rangle \) and an energetically lowest-lying photoexcited state \( |e\rangle \).

The energy needed for exciting a chromophore from its electronic ground state to its first optically allowed excited state is the so-called transition energy. For the \( n \)-th chromophore the transition energy is \( \omega_{0-0} + D + \Delta_n \), where \( \omega_{0-0} \) is the gas-phase 0–0 transition energy and \( D \) is the gas–to–crystal shift that arises from the difference between Coulomb interactions in the excited state and Coulomb interactions in the ground state. To distinguish these interactions from the resonant interactions that cause excitation transfer, they are often referred to as non-resonant interactions. The randomly assigned transition energy offsets \( \Delta_n \) account for fluctuations in transition energies along the aggregates. We address the origin and form of this disorder below.

Excitonic coupling between chromophores has a delocalizing effect on excitations. For the OPV aggregates, the excitonic coupling between chromophores \( n \) and \( m \), \( J_{nm} \), has been evaluated in refs 13 and 10 by combining a coupled cluster single and double (CCSD) approach to the INDO (Intermediate Neglect of Differential Overlap) Hamiltonian on the basis of model geometric structures. The nearest-neighbor coupling between superimposed molecules for \( \phi = 14^\circ \) was found to be about 40 meV and the coupling between two chromophores within an H-bonded pair, \( J_{\text{dim}} \), was found to be only -7.5 meV. Hence, the calculated intrastrand coupling is much larger than the coupling between the strands.

Each chromophore couples to a high-energy intramolecular symmetric ring breathing/vinyl stretching vibrational mode with energy \( \omega_0 = 0.172 \text{ eV} (\sim 1400 \text{ cm}^{-1}) \) and Huang-Rhys (HR) factor \( \lambda^2 \). The Huang-Rhys factor is a measure for the shift in the equilibrium configuration of the ground- and excited-state nuclear arrangements. We use a Huang-Rhys factor of \( \lambda^2 = 1.2 \). This value, together with the cubic frequency dependence of the emission rate, yields roughly equal single-molecule 0–0 and 0–1 emission peak intensities, as is found for OPV4 molecules in solution.\textsuperscript{16} We treat this vibrational mode within the linear exciton-phonon coupling approximation. This mode is responsible for the formation of polaronic excitons, which are also called neutral polarons.

We are now ready to write down the aggregate Hamiltonian that includes disorder in the transition energies, excitonic coupling between chromophores, and the above-mentioned exciton-phonon coupling. Within a representation in which one chromophore is excited, the Hamiltonian
4.2 Model for helical OPV4 aggregates

reads:

\[
H = \omega_0 \sum_{n=1}^{N} b_n^\dagger b_n + \omega_0 \lambda \sum_{n=1}^{N} (b_n^\dagger + b_n) |n\rangle \langle n| + \\
\sum_{n=1}^{N} \sum_{m=1}^{N} (\Delta_m \delta_{nm} + J_{nm}) |m\rangle \langle m| + \omega_{0-0} + D + \lambda^2 \omega_0,
\]

(4.1)

where we have taken \( \hbar = 1 \). The first term in this Hamiltonian represents the vibrational energy due to the high-energy vibrational mode and the second term describes the linear exciton-phonon coupling associated with this mode. \( b_n^\dagger \) and \( b_n \) are the creation and annihilation operator, respectively, for vibrational quanta within the harmonic ground-state nuclear potential of the \( n \)-th chromophore. The pure electronic state \( |n\rangle \) denotes that the \( n \)-th chromophore is electronically excited while all other chromophores remain in the electronic ground state, \( |n\rangle \equiv |e_n\rangle \prod_{m\neq n} |g_m\rangle \). Originally, the Hamiltonian in eq 4.1 (without disorder) was used by Holstein to study charged-polaron motion in one-dimensional molecular crystals.\textsuperscript{17} Therefore, from here on we will refer to eq 4.1 as the disordered Holstein Hamiltonian.

The basis set of the disordered Holstein Hamiltonian can be divided into so-called \( k \)-particle states, which were originally introduced by Philpott.\textsuperscript{18} A \( k \)-particle state consists of one vibronically (both electronically and vibrationally) excited chromophore and \( k - 1 \) vibrationally excited chromophores. One-particle states are denoted by \( |n, \tilde{\nu}\rangle \), with

\[
|n, \tilde{\nu}\rangle \equiv |e_n, \tilde{\nu}\rangle \otimes \prod_{m\neq n} |g_m, \nu_m = 0\rangle,
\]

(4.2)

and consist of a vibronic excitation at chromophore \( n \) containing \( \tilde{\nu} \) vibrational quanta in the shifted excited-state (denoted by the \( \sim \) on top of the \( \nu \)) nuclear potential. All other chromophores remain electronically and vibrationally unexcited. Two-particle states are denoted by \( |n, \tilde{\nu}; n', \nu'\rangle \), with

\[
|n, \tilde{\nu}; n', \nu'\rangle \equiv |e_n, \tilde{\nu}\rangle \otimes |g_{n'}, \nu'\rangle \otimes \prod_{m\neq n, n'} |g_m, \nu_m = 0\rangle.
\]

(4.3)

In addition to a vibronic excitation at chromophore \( n \), these two-particle states have a vibrational excitation at chromophore \( n' \) containing \( \nu' \) vibrational quanta in the ground-state nuclear potential (\( \nu' \geq 1 \)). We have shown these two excitation types in Figure 1.10.

The Holstein Hamiltonian only couples \( k \)-particle states to \( l \)-particle states with \( l = k \), \( l = k + 1 \) and \( l = k - 1 \), the latter requiring that \( k > 1 \). This demonstrates that there is a coupling hierarchy among \( k \)-particle states that leads naturally to a \( k \)-particle approximation in which the basis set is truncated to include only \( k' \)-particle states with \( k' \leq k \). In this thesis we apply the two-particle approximation (TPA) to represent the eigenstates of the disordered Holstein Hamiltonian.\textsuperscript{18,19} Within this approximation, the \( \alpha \)-th eigenstate of \( H \) is expanded as

\[
|\psi^{(\alpha)}\rangle = \sum_{n, \tilde{\nu}} c_{n, \tilde{\nu}}^{(\alpha)} |n, \tilde{\nu}\rangle + \sum_{n, \tilde{\nu}} \sum_{n', \nu'} c_{n, \tilde{\nu}; n', \nu'}^{(\alpha)} |n, \tilde{\nu}; n', \nu'\rangle.
\]

(4.4)
The two-particle approximation is highly accurate in the intermediate coupling regime that is appropriate for OPV helices.\textsuperscript{19} In this regime the vibrational energy $\omega_0$, the nuclear relaxation energy $\lambda^2 \omega_0$ and the free exciton bandwidth, $W$, are all comparable in magnitude. The free exciton bandwidth, $W$, is the energy difference between the highest-energy and lowest-energy exciton when disorder and electron-phonon coupling are absent. For example, $W$ equals $4 J_0$ in a long linear single-stranded aggregate with only nearest-neighbor coupling ($J_0$). Here, we consider double-stranded aggregates with extended interactions taken from ref 10. We find $W = 0.15$ eV by diagonalizing the Hamiltonian eq 4.1 after setting $\Delta_n$, $\lambda^2$, and $\omega_0$ equal to zero.

The transition energies of two OPV molecules forming an H-bonded pair were assumed to be equal in ref 10. Because in addition interstrand couplings are relatively weak as compared to intrastrand couplings, a single-strand approximation (SSA) was used to model the photophysics of the OPV aggregates.\textsuperscript{10} The SSA treats the OPV helix as an effective single strand of $N$ chromophoric units, with each unit representing an H-bonded pair. We study the influence of non-equal transition energies on the aggregate emission and therefore we model the OPV helix as a double-stranded aggregate. An aggregate consisting of $L$ dimers contains then $N = 2L$ chromophores. In our modeling, the first strand contains the chromophores $n = 1$ to $n = L$, whereas the second strand contains the chromophores $n = L + 1$ to $n = 2L$. The chromophores are numbered such that the $n$–th and $(n + L)$–th chromophore form an H-bonded pair.

The disorder in the transition energies, having a localizing effect on excitations, is caused by thermally induced deformations of each chromophore (e.g. by bending and twisting), fluctuations of the conformations of the side groups of the chromophores, and by randomness in the direct environment of the chromophores because of the presence of the solvent. This disorder is modeled by a Gaussian distribution of the chromophore transition energies. We allow for spatial correlation between the transition energies by employing a joint Gaussian distribution function\textsuperscript{20}

\[
P(\Delta_1, \ldots, \Delta_N) = \frac{1}{(2\pi)^{N/2}} \frac{1}{\sqrt{\det A}} \exp \left( -\frac{1}{2} \sum_{n,m=1}^{N} (A^{-1})_{nm} \Delta_n \Delta_m \right),
\]

where $(A^{-1})_{nm}$ is the $nm$-th element of the inverse covariance matrix. The matrix elements of the covariance matrix are given by

\[
A_{nm} \equiv \langle \Delta_n \Delta_m \rangle_C = \begin{cases} 
\sigma^2 e^{-|n-m|/l_0} & \text{if } n, m \leq L \text{ or } n, m > L; \\
\sigma^2 e^{-1/c} e^{-|n-m+L|/l_0} & \text{if } n \leq L \text{ and } m > L; \\
\sigma^2 e^{-1/c} e^{-|n-m-L|/l_0} & \text{if } n > L \text{ and } m \leq L.
\end{cases}
\]

Here, $\langle \ldots \rangle_C$ denotes an average over random distributions, and $\sigma$ is the standard deviation of the Gaussian distribution\textsuperscript{1}. In ref 10 the aggregates were modeled within the SSA and the covariance matrix was given by $\sigma^2 \exp(-|n - m|/l_0)$, with $l_0$ the spatial correlation length for intrastrand disorder in dimensionless units of the lattice spacing. This form was originally used by Knapp in a study of the line shapes of $J$-aggregates.\textsuperscript{20} We model the helices as double-stranded aggregates and allow also for correlation between the transition energies within each aggregate.

\textsuperscript{1}Note that in ref 10 a $\sigma$ was defined that is $\sqrt{2}$ times the $\sigma$ used in eq 4.6.
4.2 Model for helical OPV4 aggregates

H-bonded pair. The corresponding correlation strength is controlled by the parameter \( c \) in eq 4.6. In our numerical calculations we generate disorder configurations according to eq 4.6. For each disorder configuration we evaluate the electronic eigenstates of \( H \) numerically. Once the eigenstates and energies are known for each configuration, we calculate the spectra by averaging over many disorder configurations. We focus on the absorption spectrum \( A(\omega) \) and the emission spectrum \( S(\omega) \).

The absorption spectrum is given by

\[
A(\omega) = \langle \mu^2 \sum_\alpha |\langle G|\hat{M}|\psi^{(\alpha)}(C)\rangle|^2 \delta(\omega - \omega^{\alpha}(C)) \rangle_C,
\]

where \( \omega^{\alpha} \) is the energy of the \( \alpha \)-th eigenstate of the disordered Holstein Hamiltonian \( H \), \( \langle G \rangle \) is the aggregate electronic and vibrational ground state, and \( \langle \cdots \rangle_C \) denotes an average over disorder configurations. The electric transition dipole moment (tdm) operator \( \hat{M} \) consists of a sum of radially directed molecular tdm vector operators,

\[
\hat{M} = \sum_n \hat{\mu}_n.
\]

Taking the \( z \)-axis along the stacking direction, the tdm operator \( \hat{\mu}_n \) of chromophore \( n \) is defined as

\[
\hat{\mu}_n = \begin{cases} 
\mu (\cos(n\phi)\hat{e}_x - \sin(n\phi)\hat{e}_y) |n\rangle\langle g_n| + \text{H.c.} & \text{if } n \leq L; \\
\hat{\mu}_{n-L} & \text{if } n > L.
\end{cases}
\]

Here \( \mu \) is the tdm of a single chromophore, \( \phi \) is the angle between two consecutive H-bonded pairs, and \( \hat{e}_x \) and \( \hat{e}_y \) are the unit vectors in the \( x \)- and \( y \)-directions.

At zero temperature, emission originates only from the lowest-energy exciton state of each aggregate, \( |\psi^{(\text{em})}\rangle \), and can terminate on any electronic ground state with \( \nu_t \) vibrational quanta. In that case the emission spectrum is given by

\[
S(\omega) = \sum_{\nu_t=0,1,2,\ldots} S^{0-\nu_t}(\omega),
\]

where the spectrum of the \( 0-\nu_t \) emission peak is given by

\[
S^{0-\nu_t}(\omega) = \langle l^{0-\nu_t}(C)\omega^3 \delta(\omega - \omega^{\text{em}}(C) + \nu_t\omega_0) \rangle_C.
\]

Here the factor \( \omega^3 \) accounts for the cubic frequency dependency of the emission rate and \( \omega^{\text{em}} \) is the 0–0 emission frequency of the lowest-energy exciton state. The frequency-independent part of the emission intensity, the emission-line strength \( l^{0-\nu_t} \), is given by

\[
l^{0-\nu_t} = \mu^2 \sum_{\{\nu_n\}} |\langle \psi^{(\text{em})}|\hat{M}\prod_n |g_n; \nu_n\rangle|^2.
\]

Emission of a photon can leave the aggregate in all vibrationally excited (electronic ground) states \( \prod_n |g_n, \nu_n\rangle \) with a total of \( \nu_t = \sum \nu_n \) vibrational quanta. We have indicated this
Optical spectra and Stokes shift in double-stranded helical assemblies

constraint by the prime on the summation in eq 4.12. At non-zero temperature, emission does not originate only from the lowest-energy exciton state but also from higher-energy exciton states, due to thermal activation. The emission spectrum at non-zero temperature is obtained by an additional Boltzmann average over all thermally accessible excited states.

We have replaced in our calculations the Dirac delta function in eqs 4.7 and 4.11 by a narrow Gaussian line shape, with "homogeneous" line width \( \sigma_H \). We have taken \( \sigma_H \) to be small enough \((\sigma_H \approx 0.014 \text{ eV})\) to guarantee that the spectral broadening is dominated by the inhomogeneous disorder, but large enough to obtain smooth spectra.

### 4.3 Properties of the 0–0 and 0–1 emission lines

The emission-line strengths are obtained by inserting the expression for the wave function, eq 4.4, into eq 4.12. For the 0–0 and 0–1 line-strengths we find, respectively,

\[
\langle I^{0-0}_C \rangle = \sum_{\delta=x,y} \left| \sum_n \sum_{\tilde{\nu}} \mu_{n,\delta} f_{\tilde{\nu},0} c_{n,\tilde{\nu}}^{(em)} \right|^2, \quad (4.13)
\]

and

\[
\langle I^{0-1}_C \rangle = \sum_{\delta=x,y} \sum_n \left| \sum_{\tilde{\nu}} \mu_{n,\delta} f_{\tilde{\nu},1} c_{n,\tilde{\nu}}^{(em)} + \sum_{\tilde{\nu}'} \mu_{n',\delta} f_{\tilde{\nu}',0} c_{n',\tilde{\nu}',n,1}^{(em)} \right|^2, \quad (4.14)
\]

Here, \( f_{\tilde{\nu},\nu} \equiv \langle \tilde{\nu} | \nu \rangle \) is the overlap between the harmonic-oscillator eigenfunction with \( \tilde{\nu} \) quanta in the shifted excited-state nuclear potential and the eigenfunction with \( \nu \) quanta in the ground-state nuclear potential, and \( \mu_{n,\delta} \) is the projection of the tdm of molecule \( n \) along the \( \delta \)-axis (x-or y-axis). The 0–0 emission intensity depends only on one-particle coefficients, whereas the 0–1 emission intensity depends both on one-particle and two-particle coefficients.

Two-particle states play a very important role in emission. This is clearly illustrated in Figure 4.1, which shows emission spectra for a full two-particle basis set (solid black curve) and a basis set consisting of only one-particle states (red dashed curve). The spectra were calculated by averaging over \( 10^4 \) disorder configurations and the temperature was taken to be \( T = 278 \text{ K} \) (room temperature). The aggregate parameters are \( \omega_0 \pm 0 + D = 2.53 \text{ eV}, \omega_0 = 0.172 \text{ eV}, l_0 = 2.0 \text{ and } c = \infty \). Eliminating two-particle states from the basis set results in an increase of about a factor of 1.5 in the 0–1 emission intensity, whereas the 0–0 emission intensity (green dotted curve) is practically equal for both basis sets. The effect is more dramatic with increasing exciton coupling. In OPV3 herringbone lattices where \( W \) is of the order of 1 eV, the sideband emission increases about 20-fold when two-particle states are omitted.

Excluding two-particle contributions from eq 4.14 increases thus the 0–1 emission intensity, leading to the conclusion that destructive interference occurs between the contributions from one- and two-particle states.

By truncating our two-particle basis set to states in which the vibronic-vibrational separation is limited and comparing to full two-particle basis-set calculations, we concluded that it is
4.3 Properties of the 0–0 and 0–1 emission lines

Figure 4.1: Calculated emission spectrum \( S(\omega) \) at \( T = 278 \) K of OPV aggregates containing 20 H-bonded pairs for a two-particle (black solid curve) and a one-particle (red dashed curve) basis set. The 0–0 emission intensity (green dotted curve) is practically equal for both basis sets. We averaged over \( 10^4 \) disorder configurations to obtain these spectra. The aggregate parameters are \( \omega_{0-0} + D = 2.53 \) eV, \( \omega_0 = 0.172 \) eV, \( \sigma = 90 \) meV, \( l_0 = 2.0 \), and \( c = \infty \). The spectra are normalized such that the intensity of the 0–1 peak of the spectrum calculated with the two-particle basis set equals one.

The 0–1 line strength in eq 4.14 consists mainly of a "sum of squares" and therefore, apart from the aforementioned one- and two-particle interference in the summand, is largely incoherent. By contrast, each polarized component of the 0-0 line strength given by eq 4.13 consists of the square of a sum over the molecular transition dipole moments weighted by one-particle coefficients. The "square of a sum" construct makes the 0-0 emission coherent in origin and therefore far more sensitive to disorder \(^7,10\) than the sideband line strengths.\(^15\) For example, the 0–0 peak vanishes completely for single-stranded achiral aggregates (\( \phi = 0^\circ \)) at zero temperature without disorder (\( \sigma = 0 \)).\(^14,23\) This is the case for ideal H-aggregates, where the emitting exciton wave function is delocalized over the entire aggregate. Because the exciton wave function alternates in sign between consecutive chromophores, there is a complete destructive interference of the 0–0 tdm. Such destructive interference cannot occur for the sideband intensities and therefore these will never vanish by symmetry. However, the sideband intensities diminish rapidly with increasing exciton bandwidth.\(^19,22,24\)

Increasing disorder leads to localization of the emitting exciton and an increase of the 0–0 peak. This is illustrated in Figure 4.2a, where we show emission spectra at \( T = 278 \) K of double-stranded aggregates consisting of 40 H-bonded pairs. To vary the disorder we have...
changed the spatial correlation length \( l_0 \), while keeping \( \sigma \) constant. We have taken equal transition energies within each dimer \( (c = \infty) \). The emission spectra were calculated using eq 4.10 and were normalized to the 0–1 emission intensity. The aggregate parameters are given in the figure caption. We observe that the 0–0 emission intensity decreases monotonically with increasing \( l_0 \). The exciton wave function becomes more delocalized with increasing \( l_0 \) because it becomes more likely that the offset difference \( \Delta_n - \Delta_m \) between chromophores \( n \) and \( m \) is small compared to the excitonic coupling \( J_{nm} \) between these chromophores. In the limit \( l_0 \to \infty \) the 0–0 peak vanishes since in this limit there is no disorder within each individual aggregate. Figure 4.2a also shows that the relative side-band emission intensities are remarkably insensitive to the disorder. In Figure 4.2b we have varied the correlation strength \( c \) while keeping the spatial correlation length fixed to \( l_0 = 2.0 \). We see that the 0–0 emission intensity depends only very weakly on \( c \), whereas the spectra red-shift by about 30 meV in going from \( c = \infty \) to \( c = 0 \).

Figure 4.2c shows emission spectra for different aggregate lengths \( L \), ranging from 10 to 50 dimers, for a spatial correlation length \( l_0 = 2.0 \). This figure shows that the relative intensities of the side-band and the 0–0 emission are quite insensitive to \( L \). Hence, the ratio of the 0–0 to 0–1 emission intensities, \( S_R \), is a reliable probe for the disorder. An approximate expression for \( S_R \) is

\[
S_R \equiv \frac{\int d\omega S^{0-0}(\omega)}{\int d\omega S^{0-1}(\omega)} \approx \frac{S(\omega_{\text{peak}})}{S(\omega_{\text{peak}} - \omega_0)}. \tag{4.15}
\]

Here \( \omega_{\text{peak}} \) is the frequency associated with the maximum of the 0–0 emission peak. This approximate expression is only valid when the vibronic peaks are well-resolved. In Figure 4.3 we have plotted \( S_R \) as a function of \( L \) at \( T = 278 \) K for several values of \( l_0 \). We have considered both the case of equal \( (c = \infty) \) and uncorrelated \( (c = 0) \) transition energies within each dimer.
4.4 The two-strand exciton coherence functions

The ratio $S_R$ decreases when the intra-stack order is increased and is remarkably constant above a certain aggregate length. The degree of correlation between the transition energies within each dimer has only a small effect on $S_R$. In section 4.6 we will use $S_R$ to determine $\sigma$ and $l_0$ for OPV aggregates by comparing our calculated spectra to the measured absorption and emission spectra.

Although $S_R$ is quite insensitive to $L$, Figure 4.2c shows that the peak positions and their widths depend significantly on $L$. With increasing $L$ the peaks show a red-shift while their widths become smaller. This behavior also occurs when the disorder is increased (decreasing $l_0$, see Figure 4.2a). In section 4.5 we will discuss these phenomena in more detail and we will also investigate the effect of interstrand correlated disorder. But first we will relate the intensity of the 0–0 emission to the exciton coherence function. This will provide us with a better understanding of the independence of $S_R$ on $L$.

4.4 The two-strand exciton coherence functions

The independence of $S_R$ on the aggregate length $L$ can be understood by considering the exciton coherence function, as introduced in ref 10 for single-stranded aggregates. We consider double-stranded aggregates and therefore we introduce here the two-strand exciton coherence functions, the intrastrand coherence function and the interstrand coherence function. For the
\( \alpha \)-th exciton state, the intrastrand coherence function is defined as
\[
C_{\text{intra}}^{(\alpha)}(s) \equiv \sum_n \langle \psi^{(\alpha)} | B_n^\dagger B_{n+s} | \psi^{(\alpha)} \rangle + \sum_n \langle \psi^{(\alpha)} | B_{n+L}^\dagger B_{n+L+s} | \psi^{(\alpha)} \rangle,
\]
where the prime on the sum indicates that \( n \) and \( n + s \) are such that \( n, n + s \leq L \). The interstrand coherence function is defined as
\[
C_{\text{inter}}^{(\alpha)}(s) \equiv \sum_n \langle \psi^{(\alpha)} | B_n^\dagger B_{n+L+s} | \psi^{(\alpha)} \rangle + \sum_n \langle \psi^{(\alpha)} | B_{n+L}^\dagger B_{n+s} | \psi^{(\alpha)} \rangle.
\]
In these expressions \( B_n^\dagger \) is the exciton creation operator given by \( B_n^\dagger \equiv |n;0,0,...,0\rangle \langle g;0,0,...,0| \). The state vector \(|n;0,0,...,0\rangle\) represents a vibronic state with the \( n \)-th chromophore excited electronically and with all chromophores (including the \( n \)-th) in the vibrational ground state of the unshifted electronic ground-state potential. The state \(|g;0,0,...,0\rangle\) represents the aggregate electronic and vibrational ground state. We note that the operators \( B_n^\dagger \) and \( B_n \) are not pure electronic operators. Hence, \( \sum_n B_n^\dagger B_n \) is not the usual exciton-number operator, and \( C_{\text{intra}}^{(\alpha)}(0) \) and \( C_{\text{inter}}^{(\alpha)}(0) \) are in general not equal to unity\(^5\).

Averaging over all disorder configurations simplifies the above expressions to
\[
\langle C_{\text{intra}}^{(\alpha)}(s) \rangle_C = 2 \left( \sum_n \langle \psi^{(\alpha)} | B_n^\dagger B_{n+s} | \psi^{(\alpha)} \rangle \right)_C,
\]
and
\[
\langle C_{\text{inter}}^{(\alpha)}(s) \rangle_C = 2 \left( \sum_n \langle \psi^{(\alpha)} | B_n^\dagger B_{n+L+s} | \psi^{(\alpha)} \rangle \right)_C.
\]
If we insert the wave function eq 4.4 into eqs 4.18 and 4.19 we find
\[
\langle C_{\text{intra}}^{(\alpha)}(s) \rangle_C = 2 \sum_n \sum_{\tilde{\nu},\tilde{\nu}'} f_{\tilde{\nu},0}^* f_{\tilde{\nu}',0} \langle \psi^{(\alpha)} | C_{n,\tilde{\nu}}^{(\alpha)} C_{n+s,\tilde{\nu}'}^{(\alpha)} \rangle_c,
\]
and
\[
\langle C_{\text{inter}}^{(\alpha)}(s) \rangle_C = 2 \sum_n \sum_{\tilde{\nu},\tilde{\nu}'} f_{\tilde{\nu},0}^* f_{\tilde{\nu}',0} \langle \psi^{(\alpha)} | C_{n,\tilde{\nu}}^{(\alpha)} C_{n+L+s,\tilde{\nu}'}^{(\alpha)} \rangle_c,
\]
showing that \( \langle C_{\text{intra}}^{(\alpha)}(s) \rangle_C \) and \( \langle C_{\text{inter}}^{(\alpha)}(s) \rangle_C \) depend only on the one-particle coefficients of the \( \alpha \)-th exciton wave function.\(^7,10\)

Figure 4.4 shows the configurationally averaged coherence functions for the lowest-energy (emitting) exciton in an aggregate containing 20 H-bonded pairs, for several values of \( \sigma \), and for uncorrelated transition energies within each dimer. The intrastrand coherence function reflects the extent of delocalization of the lowest-energy (emitting) exciton along the strand that contains its “center-of-mass”, whereas the interstrand coherence function reflects the extent of delocalization of the emitting exciton over the other strand. We see that with decreasing disorder the exciton becomes more delocalized and that the coherence functions develop a phase

\(^5\)The expectation value of the usual exciton-number operator equals unity for every one-exciton state \(|\psi^{(\alpha)}\rangle\).
4.4 The two-strand exciton coherence functions

The two-strand exciton coherence functions

\[ L_{coh} = 0.8 \]
\[ L_{coh} = 3.0 \]
\[ L_{coh} = 9.5 \]

\[ \text{σ} = 90 \text{ meV} \]
\[ \text{σ} = 9 \text{ meV} \]
\[ \text{σ} = 0.9 \text{ meV} \]

**Figure 4.4:** Configurationally averaged intrastrand (a) and interstrand (b) coherence function for the emitting (lowest-energy) exciton in an aggregate containing 20 dimers. Note that the graphs have a different scale. The coherence functions are shown for several values of \( \sigma \). The transition energies within each dimer are uncorrelated (\( c = 0 \)) and the intrastrand correlation length is \( b_0 = 2.0 \). All other parameters are identical to those used in Figure 4.2.

 alternation that is characteristic of the lowest-energy exciton in an ideal H-aggregate. The coherence function covers practically the entire aggregate if disorder is absent (not shown here). For large disorder, the exciton is delocalized over only a few chromophores. In Figure 4.5 we show the coherence function for the emitting (lowest-energy) exciton, \( \langle C^{(em)}_{\text{intra}}(s) \rangle \), for \( \sigma = 90 \) meV and several values of \( b_0 \) in an aggregate containing 20 H-bonded pairs. We see that with increasing disorder (decreasing \( b_0 \)) the exciton becomes more localized. In the limit of extreme disorder, \( \langle C^{(em)}_{\text{intra}}(s) \rangle \) approaches \( \exp(-\lambda^2) \delta_{s0} \), and the exciton becomes localized on a single chromophore. The exponential factor \( \exp(-\lambda^2) \) indicates that the exciton is then fully relaxed to the minimum of the shifted excited-state nuclear potential with \( \tilde{\nu} = 0 \) vibrational quanta.

The value of the intrastrand coherence function at \( s = 0 \), \( \langle C^{(em)}_{\text{intra}}(0) \rangle \), contains information about the extent of the nuclear relaxation at the site of the vibronic excitation. In the limit of very weak excitonic coupling (\( W \ll \lambda^2 \omega_0 \)) it is straightforward to show that \( \langle C^{(em)}_{\text{intra}}(0) \rangle \) reduces to \( \exp(-\lambda^2) \). The exciton is then localized on a single chromophore and has fully relaxed in the shifted excited-state nuclear potential. This result does not depend on the strength of the disorder. Increasing excitonic coupling leads to a diminishing vibronic relaxation and this causes \( \langle C^{(em)}_{\text{intra}}(0) \rangle \) to increase beyond \( \exp(-\lambda^2) \). In the limit of strong excitonic coupling (\( W \gg \lambda^2 \omega_0, \sigma \)) we have \( \langle C^{(em)}_{\text{intra}}(0) \rangle = 1 \), which corresponds to a free exciton without accompanying nuclear relaxation.

When the disorder strength \( \sigma \) is smaller than the magnitude of the intradimer coupling \( |J_{\text{dim}}| = 7.5 \text{ meV} \), the exciton delocalizes over both strands. This can be observed in Figure 4.4b for the case of \( \sigma = 0.9 \) meV. The exciton is still mainly delocalized on the strand that
Figure 4.5: Configurationally averaged intrastrand coherence function for the emitting (lowest-energy) exciton in an aggregate containing 20 dimers, shown for $\sigma = 90$ meV and several values of $l_0$. The transition energies within each dimer are equal ($c = \infty$). All other parameters are identical to those used in Figure 4.2.

contains its center-of-mass, but the significant magnitude of the interstrand coherence function indicates that the exciton is also delocalized over the other strand (note that the scale of Figure 4.4a and b differ by a factor of 5). Delocalization over both strands is more evident for the case that the transition energies within each dimer are equal. In Figure 4.6 we show $\langle C_{\text{em}}(s) \rangle_C$ for $l_0 = 2.0$ and several values of the intra-dimer correlation strength $c$, in an aggregate of length $L = 20$. The interstrand coherence function is a copy of the intrastrand coherence function, but with a smaller magnitude (see Figure 4.5). The magnitudes of these coherence functions become equal when the transition energies within each dimer are equal ($c = \infty$). Within each strand the exciton is delocalized over only a few chromophores.

The 0–0 emission-line strength of the lowest-energy exciton state is related to the exciton coherence functions by

$$\langle I^{0-0} \rangle_C = \sum_s \langle C_{\text{intra}}(s) \rangle_C \cos(\phi s) + \sum_s \langle C_{\text{inter}}(s) \rangle_C \cos(\phi s).$$

(4.22)

This relationship can be established by comparing the definition of the 0–0 emission-line strength in eq 4.12 with the definitions of the intrastrand and interstrand coherence function in eq 4.16 and eq 4.17, respectively. Equation 4.22 is a generalization of the single-strand relationship derived in ref 7 and enables us to understand the decrease of the 0–0 emission intensity with increasing order in terms of the coherence functions for the emitting exciton. With increasing order, the width of the coherence functions increases. This leads to a more effective cancelation of the positive and negative terms in the sums in eq 4.22, resulting in a decreased 0–0 emission
4.4 The two-strand exciton coherence functions

Figure 4.6: Configurationally averaged interstrand coherence function for the emitting (lowest-energy) exciton in an aggregate containing 20 dimers, shown for $\sigma = 90$ meV, $l_0 = 2.0$, and several values of $c$. All other parameters are identical to those used in Figure 4.2.

Intensity, as we have observed in Figure 4.2 and Figure 4.3. We have also seen that for $\sigma = 90$ meV the $\langle C_{\text{inter}}^{(em)}(s)\rangle_c$ is zero when the transition energies within each dimer are uncorrelated ($c = 0$). In that case, eq 4.22 contains only a contribution from $\langle C_{\text{intra}}^{(em)}(s)\rangle_c$, explaining why the peak ratio $S_R$ is lower for $c = 0$, see Figure 4.3.

To explain the insensitivity of $S_R$ to the aggregate size $L$, we introduce the coherence length of the emitting exciton, $L_{\text{coh}}$, which is a measure of the spatial extent of the oscillations in the intrastrand coherence function $\langle C_{\text{intra}}^{(em)}(s)\rangle_c$. The coherence length can be defined in different ways (see ref 10), but here we take the coherence length $L_{\text{coh}}$ (in units of the separation between consecutive dimers) as

$$L_{\text{coh}} \equiv N_{\text{coh}} - 1,$$

with the coherence number $N_{\text{coh}}$ defined as

$$N_{\text{coh}} \equiv \frac{1}{\langle C_{\text{intra}}^{(em)}(0)\rangle_c} \sum_{s=-N+1}^{N-1} \left| \langle C_{\text{intra}}^{(em)}(s)\rangle_c \right| .$$

For the intrastrand coherence functions shown in Figure 4.4a, the coherence length varies from $L_{\text{coh}} = 0.8$ when $\sigma = 90$ meV, up to $L_{\text{coh}} = 9.5$ when $\sigma = 0.9$ meV. In Figure 4.5 we show $\langle C_{\text{intra}}^{(em)}(s)\rangle_c$ for varying $l_0$. The coherence length varies from $L_{\text{coh}} = 0.6$ when $l_0 = 0$, up to $L_{\text{coh}} = 1.2$ when $l_0 = 10$. We have found that the coherence functions practically do not change with aggregate size $L$ if $L$ is much larger than $L_{\text{coh}}$, accounting for the independence of $S_R$ on $L$ (see the inset of Figure 4.3).

The results presented in the previous section, and in the remainder of this chapter, are obtained for $T = 278$ K. In that case emission occurs from a Boltzmann distribution over all
thermally accessible excited states, and not only from the lowest-energy exciton state that we studied with the coherence function. However, because at $T = 278$ K the lowest-energy exciton state still yields the dominant contribution to the emission, the qualitative conclusions drawn from our study of the exciton coherence function remain valid.

4.5 Aggregate-length dependent Stokes shift and line-width narrowing

We observed in Figure 4.2 that with increasing aggregate length $L$ the emission spectra exhibit a red-shift, while the emission lines become narrower. Since we assume that emission takes place from a Boltzmann distribution over the lowest-energy exciton states, the increasing red-shift is due to an enhanced probability that an exciton finds chromophores with very low transition energies. To investigate this further we consider an aggregate consisting of $N = 2L$ chromophores with transition energies taken from the Gaussian distribution with standard deviation $\sigma$. We take the transition energies within each H-bonded pair equal and we assume that emission takes place from the lowest-energy exciton state. To estimate the energy of this state, we neglect the excitonic coupling. In that case, emission takes place from the lowest-energy chromophore in the set $[\Delta_1, \Delta_2, ..., \Delta_N]$. The emission-line shape for each vibronic peak in the fluorescence spectra should then reflect the probability distribution, $L(\Delta)$, to find $\Delta$ as the lowest value in this set. If $P(\Delta_1, ..., \Delta_N)$ is the generally correlated distribution function in eq 4.5, then the distribution $L(\Delta)$ can be found by integrating $P$ over all configurations in which $N − 1$ transition energies are larger than $\Delta$, \(^{25}\)

$$L(\Delta) = N\int_{\Delta}^{\infty} d\Delta_2 \int_{\Delta}^{\infty} d\Delta_3 \cdots \int_{\Delta}^{\infty} d\Delta_N P(\Delta, \Delta_2, \Delta_3, ..., \Delta_N).$$

(4.25)

The factor $N$ in eq 4.25 takes into account the equal probability for each element in the set $[\Delta_1, \Delta_2, ..., \Delta_N]$ to have the lowest value. If there is no spatial correlation ($l_0 = 0$), then $P(\Delta_1, ..., \Delta_N)$ is the product of $N$ Gaussian distribution functions $G(\Delta_N)$ with standard deviation $\sigma$, and $L(\Delta)$ is given by

$$L(\Delta) = NG(\Delta) \left[ \int_{\Delta}^{\infty} G(\Delta') d\Delta' \right]^{N-1} = NG(\Delta) \frac{\text{erfc}(\Delta/\sqrt{2}\sigma)^{N-1}}{2^{N-1}},$$

(4.26)

where erfc($x$) is the complementary error function. We show this distribution $L(\Delta)$ in Figure 4.7 for various values of $N$. It is clear from Figure 4.7 that multiplication of $G(\Delta)$ by the error function results both in a red-shift and a line-width narrowing with increasing $N$.

Figure 4.8 shows how the 0–1 peak position, $E_{0-1}$, and its line width, $\Gamma$, change with the aggregate length $L$ and the spatial correlation length $l_0$, for the case that the transition energies within each H-bonded pair are taken equal. The line width $\Gamma$ is defined as the full width at $1/e$ of the maximum of the 0–1 peak. We have plotted the red-shift and width of the 0–1 emission line, since this emission line has the highest intensity and is therefore the least affected by overlap with other emission lines. The peak position and the line width are
4.5 Aggregate-length dependent Stokes shift and line-width narrowing

Figure 4.7: The distribution function $L(\Delta)$ of eq 4.26 to find $\Delta$ as lowest value in a set of $N$ random numbers drawn from a Gaussian distribution with standard deviation $\sigma$.

calculated by evaluating the full spectrum in eq 4.10 numerically using the eigenstates and eigenenergies obtained by diagonalizing the Hamiltonian eq 4.1. We have averaged over $10^4$ disorder configurations, which is sufficient to suppress numerical noise to less than 0.005 eV. The dashed lines in Figure 4.8 correspond to the maximum and full width of the distribution $L(\omega - \omega_{0-0} - D + \omega_0)$ of eq 4.26.

Figure 4.8a shows that $E^{0-1}$ depends strongly both on $L$ and $l_0$. The peak position $E^{0-1}$ red-shifts monotonically with $L$ for the reason discussed above. For fixed $L$, $E^{0-1}$ also red-shifts with decreasing $l_0$, because a decrease of $l_0$ effectively corresponds to larger disorder. Conversely, when $l_0$ is increased, groups of molecules with similar energies form. This means that the aggregate length $L$ for which the same lowest-energy exciton state is obtained as with $l_0 = 0$ increases. Figure 4.8b shows that the line width $\Gamma$, which is approximately the same for all emission peaks in the fluorescence, decreases with increasing aggregate length $L$ and decreasing $l_0$. This behavior is predicted by the distribution $L(\Delta)$, see Figure 4.7 and the dashed curves in Figure 4.8. The distribution $L(\Delta)$ predicts a smaller line width for the emission lines because it corresponds to emission from the lowest-energy chromophore. At non-zero temperature, emission also takes place from thermally excited states, resulting in thermal broadening of the emission lines. Although thermal broadening is the main cause, the emission lines are also broadened due to the homogeneous broadening in the numerical calculations when the delta function in eq 4.11 is replaced with a Gaussian with standard deviation $\sigma_H \approx 0.014$ eV.

Figure 4.9 shows how the 0–1 peak position changes with aggregate length $L$ for different correlation strengths $c$ between the transition energies within each H-bonded pair. We have used two values of the spatial correlation length, $l_0 = 2$ and 10. For fixed $L$ and $l_0$, $E^{0-1}$ red-shifts with decreasing $c$, i.e. decreasing correlation. The effect is quite dramatic, since for the curves with $l_0 = 2$ roughly the same red-shift is obtained for $c = \infty$ at a given aggregate
Figure 4.8: The 0–1 peak position (a) and line width (b) as a function of aggregate length $L$ at $T = 278$ K for several values of the spatial correlation length $l_0$. The aggregate parameters are $\omega_{0-0} + D = 2.53$ eV, $\omega_0 = 0.172$ eV, $\sigma = 90$ meV, and the transition energies within each dimer are taken equal ($c = \infty$). We averaged over $10^4$ disorder configurations. The dashed lines correspond to the lowest-energy exciton distribution $L(\Delta')$ given by eq 4.26, with $\Delta' = \omega - \omega_{0-0} - D + \omega_0$.

Interstrand correlation has thus a dramatic effect on the dependence of the Stokes shift on aggregate length. The single-stranded model of ref 10 does not take into account this correlation and therefore cannot describe this effect.

### 4.6 Comparison with experiment

Figure 4.10 shows the measured absorption (open triangles) and emission (open dots) spectra of OPV4 aggregates at $T = 278$ K. At this temperature, the solution consists mainly of long helical aggregates. These experimental spectra were theoretically modeled in ref 10. The calculations in that work were based on aggregates containing $L = 20$ chromophoric units, with each unit representing an H-bonded pair of OPV molecules (equivalent to our case with $c = \infty$). The measured absorption was used to determine the transition energy $\omega_{0-0} + D$ and the disorder strength $\sigma$. Since the ratio between the 0–0 and 0–1 emission intensities, $S_R$, is very sensitive to disorder, the spatial correlation length $l_0$ was extracted from the measured value of $S_R$ (the absorption spectrum is practically independent of $l_0$). A fair agreement with the experimental spectra was obtained with the parameters $\omega_{0-0} + D = 2.53$ eV, $\sigma = 85$ meV, and $l_0 = 4.5$. However, the theoretically obtained Stokes shift was smaller than the measured

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*Note that the $\sigma$ defined in ref 10 is $\sqrt{2}$ times the $\sigma$ used in eq 4.6.*
4.6 Comparison with experiment

Figure 4.9: The 0–1 peak position as a function of aggregate length \( L \) at \( T = 278 \) K for spatial correlation lengths \( l_0 = 2 \) and 10. The correlations within each dimer varies from uncorrelated \( (c = 0) \) to equal \( (c = \infty) \) transition energies. All other parameters are the same as those used in Figure 4.8.

value by about 50 meV.

As we have seen in the previous section, the Stokes shift depends on the aggregate size and on the disorder strength. Therefore, we varied the aggregate size in our calculations. In addition, we properly modeled the OPV helices as double-stranded aggregates. The absorption was modeled by an aggregate containing \( L = 20 \) H-bonded pairs and we found as best fit parameters almost the same values as in ref 10: \( \omega_{0,0} + D = 2.53 \) eV and \( \sigma = 90 \) meV, the latter value being only 5 meV higher than in ref 10. Both the spatial correlation length along the aggregate \( l_0 \) and the parameter \( c \) for the correlation strength between the excitation energies within each dimer have a negligible effect on the absorption spectrum. Figure 4.10 shows the calculated absorption spectrum (red line). The disagreement with experiment in the high-energy region is due to excited states that are not included in the theory. We found that by simply increasing the aggregate size in the calculations to reproduce the measured Stokes shift, while assuming equal transition energies within each dimer and using the best fit value for the spatial correlation length \( l_0 = 4.5 \) as obtained in ref 10, a ratio of \( S_R \) is obtained that is slightly lower than that found in experiment.

A higher ratio \( S_R \) can be achieved by decreasing \( l_0 \). By decreasing \( l_0 \) to 2.0 and still assuming equal transition energies within each dimer, we modeled the emission spectrum with an aggregate containing 35 H-bonded pairs. Figure 4.10 shows the resulting emission spectrum (red line). The calculated spectrum now reproduces both the experimental ratio \( S_R \) and the Stokes shift. However, the width of the emission lines is still not well reproduced. We have investigated whether a larger disorder strength results in a better reproduction of these line
Figure 4.10: Experimental absorption ($A(\omega)$, triangles) and emission ($S(\omega)$, circles) spectra of an OPV4 solution in dodecane ([OPV4] = 2 \cdot 10^{-5} M) at $T = 278$ K, reproduced from ref 10, and our calculated spectra (red lines). The calculated emission spectrum is based on an aggregate containing 35 H-bonded pairs and the parameters used are $\sigma = 0.090$ eV, $\omega_{0-0} + D = 2.53$ eV, $\omega_0 = 0.172$ eV, and $l_0 = 2.0$. The transition energies within each dimer are taken equal ($c = \infty$). We used an aggregate containing 20 H-bonded pairs to calculate the absorption spectrum, with all other parameters the same as those used for emission.

widths. A larger disorder strength indeed broadens the emission lines but we were not able to obtain a reasonable agreement with the emission-line shape at the high-energy end of the spectrum.

We checked that the intrastrand coherence function shown in Figure 4.5, corresponding to 20 H-bonded pairs, practically does not change if it is calculated for an aggregate containing 35 H-bonded pairs. The exciton coherence function enables us to determine the coherence length $L_{coh}$ of the emitting exciton (eq 4.23). We find that $L_{coh}$ is only one lattice spacing along the stacking direction (see Figure 4.5). The coherence length measures the spatial extent of the oscillations in the intrastrand coherence function. This indicates that the exciton is delocalized over not more than two neighboring OPV molecules along a strand, which is in agreement with the results obtained in ref 10 with the parameters $\sigma = 85$ meV and $l_0 = 4.5$.

At a temperature of 278 K, the solution consists in general of aggregates containing hundreds of H-bonded pairs. Here, we find that with an aggregate containing 35 H-bonded pairs the measured Stokes shift can be reproduced. With shorter aggregates, and assuming that the transition energies with each dimer are equal, the measured Stokes shift cannot be reproduced, since the probability of finding a low-energy exciton state is reduced. With longer aggregates the Stokes shift exceeds the measured value. The reason why the measured Stokes shift cannot be reproduced for very long aggregates is that the excitons, created at a high energy by the
laser pulse, cannot relax to the lowest-energy exciton states within their lifetime. Therefore, the aggregate size of 35 H-bonded pairs, which corresponds to about 13 nm, should be a measure for the exciton diffusion length. However, we must note that we are not able to conclude from our comparison with experiment whether the transition energies within each dimer are equal or uncorrelated. The measured Stokes shift can also be reproduced with an aggregate containing about 17 H-bonded pairs, corresponding to about 6 nm, when the energies within each dimer are uncorrelated. Since these are the two extremes, we conclude from our analysis that the exciton diffusion length is in the range 6-13 nm. In the previous chapter we estimated the exciton diffusion length to be about 6 nm (17 H-bonded pairs) by modeling the H-bonded pairs as single chromophores ($c = \infty$). The main reason why we obtained this lower value is that the average transition energy of the chromophores in the aggregates was estimated to be lower ($\omega_0 - \omega_1 + D = 2.48 \text{ eV}$). In ref 10, the measured Stokes shift was not reproduced and accordingly the exciton diffusion length could not be estimated. We have seen that the Stokes shift, and with that the exciton diffusion length, depends strongly on the interstrand correlation. This correlation is not included in the single-stranded model of ref 10.

Although we are able to reproduce the measured Stokes shift, the ratio $S_R$, and the position of the emission lines, we are not able to reproduce the emission-line widths accurately. Apart from this, the intensity of the calculated 0–2 emission line is significantly lower than observed in experiment. We suggest that the discrepancy is due to our assumption of a Boltzmann distribution for the emitting states, while using an aggregate length that is much shorter than the actual lengths in the experiment. In a fluorescence experiment, a high-energy exciton is created on the aggregate by a laser pulse. During its relaxation, the exciton will diffuse to low-energy states in different regions of the aggregates. The experimental Stokes shift is reproduced with an aggregate length of 35 (or 17) H-bonded pairs from which we concluded that this length is the average distance covered by the excitons. However, occasionally the exciton might diffuse much further and find states with very low energy within the long aggregate. The occasional emission from these states with very low energy could be responsible for the higher 0–2 emission peak observed in experiment. Moreover, this would also broaden the emission-line widths. Up to now this is a speculative explanation. In order to demonstrate its possible consequence, we have added the original calculated emission spectrum of Figure 4.10 and the same spectrum but red-shifted over 0.1 eV, with a weight ratio 2:1. Figure 4.11 shows the resulting spectrum, which agrees surprisingly well with the experimental emission spectrum. In particular, the intensities of the 0–2 emission line now agree very well. Of course, this simple addition of the original and shifted spectrum is presently an ad hoc procedure to account for exciton migration. It would be very interesting to extend the approach followed by Beljonne and collaborators to study exciton diffusion along an OPV stack for a tight-binding Hamiltonian to the disordered Holstein model and to see if this results in better agreement with experiment.

An alternative explanation for the higher 0–2 emission peak in experiment and the broader emission lines, as compared to our calculations, could be the clustering of helical aggregates. At low temperature ($T = 278 \text{ K}$) the helical aggregates are very long and clustering of the helical aggregates cannot be ruled out. In that case we expect the emission spectrum to be composed of single-aggregate emission and emission from clustered aggregates. The latter must be further red-shifted because excitons diffuse not only along the long aggregates but
Figure 4.11: The experimental emission spectra (circles) of an OPV4 solution in dodecane (ref 10) and our calculated spectra. The red dashed line is the original calculated spectrum in Figure 4.10, whereas the green dotted line is the same spectrum but red-shifted over 0.1 eV. The blue full line is the sum of these spectra with a weight ratio of 2:1.

occasionally they can also hop to adjacent aggregates, making it easier for these excitons to find low-energy states. This leads to the superposition of at least two emission spectra, of which one is significantly red-shifted. Finally, due to thermal fluctuations it is possible that the aggregates are not perfectly helical (see chapter 3). In that case there are regions within the aggregates where the dimers do not have fixed orientations with respect to each other. This possibly results in regions with more disorder, which increases the probability of low-energy trap emission.

4.7 Conclusions and outlook

We have studied the emission spectra of helical OPV4 aggregates using a disordered Holstein Hamiltonian, with spatially correlated disorder in the chromophore transition energies. The emission spectra are characterized by a clear vibronic progression. Whereas the coherent 0–0 emission is very sensitive to disorder, the sideband emission is far less so. This property makes the ratio of the 0–0 and 0–1 emission peak intensities, $S_R$, a reliable probe for disorder. The sensitivity of the 0–0 emission intensity to disorder derives from the unique nature of this emission line in molecular aggregates: it depends entirely on the coherence of the emitting exciton. Moreover, the ratio $S_R$ is also very insensitive to the aggregate length, because the coherence size of the emitting exciton is in general much smaller than the aggregate size. We have found only a weak dependence of the ratio $S_R$ on the degree of correlation between the transition energies within each dimer.
We have found that with increasing aggregate length the emission spectra red-shift while the emission lines become narrower. Since we assume that emission takes place from a Boltzmann distribution of the lowest-energy excited states, this increasing red-shift with increasing aggregate size (and with increasing disorder) is due to an enhanced probability that an exciton finds a state with very low transition energy. We have found that the degree of correlation between the transition energies within each dimer has a large effect on the red-shift of the emission spectra. The same red-shift can be achieved with about half the aggregate length for the case that these energies are uncorrelated, as compared to the case of equal transition energies.

We have compared our calculations to experiment and we were able to reproduce the measured Stokes shift and the ratio $S_R$. From this comparison we were not able to conclude whether the transition energies within each dimer are equal or uncorrelated. The experimental Stokes shift is reproduced by our calculations for an aggregate containing 17 (uncorrelated energies) and 35 (equal energies) H-bonded pairs, corresponding to lengths of about 6 nm and 13 nm, respectively. We are unable to reproduce the Stokes shift with aggregates of shorter lengths, since the probability of finding low-energy states is then reduced. A too large Stokes shift is obtained with longer aggregates and we suggest that in longer aggregates the excitons are not able to relax to the lowest-energy states within their lifetime. Therefore, we interpret the values of 17 (6 nm) and 35 (13 nm) H-bonded pairs as a measure for the exciton diffusion length. Hence, we suggest that this diffusion length is in the range 6-13 nm. The coherence length of the emitting exciton was obtained from the exciton coherence function and we conclude that the exciton is delocalized over not more than two neighboring OPV molecules along a strand. On the basis of these results we suggest that the exciton migration is an incoherent diffusive process between small coherent domains.

References


Optical spectra and Stokes shift in double-stranded helical assemblies


Chapter 5

Dynamics of exciton-polarons in helical supramolecular assemblies

We study the dynamics of excitations in helical π-stacked assemblies of chiral oligo(p-phenylene-vinylene) derivatives (OPV). Excitations in these assemblies are vibrationally dressed excitons, or exciton-polarons, due to a strong coupling of the excitons to a high-energy intramolecular vibration. We develop a theory in which transitions between exciton states are assumed to occur by weak coupling of the excitons to low-energy acoustic phonons of the solvent and/or the assembly. The evolution in time of an excitation is obtained by solving a Pauli master equation. Our theory is able to reproduce the experimental polarization anisotropy decay in OPV4 aggregates. We study the migration of excitons along the helical assemblies by evaluating their mean squared displacement. We find that excitons cover a distance of about 4 nm within the first 20 ps after a high-energy excitation while relaxing to lower energy states, followed by a more diffusion-like motion at later times. From our analysis we estimate that the exciton diffusion length is about 9 nm. By analyzing the changes in the emission spectral line shapes with time, we find that the emission spectra exhibit a dynamic Stokes shift and that the 0–0 emission peak diminishes with time relative to the sideband emission.*

*Manuscript in preparation
5.1 Introduction

Organic $\pi$-conjugated materials are nowadays a well-established class of functional materials and have great potential as active components in several optoelectronic devices such as organic field-effect transistors,\textsuperscript{1,2} light-emitting diodes,\textsuperscript{3,4} photovoltaic cells,\textsuperscript{5,6} and sensors.\textsuperscript{7,8} An indispensable ingredient for designing and optimizing high-performance organic-based optoelectronic devices is a good understanding of the complicated nature of energy and charge transport in organic materials. Whether considering energy or charge transport, organic materials have an important feature that discerns them from their inorganic counterparts: they are soft, meaning that the presence of a charge or electronic excitation induces a significant rearrangement of the nuclei in the participating molecules via non-adiabatic electron-phonon coupling.\textsuperscript{9,10} This leads to a strong enhancement of the effective mass and a narrowing of the bandwidth, which results in localization of charges and electronic excitations. Therefore, a detailed understanding of the coupling between electronic excitations and the nuclear framework over which they travel is crucial for a proper understanding of energy and charge transport in organic materials. This requires a theoretical approach that surpasses the common Born-Oppenheimer approximation and treats electron-phonon coupling fully quantum-mechanically.

An excellent system for studying the transport of electronic excitations in organic materials are chiral stacks of $\pi$-conjugated oligo($p$-phenylene-vinylene) (OPV) derivatives.\textsuperscript{11,12} Figure 1.3 features a schematic representation of the OPV4 molecules. OPV molecules are functionalized on one end with an ureidotriazine group that enables a molecule to engage in four hydrogen bonds with another molecule. These H-bonded pairs form the rungs of the helical OPV assemblies. Their well-defined architecture make OPV helices ideal systems for testing theoretical models of energy transport. A clear vibronic progression in the optical spectra of OPV helices, in particular UV/vis absorption, fluorescence and circular dichroism spectra, reveals a strong coupling of excitations to a symmetric ring breathing/vinyl stretching mode with an energy of $0.17$ eV ($\sim 1400$ cm$^{-1}$).\textsuperscript{12,13} Excitations in OPV helices are thus vibrationally dressed excitons or exciton-polarons. The spectral line shapes of the absorption, emission, and circular dichroism spectra were successfully reproduced in ref 13 by employing the Holstein Hamiltonian with spatially correlated disorder. This Hamiltonian treats excitonic coupling, energetic disorder, and exciton-phonon coupling on equal footing and thus surpasses the common Born-Oppenheimer approximation. In the previous chapter, we have used the disordered Holstein Hamiltonian to analyze the Stokes-shift in the optical spectra and the coherence size of the emitting exciton. Our analysis suggested that exciton migration along helical OPV assemblies is a diffusive process between small coherent domains.

Several experimental studies have demonstrated that helical OPV assemblies are relatively efficient pathways for exciton transport. Time-resolved spectroscopy studies on OPV helices have shown fast diffusion of excitons in these supramolecular assemblies, leading to exciton trapping and fluorescence depolarization.\textsuperscript{14,15} Femtosecond transient absorption spectroscopy was used to demonstrate that bimolecular exciton annihilation dynamics in OPV helices is dominated by a combination of exciton diffusion over nearest-neighbor distances and resonance energy transfer over long distances.\textsuperscript{16} That intermolecular ordering has a substantial influence on the exciton dynamics was shown by comparing the optical properties of OPV assemblies with
In order to theoretically study the dynamics of excitons in OPV helices we will employ a Pauli master equation to describe transitions between exciton eigenstates of the Holstein Hamiltonian. We assume that the transition of excitons is induced by low energy acoustic phonons in the solvent and/or in the aggregate. A similar approach as will be developed in this chapter was very successful in describing the relaxation of Frenkel excitons in linear J-aggregates of cyanine dyes.\textsuperscript{19–21} Beljonne and coworkers also used a Pauli master equation approach to analyze the fluorescence anisotropy decay in OPV aggregates. They showed that the experimental fluorescence anisotropy decay could only be reproduced theoretically by assuming Förster transfer\textsuperscript{22} from localized donors to delocalized acceptors.\textsuperscript{23} Our approach consistently considers both the donors and acceptors as delocalized entities, but, more importantly, also takes into account polaronic effects due to strong coupling of the exciton to intramolecular vibrations. This exciton-phonon coupling was neglected in ref \textsuperscript{23} and their approach is therefore incapable to properly account for changes in the emission line shapes of OPV helices with time.

Our theory for the dynamics of exciton-polarons in helical OPV assemblies includes strong coupling of the exciton to intramolecular vibrations as well as the weak coupling to acoustic phonons in the solvent and/or the aggregate that induces transitions between exciton states. The inclusion of strong exciton-phonon coupling makes our theory an extension of the approach of Knoester and coworkers\textsuperscript{19–21,24} in the sense that we take into account polaronic effects. Our theory is able to reproduce the experimental polarization anisotropy decay in OPV4 aggregates and enables us to study the migration of exciton-polarons along the helical assemblies, showing that exciton-polarons diffuse significantly slower than ‘free’ excitons. We will calculate emission spectral line shapes as a function of time, showing that the relaxation of excitons results in a dynamic Stokes-shift of the emission lines and that the intensity of the 0–0 emission peak diminishes with time relatively to the sideband emission. Experimentally, a dynamic Stokes-shift and diminishing 0–0 emission intensity have been observed in thin films of polythiophene (PT) derivatives.\textsuperscript{25} This system is similar to OPV helices in the sense that the photophysics of thin PT films is interpreted in terms of the disordered Holstein model as well.\textsuperscript{9,26}

The outline of this chapter is as follows. First, in section 5.2, we concisely review the disordered Holstein model. In section 5.3 we introduce the Pauli master equation to study exciton dynamics in one-dimensional helical aggregates. In section 5.4 we apply our theory to helical OPV4 aggregates, and we study the polarization anisotropy decay and the migration of exciton-polarons along the helical stacks. We study the dynamic Stokes-shift and 0–0 emission in section 5.5. Finally, in section 5.6 we state our main conclusions and we give an outlook.

5.2 Disordered Holstein model for OPV helices

Figure 1.3 features a schematic representation of the helical OPV4 aggregates. Each rung of the helical assembly is formed by an H-bonded pair of OPV molecules. The intermolecular distance $d_i$ and angle $\phi$ between two consecutive H-bonded pairs along the stacks are $d_i = 0.375$ nm and
The photophysics of OPV aggregates is described with the disordered Holstein model. We introduced this model in the previous chapter to study the optical spectra of the helical assemblies as double-stranded aggregates. In the present chapter we follow ref 13 and associate each H-bonded pair with a single chromophoric unit. This means that we assume the transition energies of the two molecules forming an H-bonded pair to be equal.

We consider each chromophore within an aggregate as a two-level system with an electronic ground state $|g\rangle$ and an energetically lowest-lying photoexcited state $|e\rangle$. The energy needed for exciting a chromophore from its electronic ground state to its first optically allowed excited state is the so-called transition energy. For the $n$-th chromophore the transition energy is $\omega_{0-0} + D + \Delta_n$, where $\omega_{0-0}$ is the gas-phase 0–0 transition energy and $D$ is the gas–to–crystal shift due to non-resonant interactions. The randomly assigned transition energy offsets $\Delta_n$ account for fluctuations in transition energies along the aggregates. These fluctuations are caused by thermally induced deformations of each chromophore (e.g. by bending and twisting), fluctuations of the conformations of the side groups of the chromophores, and by randomness in the direct environment of the chromophores because of the presence of the solvent. We assume that the chromophore transition energies are distributed randomly, but with spatial correlation. Following ref 13, we draw the transition energy offsets $\Delta_n$ from a joint Gaussian distribution:

$$P(\Delta_1, ..., \Delta_N) = \left[\frac{1}{2\pi}\right]^N \frac{1}{\sqrt{\det A}} \exp\left[-\frac{1}{2} \sum_{n,m=1}^{N} (A^{-1})_{nm} \Delta_n \Delta_m\right],$$

(5.1)

where $(A^{-1})_{nm}$ is the $nm$-th element of the inverse covariance matrix. The matrix elements of the covariance matrix are given by $A_{nm} \equiv \sigma^2 \exp(-|n - m|/l_0)$, with $\sigma$ the standard deviation of the Gaussian distribution and $l_0$ the spatial correlation length in units of the lattice spacing. This form was originally used by Knapp in a study of the line shapes of $J$-aggregates.

The localizing effect of energetic disorder is balanced against the delocalizing effect of excitonic coupling between chromophores. For the OPV4 aggregates, the excitonic coupling between chromophores $n$ and $m$, $J_{nm}$, has been evaluated in refs 23 and 13 by combining a coupled cluster single and double (CCSD) approach to the INDO Hamiltonian on the basis of model geometric structures. The nearest-neighbor coupling between superimposed molecules for $\phi = 14^\circ$ was found to be about 40 meV and the coupling between two chromophores within an H-bonded pair, $J_{dim}$, was found to be only $-7.5$ meV. Hence, the calculated intrastrand coupling is much larger than the coupling between the strands.

Each chromophore couples to a high-energy intramolecular symmetric ring breathing/vinyl stretching vibrational mode with energy $\omega_0 = 0.172$ eV ($\sim 1400$ cm$^{-1}$) and Huang-Rhys (HR) factor $\lambda^2$. The Huang-Rhys factor is a measure for the shift in the equilibrium configuration of the ground and excited state nuclear arrangements. We use a Huang-Rhys factor of $\lambda^2 = 1.2$. This value, together with the cubic frequency dependence of the emission rate, yields roughly equal single-molecule 0–0 and 0–1 emission peak intensities, as is found for OPV4 molecules in solution. We treat this vibrational mode within the linear exciton-phonon coupling approximation. This mode is responsible for the formation of exciton-polarons, which are also called neutral polarons.\footnote{Note that in ref 13 a $\sigma$ was defined that is $\sqrt{2}$ times the $\sigma$ used in eq 5.1.}
We now have all the ingredients to write down the aggregate Hamiltonian that includes disorder in the transition energies, excitonic coupling between chromophores, and the above-mentioned exciton-phonon coupling. Within a representation in which one chromophore is excited, the Hamiltonian is given by

\[ H = \omega_0 \sum_{n=1}^{N} b_n^\dagger b_n + \omega_0 \lambda \sum_{n=1}^{N} (b_n^\dagger + b_n) |n\rangle \langle n| + \sum_{n=1}^{N} \sum_{m=1}^{N} (\Delta_m \delta_{nm} + J_{nm}) |m\rangle \langle n| + \omega_{0-0} + D + \lambda^2 \omega_0, \tag{5.2} \]

where we have taken \( \hbar = 1 \). The first term in this Hamiltonian represents the energy due to the high-energy vibrational mode and the second term describes the linear exciton-phonon coupling associated with this mode. \( b_n^\dagger \) and \( b_n \) are the creation and annihilation operator, respectively, for vibrational quanta within the harmonic ground-state nuclear potential of the \( n \)-th chromophore.

In the pure electronic state \( |n\rangle \) the \( n \)-th chromophore is electronically excited while all other chromophores remain in the electronic ground state, \( |n\rangle \equiv |e_n\rangle \prod_{m \neq n} |g_m\rangle \). Originally, the Hamiltonian in eq 5.2 (without disorder) was used by Holstein to study charged polaron motion in one-dimensional molecular crystals.\(^{29}\)

We use the two-particle approximation (TPA) to represent the eigenstates of the disordered Holstein Hamiltonian.\(^ {30,31}\) Within this approximation, the \( \alpha \)-th eigenstate of \( H \) is expanded as

\[ |\psi^{(\alpha)}\rangle = \sum_{n,\tilde{\nu}} c_{n,\tilde{\nu}}^{(\alpha)} |n, \tilde{\nu}\rangle + \sum_{n,\tilde{\nu}} \sum_{n',\nu'} c_{n,\tilde{\nu},n',\nu'}^{(\alpha)} |n, \tilde{\nu}; n', \nu'\rangle. \tag{5.3} \]

The first term of this expansion represents the one-particle states. A one-particle state \( |n, \tilde{\nu}\rangle \) consists of a vibronic (both electronic and vibrational) excitation at chromophore \( n \) containing \( \tilde{\nu} \) vibrational quanta in the shifted excited state nuclear potential, while all other chromophores remain electronically and vibrationally unexcited. The second term represents the two-particle states. In addition to a vibronic excitation at chromophore \( n \), a two-particle state \( |n, \tilde{\nu}; n', \nu'\rangle \) has a vibrational excitation at chromophore \( n' \) containing \( \nu' \) vibrational quanta in the ground state nuclear potential (\( \nu' \geq 1 \)). Figure 1.10 features the two excitation types. The two-particle approximation is highly accurate in the intermediate coupling regime that is appropriate for OPV helices.\(^ {31}\) In this regime the vibrational energy \( \omega_0 \), the nuclear relaxation energy \( \lambda^2 \omega_0 \) and the free exciton bandwidth, \( W \), are all comparable in magnitude. The free exciton bandwidth, \( W \), is the energy difference between the highest-energy and lowest-energy exciton when disorder and electron-phonon coupling are absent. For example, \( W = 4J_0 \) in a long linear single-stranded aggregate with only nearest-neighbor coupling (\( J_0 \)). We find \( W = 0.15 \) eV for OPV4 helices by diagonalizing the Holstein Hamiltonian after setting \( \Delta_n, \lambda^2, \) and \( \omega_0 \) equal to zero.

### 5.3 Model for exciton dynamics

Helical OPV aggregates are not isolated but surrounded by solvent molecules. Thermal motion of both the surrounding solvent molecules and the molecules of the aggregates themselves...
leads to additional fluctuations in the chromophore transition energies and to fluctuations in the excitonic couplings $J_{nm}$. This causes transitions of excitons from one eigenstate $|\psi^{(a)}\rangle$ to other eigenstates $|\psi^{(b)}\rangle$. In this chapter we neglect fluctuations in the excitonic couplings for the sake of simplicity and consider only on-site coupling of the exciton to vibrations. Within a linear-coupling approximation, the interaction Hamiltonian reads

$$H_{\text{int}} = \sum_{n=1}^{N} \sum_{q} V_{q}^{n} |n\rangle \langle n| (a_{q}^\dagger + a_{q}),$$  \hspace{1cm} (5.4)$$

where $a_{n}^\dagger$ ($a_{n}$) is the creation (annihilation) operator for a phonon in normal mode $q$ and $V_{q}^{n}$ is the on-site coupling constant of the normal phonon mode $q$ to the $n$-th chromophore. In principle, the $q$-summation runs over all normal phonon modes of the aggregate and solvent. The helical aggregates are one-dimensional in nature and the degrees of freedom associated with these aggregates are therefore much smaller than those associated with the solvent. Therefore, the density of states of the solvent vibrations is much larger than that of the aggregate vibrations and we may presume that coupling to the solvent vibrations is the dominant contribution to the transitions between exciton states.

We assume that the coupling to acoustic phonons in the solvent is sufficiently weak, so that we may treat this coupling as a perturbation. In that case, the transitions between exciton eigenstates $|\psi^{(a)}\rangle$ and $|\psi^{(b)}\rangle$ of the disordered Holstein Hamiltonian can be described by a Pauli master equation for the populations $P_{\alpha}(t)$ of the exciton states,

$$\frac{\partial P_{\alpha}}{\partial t} = -\gamma_{\alpha} P_{\alpha} + \sum_{\beta} \left( W_{\alpha\beta} P_{\beta} - W_{\beta\alpha} P_{\alpha} \right).$$  \hspace{1cm} (5.5)$$

Here, $W_{\alpha\beta}$ is the transition rate from the exciton state $|\psi^{(b)}\rangle$ to state $|\psi^{(a)}\rangle$ and $\gamma_{\alpha}$ is the radiative decay rate of exciton state $|\psi^{(a)}\rangle$. We will apply our theory to OPV4 helices, for which the radiative decay rate was found to be $7 \cdot 10^{7} \text{s}^{-1}$.\(^{32}\) In this chapter we will study the dynamics of excitons in OPV helices on timescales of the order of a few nanoseconds and therefore we can safely neglect the radiative decay term in eq 5.5. The transition rates may be obtained by applying Fermi’s Golden rule. The result becomes particularly simple if we consider the solvent as a disordered host medium in which the coupling constants $V_{q}^{n}$ are stochastic variables without any correlation between the various chromophore sites. In that case the transition rates are given by

$$W_{\alpha\beta} = W_{0} S(\omega_{\alpha\beta}) \sum_{n=1}^{N} |\langle n|\psi^{(\alpha)}\rangle|^{2} |\langle n|\psi^{(\beta)}\rangle|^{2} \times \begin{cases} n(\omega_{\alpha\beta}) & \text{if } \omega_{\alpha\beta} > 0, \\ 1 + n(-\omega_{\alpha\beta}) & \text{if } \omega_{\alpha\beta} < 0, \end{cases}$$  \hspace{1cm} (5.6)$$

where $\omega_{\alpha\beta} = \omega_{\alpha} - \omega_{\beta}$ and $n(\omega) = [\exp(\omega/k_{B} T) - 1]^{-1}$ is the mean occupation number of a phonon state with energy $\omega$. The presence of the factors $n(\omega)$ and $1 + n(-\omega)$ ensures that the transition rates $W_{\alpha\beta}$ obey the principle of detailed balance. This means that in absence of radiative decay ($\gamma_{\alpha} = 0$), the exciton population will eventually reach an equilibrium that is characterized by the Boltzmann distribution over energy. The spectral factor $S(\omega)$ depends on
5.4 Exciton-polaron diffusion in helical OPV4 aggregates

both the details of the exciton-phonon coupling and the phonon density of states. We follow ref 19 and assume that coupling to low-energy acoustic phonons in the solvent dominates the exciton transitions. In that case the spectral factor is given by \( S(\omega) = \frac{\omega}{J}^3 \), where \( J \) is the nearest-neighbor excitonic coupling. The \( \omega^3 \) scaling originates from the fact that \(|V_q|^2\) scales with \( \omega \) for low energy acoustic phonons and that within the Debye model the phonon density of states scales with \( \omega^2 \). We use this Debye-like spectral factor with an additional exponential cut-off factor,

\[
S(\omega) = \frac{\omega}{J}^3 \exp\left(-\frac{\omega}{\omega_c}\right),
\]

where \( \omega_c \) is the cut-off energy. This exponential cut-off factor suppresses arbitrarily high, unphysical acoustic phonon modes. The remaining prefactor \( W_0 \) in eq 5.6 is a measure for the overall strength of the phonon-assisted exciton transition rate and it depends on the microscopic details of the exciton-phonon coupling. We consider \( W_0 \) and the cut-off energy \( \omega_c \) as free parameters of our model that may be used to fit the experimental data.

The factor \( \sum_{n=1}^{N} |\langle n|\psi^{(\alpha)}\rangle|^2 |\langle n|\psi^{(\beta)}\rangle|^2 \) in eq 5.6 represents the overlap of exciton probabilities for the exciton states \( |\psi^{(\alpha)}\rangle \) and \( |\psi^{(\beta)}\rangle \), where \( |\langle n|\psi^{(\alpha)}\rangle|^2 \) is given by

\[
|\langle n|\psi^{(\alpha)}\rangle|^2 = \sum_{\tilde{\nu}} |c^{(\alpha)}_{n,\tilde{\nu}}|^2 + \sum_{\tilde{\nu}} \sum_{n',\tilde{\nu}'} |c^{(\alpha)}_{n',\tilde{\nu}'}|^2.
\]

This overlap factor plays an important role in the exciton dynamics. It indicates that transitions between weakly delocalized states are only efficient for states that are spatially close. The magnitude of the overlap factor is mainly determined by the amount of disorder and the strength of the exciton-phonon coupling. Both energetic disorder and coupling of the exciton to intramolecular vibrations have a localizing effect and the more localized the excitons are, the more spatially close the exciton states have to be for efficient transfer between exciton states by scattering with acoustical phonons.

5.4 Exciton-polaron diffusion in helical OPV4 aggregates

We will employ our theory to study exciton diffusion in helical OPV4 aggregates. In the previous chapter we used the disordered Holstein Hamiltonian to account for the spectral line shapes of the steady-state absorption and emission spectra. Good agreement with the experimental absorption and emission spectra was obtained with the aggregate parameters \( \omega_{0-0} + D = 2.53 \) eV, \( \sigma = 90 \) meV and \( l_0 = 2.0 \), and we adopt these values here. The relaxation model contains two additional free parameters, the overall strength of the exciton transition rate \( W_0 \) and the cut-off energy \( \omega_c \). We determine these parameters by fitting our model to the experimental polarization anisotropy.

The observation of photoluminescence from helical assemblies depends on two processes, the absorption of light by an aggregate and the subsequent emission of light. Due to the helical nature of the aggregate, the probability of absorption of polarized light varies along the stacking direction. Light that is emitted directly after excitation will have the same polarization as the absorbed light. However, most excitons do not decay immediately, but diffuse over the
Figure 5.1: Time-dependent polarization anisotropy for OPV4 helices in dodecane solution ($10^{-4}$ M) at room temperature ($T = 293$ K). The symbols represent the experimentally obtained polarization anisotropy, adopted from ref 23, and the solid line represents the calculated polarization anisotropy. Aggregate parameters are $\omega_{0-0} + D = 2.53$ eV, $\sigma = 90$ meV, $l_0 = 2$, $\lambda^2 = 1.2$ and $\omega_0 = 0.172$ eV, which are obtained from our analysis in the previous chapter. The aggregate length in the calculations is $N = 200$ molecular units and the parameters of the relaxation model are set equal to $\omega_c = 20$ meV and $W_0 = 29.5J$, with $J = 33.4$ meV the nearest-neighbor coupling. With these parameters, a good fit with experiment is obtained. The excitation energy is $\omega_{exc} = 3.1$ eV.

helical assembly before radiative decay occurs. This leads to depolarization of the emitted light and hence the photoluminescence depolarization rate provides insight in the efficiency of exciton diffusion along the helical stacks. Figure 5.1 shows the experimental time-dependent polarization anisotropy of OPV4 dissolved in dodecane solution ($10^{-4}$M) at room temperature (open symbols). A 15-fs pulse of polarized light with an energy of 3.1 eV was used to excite the sample. Following ref 23 we define the polarization anisotropy as

$$r(t) \equiv \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)}.$$  \hspace{1cm} (5.9)$$

Here, $I_{\parallel}(t)$ and $I_{\perp}(t)$ are the intensities of respectively the parallel component and the perpendicular component in one direction of the light emission with respect to the excitation laser polarization.

In appendix A of this chapter we derive an expression for the time-dependent polarization anisotropy of the helical aggregates under consideration. This derivation is based on ref 33, in which the depolarization of fluorescence was studied in a dilute gas of linear molecules. Our derivation assumes that the helical aggregates are oriented isotropically in solution. The final
result reads
\[ r(t) = \sum_{\alpha} P_{\alpha}(t) \left[ \frac{3}{5} \sum_{\nu_1} \sum_{\nu_2} (\omega_0 - \nu_t \omega_1)^3 |\hat{\mu}_{\text{abs}}^{(\nu_1)} \cdot \hat{\mu}_{\text{em}}^{(\nu_0)}(\nu_1)|^2 - \frac{1}{5} \right]. \] (5.10)

Here, \( \omega_0 \) is the energy of the \( \alpha \)-th exciton eigenstate, \( \hat{\mu}_{\text{abs}}^{(\nu)} = \langle G | \hat{M} | \psi^{(\nu)} \rangle \) the transition dipole moment giving rise to absorption from the aggregate electronic and vibrational ground state \( |G\rangle \) to the \( \nu \)-th exciton eigenstate \( |\psi^{(\nu)}\rangle \), and \( \hat{\mu}_{\text{em}}^{(\nu)}(\nu_1) = \langle \psi^{(\nu)} | \hat{M} \prod_{\nu} |g_{\nu}; \nu_{\nu} \rangle \) the transition dipole moment for emission from the \( \alpha \)-th exciton eigenstate to one of the states \( \prod_{\nu} |g_{\nu}; \nu_{\nu} \rangle \), which are vibrationally excited but electronically de-excited. The prime in the summations indicates the constraint \( \sum_{\nu} \nu_{\nu} = \nu_t \), with \( \nu_t \) the total number of vibrational quanta in the states \( \prod_{\nu} |g_{\nu}; \nu_{\nu} \rangle \). The electric transition dipole moment (tdm) operator \( \hat{M} \) consists of a sum of radially directed molecular tdm vector operators,
\[ \hat{M} = \sum_{\nu} \mu \left( \cos(n\phi) \hat{e}_x - \sin(n\phi) \hat{e}_y \right) |n\rangle \langle g| + \text{H.c.} \] (5.11)

Here, \( \hat{e}_x \) and \( \hat{e}_y \) are the unit vectors in the \( x \)- and \( y \)-directions. This definition of the tdm operator assumes the \( z \)-axis to be along the stacking direction and corresponds to a left-handed (right-handed) helix for \( \phi > 0 \) (\( \phi < 0 \)).

The solid lines in Figure 5.1 indicate the calculated polarization anisotropy as a function of time for OPV4 aggregates (solid line). In the calculations we have used an aggregate containing \( N = 200 \) chromophores. This aggregate size amply exceeds the mean exciton diffusion length of \( N = 35 \) chromophores, as estimated from our analysis in the previous chapter. Unfortunately, an aggregate containing \( N = 200 \) chromophores leads to an enormous two-particle basis set, making the diagonalization of the Holstein Hamiltonian practically unfeasible. Therefore, we have limited the basis set to include only one-particle states. We then calculate the time-dependent polarization anisotropy as follows. Firstly, we determine the exciton eigenstate \( \psi^{(\nu)} \) of which the energy is closest to \( \omega_{\text{exc}} = 3.1 \) eV, the excitation energy of the laser used in experiment. The population of this eigenstate at time \( t = 0 \) is set equal to one, \( P_{\alpha}(t = 0) = 1 \), while the populations of the other exciton eigenstates are set equal to zero, \( P_{\alpha \neq \nu}(t = 0) = 0 \). Then, the time evolution of the exciton populations is obtained by solving the Pauli master equation. Once the exciton populations are known, we calculate the time-dependent polarization anisotropy for this disorder configuration using eq 5.10. This procedure is repeated for each disorder configuration and we finally obtain the time-dependent polarization anisotropy by averaging over \( 10^4 \) disorder configurations. A good fit of the experimental data is obtained by setting the parameters of the relaxation model equal to \( W_0 = 29.5J \) and \( \omega_c = 20 \) meV, with \( J = 33.4 \) meV the nearest-neighbor coupling.

Since we use a Debye density of states for the acoustic phonon modes in the solvent, the cut-off frequency \( \omega_c \) should be of the same order of magnitude as the Debye frequency \( \omega_D \). We may obtain a rough estimate of the Debye frequency by considering the solvent as a lattice, with each dodecane molecule treated as a point-like particle located at a lattice point. In that case, we find a Debye frequency equal to \( \omega_D = (6\pi^2 \rho N_A / M_{\text{molar}})^{1/3} \nu_s = 4.6 \) meV, with
Dynamics of exciton-polarons in helical supramolecular assemblies

Figure 5.2: Calculated mean squared displacement, $d^2(t)$, along OPV4 helices as a function of time at room temperature ($T = 293$ K) for several values of the Huang-Rhys factor $\lambda^2$. All other parameters are the same as those used in Figure 5.1.

$\rho = 0.75$ g cm$^{-3}$ and $M_{\text{molar}} = 170.34$ g mol$^{-1}$ the density and molar mass of dodecane, respectively, $N_A$ Avogadro’s number, and $\nu_s = 1297.8$ m s$^{-1}$ the sound velocity in dodecane at room temperature. With these numbers we find that our rough estimate of the Debye frequency is of the same order of magnitude as the cut-off frequency $\omega_c$.

The time-dependent polarization anisotropy shows a fast decrease within the first 20 ps. This hints at an initial rapid motion of the hot exciton followed by a more diffusion-like motion along the stacks once the exciton has cooled down. The inset of Figure 5.1 displays the average energy of the exciton,

$$E(t) = \sum_\alpha \omega_\alpha P_\alpha(t),$$

as a function of time, showing that the average energy indeed drops rapidly within the first 20 ps and decreases more gradually at later times.

To study the migration of excitons along the helical stacks we also calculate the mean squared displacement $d^2(t)$ as a function of time. The numerical solution of the Pauli master equation has provided us with the time evolution of the populations $P_\alpha(t)$ of each eigenstate $|\psi^{(\alpha)}\rangle$. Since $|\langle n|\psi^{(\alpha)}\rangle|^2$ is the probability to find an exciton in the $\alpha$-th eigenstate on site $n$, the time evolution of exciton populations $P_n^{\text{site}}(t)$ at each site can be calculated via

$$P_n^{\text{site}}(t) = \sum_\alpha P_\alpha(t)|\langle n|\psi^{(\alpha)}\rangle|^2.$$
Figure 5.3: Calculated mean squared displacement, $d^2(t)$, along OPV4 helices as a function time at room temperature ($T = 293$ K) for several values of spatial correlation length $l_0$. All other parameters are the same as those used in Figure 5.1.

The mean squared displacement within this approach is then given by

$$d^2(t) = d^2 \langle n^2 \rangle(t) - \langle d_i(n(t)) \rangle^2 = \sum_n (n d_i)^2 P_{\text{site}}(t) - \left( \sum_n n d_i P_{\text{site}}(t) \right)^2,$$

(5.14)

with $n$ the site number and $d_i$ the intermolecular distance between two consecutive dimers. The procedure followed to calculate the mean squared displacement is identical to that followed to obtain the time-dependent polarization anisotropy.

Figure 5.2 shows the mean squared displacement $d^2(t)$ as a function of time for several values of the Huang-Rhys factor $\lambda$. We recognize two regimes. Within the first 20 ps $d^2(t)$ evolves strongly with time and the excitons migrate over a distance of about $\sqrt{d^2(t)} = 4$-5 nm. The rapid initial motion is due to the high probability for excitons to find eigenstates with a lower energy, resulting in a fast migration. This observation is consistent with the fast initial decay of the average energy of the exciton, as shown in the inset of Figure 5.1. After the first 20 ps, $d^2(t)$ starts a much slower increase, indicating a more diffusion-like motion of the excitons. The strength of the coupling of the exciton to intramolecular vibrations, represented by the magnitude of the Huang-Rhys factor $\lambda$, has a significant effect on the fast initial motion of the exciton as well as on the more diffusion-like motion at later times. Excitons migrate slower along the helical stacks when the exciton-phonon coupling is stronger, because of the larger induced distortions in the nuclear framework over which they travel.

Decrease of the correlation length $l_0$ of the energetic disorder has a localizing effect on excitons as well and accordingly slows down the exciton migration. Figure 5.3 shows $d^2(t)$ for several values of the correlation length $l_0$ and demonstrates that exciton migration is faster
Figure 5.4: Calculated mean squared displacement, $d^2(t)$, along OPV4 helices as a function of time at room temperature ($T = 293$ K) for $\lambda^2 = 1.2$. All other parameters are the same as those used in Figure 5.1. The numbers next to the red dots indicate the mean exciton diffusion length, represented by $\sqrt{\langle d^2(t) \rangle}$, at $t = 1, 2, 5, 10, 15, \text{ and } 20 \text{ ns}$.

The amount of energetic disorder within individual aggregates is determined by the extent of spatial correlation in the disorder. All chromophore transition energies within an individual aggregate are equal if $l_0 = \infty$, whereas they are completely uncorrelated if $l_0 = 0$. Our theory describes transitions between weakly delocalized exciton states. Excitons are spatially more delocalized for larger $l_0$, leading to more efficient transitions between exciton states that are spatially further apart. Less energetic disorder thus results in a more rapid movement of excitons along the helical stacks.

In the previous chapter we concluded from our analysis of the Stokes shift that the exciton diffusion length is about 13 nm in OPV4 aggregates when the transition energies within each H-bonded pair are equal. Figure 5.4 displays the mean squared displacement of exciton-polarons in OPV4 helices up to 20 nanoseconds and the exciton diffusion length, represented by $\sqrt{\langle d^2(t) \rangle}$, is given at some fixed times. It was found in ref 32 that the radiative decay rate of excitons in OPV4 helices is $k_r = 7 \cdot 10^7 \text{ s}^{-1}$. This means that half of the excitons have decayed radiatively within the first 9.9 ns and we may thus conclude that only about half of the excitons travel distances that exceed 9 nanometers. If we take this length as a measure for the mean exciton diffusion length we find that our theory predicts a lower exciton diffusion length than we obtained from our analysis of the Stokes shift in the previous chapter.

So far the one-particle basis set has been used to study exciton dynamics. However, it was demonstrated in Figure 4.1 of the previous chapter that two-particle states play an important role in obtaining accurate emission line shapes of OPV helices and the one-particle basis set is therefore not appropriate for describing the emission spectra. In the present chapter we were forced to use the one-particle basis set, because diagonalization of the Holstein Hamiltonian
Figure 5.5: Average energy of the exciton, $E(t)$, as a function of time in an aggregate containing $N = 15$ chromophores for different excitation energies $\omega_{\text{exc}}$. All other parameters are the same as those used in Figure 5.1. For each $\omega_{\text{exc}}$, $E(t)$ is shown both for the single-particle approximation (SPA, open symbols) and two-particle approximation (TPA, solid lines).

within the two-particle approximation (TPA) is practically unfeasible for the aggregate size studied here ($N = 200$). However, we should ask ourselves the question whether the single-particle approximation (SPA, only one-particle states) is appropriate for studying exciton dynamics in OPV helices. Figure 5.5 shows the average energy of the exciton, $E(t)$, as a function of time in an aggregate containing $N = 15$ chromophores for different excitation energies $\omega_{\text{exc}}$. The relatively small aggregate length makes it possible to calculate $E(t)$ within the two-particle approximation (TPA). All other parameters in the calculations are the same as those used above and for each $\omega_{\text{exc}}$ we have calculated $E(t)$ both within the SPA and TPA. We observe in Figure 5.5 that within the SPA the exciton relaxes much more rapidly to lower-lying excited states than within the TPA, if the aggregate is excited in its second or third vibronic band, corresponding to $\omega_{\text{exc}} = 2.7$ eV and $\omega_{\text{exc}} = 2.9$ eV, respectively. However, for excitation within the first vibronic band ($\omega_{\text{exc}} = 2.5$ eV), the exciton relaxation curve within the SPA is almost identical to that within the TPA. This suggests that, although the one-particle basis set is not accurate enough for describing emission, this basis set is suitable for studying migration of excitons in the first vibronic band. Since the SPA predicts a much more rapid relaxation of a high-energy exciton than the TPA, we expect that our estimate of the parameters $\mathcal{W}_0$ and $\omega_c$ is not quite correct. If these parameters would be chosen such that our theory reproduces the experimental polarization anisotropy within the TPA, we would obtain a much faster motion in the aggregate once the exciton has cooled down. This could explain why we obtain a lower mean exciton diffusion length from the analysis in this chapter as compared to the previous chapter.
5.5 Dynamic Stokes shift and 0–0 emission

In a typical time-resolved photoluminescence experiment, the sample is excited by a pulsed laser with an energy above the optical gap of the constituting molecules, creating a high-energy exciton on the aggregate. This exciton relaxes with time to energetically lower-lying exciton eigenstates of the aggregate before radiative decay occurs. Due to this relaxation, we expect to see that the emission spectra exhibit a red-shift as time proceeds. A dynamic Stokes shift was indeed observed in thin films of polythiophene (PT) derivatives by studying the time evolution of the emission spectra at low temperature (10 K) after initial pulsed excitation. It was also observed that the high-energy 0–0 emission peak diminishes relative to the 0–1 peak with time.

The photophysics of PT films can be interpreted within the disordered Holstein model as well, since excitations in PT films also couple strongly to an intramolecular vibrational mode with an energy of about 0.17 eV. Therefore, we expect that the dynamic Stokes shift and the diminishing 0–0 emission are quite general phenomena. In this section we employ our theory for exciton dynamics to study the time-dependent emission spectra of OPV helices and we will see that our theory enables us to qualitatively understand the observations in the time-dependent emission spectra of thin PT films as well.

In order to obtain the time-dependent emission spectrum \( S(\omega, t) \), we evaluate the time evolution of the exciton populations \( P_\alpha(t) \) by solving the Pauli master equation for many disorder configurations and average accordingly,

\[
S(\omega, t) = \langle \sum_\alpha P_\alpha(t) \sum_{\nu_t=0,1,2,...} \omega^3 I_{\alpha}^{0-\nu_t} \delta(\omega - \omega_\alpha(C) + \nu_t \omega_0) \rangle_C. \tag{5.15}
\]

Here, the line strength for emission from the \( \alpha \)-th exciton eigenstate to the electronic ground state with \( \nu_t \) vibrations, \( I_{\alpha}^{0-\nu_t} \), is given by

\[
I_{\alpha}^{0-\nu_t} = \mu^{-2} \sum'_{\{\nu_t\}} \langle \psi^{(\alpha)} | \hat{M} \prod_n |g_n; \nu_n\rangle^2. \tag{5.16}
\]

Emission of a photon can leave the aggregate in all vibrationally excited but electronic ground states \( \prod_n |g_n; \nu_n\rangle \) with a total of \( \nu_t = \sum_n \nu_n \) vibrational quanta. As before, we have indicated this constraint by the prime on the summation in eq 5.16. The factor \( \omega^3 \) in eq 5.15 accounts for the cubic frequency dependency of the emission rate.

Figure 5.6 shows emission spectral line shapes \( S(\omega, t) \) for an OPV aggregate containing \( N = 20 \) chromophores without energetic disorder (\( \sigma = 0 \)) at different times. We have excited the energetically highest exciton state in the first vibronic band at \( t = 0 \) by setting \( P_N(t=0) = 1 \) while \( P_{\alpha \neq N}(0) = 0 \). The overall exciton transition rate is set to \( W_0 = 3J \), with \( J = 33.4 \) meV the nearest-neighbor excitonic coupling. All other parameters are the same as those used in Figure 5.1 and we used the two-particle basis set to calculate the spectra. The width of the emission lines is determined by the homogeneous line width, which is set to \( \sigma_H = 14 \) meV. Figure 5.6 shows that, apart from the 0–0 emission peak, all peaks red-shift with time. The red-shift of the emission peaks is easily understood by the relaxation of the exciton to energetically lower-lying excited states. After a certain time, the exciton population will reach an equilibrium
**5.5 Dynamic Stokes shift and 0–0 emission**

Figure 5.6: Emission spectral line shapes $S(\omega, t)$ for an OPV aggregate containing $N = 20$ chromophores without energetic disorder ($\sigma = 0$) at different times after excitation. The energetically highest exciton state in the first vibronic band is excited at $t = 0$. The overall exciton transition rate is set equal to $W_0 = 3J$, with $J = 33.4$ meV the nearest-neighbor excitonic coupling. All other parameters are the same as those used in Figure 5.1 and the two-particle basis set is used to calculate the spectra. The width of the emission lines is determined by the homogeneous line width, which is set to equal $\sigma_H = 14$ meV.

that is characterized by a Boltzmann distribution over energy. The spectra at 50 ps and 100 ps in Figure 5.6 are identical and show no further red-shift, indicating that thermal equilibrium has been reached before 50 ps.

Figure 5.6 shows that over time the intensity of the 0–0 peak diminishes relative to the 0–1 peak. We can understand this by recalling our discussion in the previous chapter about the properties of the 0–0 and 0–1 emission lines. Achiral aggregates ($\phi = 0$) without energetic disorder are ideal H-aggregates. The 0–0 emission is optically allowed from the state with wavevector $k = 0$ only. In the case of ideal H-aggregates, the $k = 0$ state is the energetically highest-lying exciton state in the first vibronic band. Emission from all other exciton states in the first vibronic band is optically forbidden because these transitions violate the selection rule $\Delta k = 0$\(^\ddagger\). The sideband emission is allowed because the 0-$n$ transitions with $n > 0$ are able to maintain momentum conservation by terminating on the electronic ground states with one or more vibrational phonons, where these phonons carry the excess momentum. In the present discussion, we consider aggregates that have a helical twist ($\phi = 14^\circ$). In that case the symmetry is broken and emission is allowed from the other exciton states in the first vibronic

\(^\ddagger\)The photon momentum is negligible because the optical wavelength is much larger than the aggregate dimensions.
band as well. However, the emission from most exciton states in the first vibronic band is
very weak since the three energetically highest-lying exciton states in the first vibronic band
still contain 85% of the oscillator strength. Just after excitation, emission arises mainly from
these exciton states, leading to a strong 0–0 emission. The exciton relaxes to energetically
lower-lying exciton states with time, resulting in a diminished 0–0 emission intensity. Once the
exciton population has reached thermal equilibrium, the remaining 0–0 emission is mainly due
to thermally excited emission from the energetically highest-lying exciton states, leading to a
negligible red-shift of the 0–0 emission peak.

Figure 5.7 shows emission spectral line shapes of a helical OPV aggregate with energetic
disorder, demonstrating a clearly discernible red-shift of the 0–0 emission line. The spectra
correspond to an aggregate containing $N = 15$ chromophores and are calculated using the
two-particle basis set. Again, the 0–0 peak decreases relative to the 0–1 peak, but now also
shows a red-shift. We have set the disorder strength in our calculations equal to $\sigma = 45$
meV, which is smaller than the disorder strength of $\sigma = 90$ meV obtained from our analysis
of the steady-state optical spectra of OPV helices in the previous chapter. The reason is that
with $\sigma = 90$ the emission lines would have a larger width and cannot be sufficiently separated
anymore. Narrowing of the emission lines would occur for larger aggregates, but it is not feasible
to study larger aggregates with the two-particle basis set. All other parameters are the same
as those used in Figure 5.1. To simulate excitation of the aggregate by a laser pulse, we excite
the aggregate in the second vibronic band using an excitation energy of $\omega_{\text{exc}} = 2.7$ eV, which is
0.17 eV (the energy of the intramolecular vibration) above the average chromophore transition
energy $\omega_{0-0} + D = 2.53$ eV. We assume a Gaussian shape for the laser pulse and we use a
standard deviation of $\sigma_{\text{exc}} = 10$ meV to characterize its width. If we take into account the
oscillator strength for absorption, then the exciton populations at $t = 0$ are given by

$$P_{\alpha}(0) = C|\langle G|\hat{M}|\psi^{(\alpha)}\rangle|^2 \exp\left[-\frac{(\omega_{\text{exc}} - \omega_{\alpha})^2}{2\sigma_{\text{exc}}^2}\right], \quad (5.17)$$

where $C$ is a constant. Finally, we normalize the exciton populations such that $\sum_{\alpha} P_{\alpha}(0) = 1$.

Introducing energetic disorder in chiral H-aggregates breaks the symmetry rules for optical
transitions further, resulting in a significant increase in the 0–0 emission.\textsuperscript{35,36} Figure 5.6
demonstrates that the 0–0 peak diminishes relative to the 0–1 peak with time also for disordered
aggregates. This is due to exciton relaxation to energetically lower-lying exciton states, since
the 0–0 oscillator strength in disordered H-aggregates decreases monotonically in going from
the band top to the band bottom.\textsuperscript{26} Furthermore, all emission lines, including the 0–0 emission
line, exhibit a clear dynamic Stokes shift. The Stokes shift of the 0–0 peak occurs because
the presence of energetic disorder leads to states at very low energy in the tail of the Gaussian
distribution to which exciton can relax, as discussed in the previous chapter. In addition to this,
the 0–0 emission from the energetically lowest-lying exciton states in disordered aggregates
contributes more significantly to the total 0–0 emission than in disorder-free aggregates. This
is due to the localizing effect of energetic disorder, which distributes the total 0–0 oscillator
strength more equally over all exciton states in the first vibronic band. In fact, the 0–0 oscillator
strength of each exciton state in the first vibronic band would be equal in the case of extreme
energetic disorder because excitations are then completely localized to a single chromophore.
5.6 Conclusions and outlook

We have studied the dynamics of photo-induced excitations in helical OPV aggregates. In particular, we have concentrated on the polarization anisotropy, the diffusion of excitations, and the changes in the emission spectra with time. Excitations in helical OPV aggregates are vibrationally dressed excitons, or exciton-polarons, that are very well described by eigenstates of the disordered Holstein Hamiltonian. This Hamiltonian includes excitonic coupling, spatially correlated energetic disorder, and strong coupling of the exciton to a high-energy intramolecular vibration. The latter is responsible for the polaronic nature of excitons in helical OPV aggregates and acts synergistically with energetic disorder in localizing the exciton-polaron to only a few chromophores.\textsuperscript{13} We have described the dynamics of the excitons by a Pauli master equation for the exciton populations and the transitions between the weakly delocalized exciton states are assumed to arise from the weak coupling of the excitons to low-energy acoustic phonons of the solvent and/or the aggregate.\textsuperscript{19–21,24}

Our theory was able to reproduce the experimental polarization anisotropy decay in OPV4 aggregates and enabled us to study the migration of excitons along the helical assemblies by calculating their mean squared displacement. We found that excitons migrate over a distance of about 4 nm within the first 20 picoseconds after a high-energy excitation. This rapid initial motion is attributed to the high probability of excitons to find eigenstates with lower energy, leading to fast energetically downhill migration. A more diffusion-like motion is observed after the first 20 picoseconds and we found that only half of the excitons live long enough to travel

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{figure57.png}
\caption{Emission spectral line shapes $S(\omega,t)$ for an OPV aggregate containing $N = 15$ chromophores with the energetic disorder strength equal to $\sigma = 45$ meV. All other parameters are the same as those used in Figure 5.1 and the two-particle basis set is used to calculate the emission spectra. The spectra are normalized such that the 0–1 emission peaks have the same height.}
\end{figure}
distances that exceed 9 nanometers. If we consider this distance as a measure for the exciton diffusion length, we conclude that our theory predicts a lower exciton diffusion length than obtained from our analysis of the Stokes shift in the previous chapter. A possible explanation is the exclusion of two-particle states in our basis set. Figure 5.5 demonstrates that exciton relaxation occurs much more rapidly in the higher vibronic bands if two-particle states are excluded whereas the exclusion of two-particle states does not affect the exciton relaxation in the lowest vibronic band. This suggests that our theory would predict a much faster motion of the relaxed exciton along the aggregate when the two-particle basis set was used to reproduce the experimental polarization anisotropy, leading to a higher mean exciton diffusion length. In addition we found that excitons migrate significantly slower with increasing strength of the coupling of the excitons to the nuclear framework over which they travel.

The large aggregate size required to study the polarization anisotropy and migration of excitons in OPV helices forced us to limit our basis set to include one-particle states only. Highly accurate emission spectra are obtained only if two-particle states are included in the basis set as well. Therefore, we have investigated whether the single-particle approximation is appropriate for studying exciton dynamics, by examining the exciton relaxation in small aggregates by means of the average energy of the exciton as a function of time. We found that after initial excitation in the first vibronic band, the exciton relaxation rate within the single-particle approximation is almost identical to the rate within the two-particle approximation. However, the single-particle approximation overestimates the relaxation rate considerably after initial excitation in higher vibronic bands. From this we conclude that two-particle states do not only play a crucial role in emission, but also in the dynamics of exciton-polarons.

We have studied the changes in the emission spectra with time in both a disorder-free and a disordered helical aggregate. In both cases, the emission spectra exhibit a dynamic Stokes shift and we found that the 0–0 emission peak diminishes relative to the sideband emission with time. This again demonstrates the usefulness of studying the 0–0 emission line in H-aggregates in obtaining information about the physics taking place in these aggregates. The relative decrease of the 0–0 emission intensity is due to exciton relaxation to energetically lower-lying excited states, because the 0–0 oscillator strength in H-aggregates decreases monotonically in going from the band top to the band bottom. The dynamic red-shift and diminishing 0–0 emission peak have been observed in thin films of polythiophene derivatives by studying the time evolution of the emission spectra at low temperature after initial pulsed excitation. Since the photophysics of polythiophene films can also be described by the disordered Holstein model, we suggest that our model can be applied to also study exciton dynamics in polythiophene films.

Appendix A: Derivation of the expression for the polarization anisotropy

In this appendix we derive the expression eq 5.10 for the time-dependent polarization anisotropy for the helical aggregates considered in this chapter. The derivation is based on ref 33, in which
the depolarization of fluorescence was studied in a dilute gas of linear molecules.

The fluorescence of helical aggregates depends on two processes, the absorption of light by the aggregate and the subsequent emission of light by the electronically excited aggregate. Due to the helical nature of the aggregate, the probability of absorption of polarized light varies along the stacking direction. If we let \( \hat{e}_i \) be a unit vector in the direction of the electric field of the polarized exciting light, and \( \vec{\mu}_{\text{abs}} = \langle G|\hat{M}|\psi^{(i)} \rangle \) the transition dipole moment giving rise to absorption from the aggregate electronic and vibrational ground state \( |G\rangle \) to the \( \iota \)-th exciton eigenstate \( |\psi^{(i)} \rangle \), then the orientation dependence of the excitation probability is given by \( \langle \hat{e}_i \cdot \vec{\mu}_{\text{abs}} \rangle^2 \). After excitation, excitons will spread over the helical assembly before radiative decay occurs. The probability of spontaneous emission from a certain exciton eigenstate \( |\psi^{(\alpha)} \rangle \) to one of the vibrationally excited but electronic ground states \( \prod_n |g_n, \nu_n \rangle \) is proportional to the factor \( (\omega_\alpha - \nu_\iota \omega_\iota)^3 |\hat{e}_f \cdot \vec{\mu}_{\text{em}}(\{\nu_n\})|^2 \), where \( \hat{e}_f \) gives the direction of the electric polarization of the emitted photon, \( \nu_\iota = \sum_n \nu_n \) is the total number of vibrational quanta in the final state, and \( \vec{\mu}_{\text{em}}(\{\nu_n\}) = \langle \psi^{(\alpha)} |\hat{M}| \prod_n |g_n, \nu_n \rangle \) is the corresponding transition dipole moment of the emission.

The total intensity of emission from the \( \alpha \)-th exciton eigenstate \( |\psi^{(\alpha)} \rangle \) is given by

\[
I^{(\alpha)} \propto \sum_{\nu_\iota} \sum_{\{\nu_n\}}' (\omega_\alpha - \nu_\iota \omega_\iota)^3 |\hat{e}_i \cdot \vec{\mu}_{\text{abs}}^{(\alpha)}|^2 |\hat{e}_i \cdot \vec{\mu}_{\text{em}}^{(\alpha)}(\{\nu_n\})|^2, \tag{5.18}
\]

where the prime on the summations indicates the constraint \( \sum_n \nu_n = \nu_\iota \). The intensity of emitted light for which the polarization is unchanged is given by

\[
I^{(\alpha)}_{||} \propto \sum_{\nu_\iota} \sum_{\{\nu_n\}}' (\omega_\alpha - \nu_\iota \omega_\iota)^3 |\hat{e}_i \cdot \vec{\mu}_{\text{abs}}^{(\alpha)}|^2 |\hat{e}_i \cdot \vec{\mu}_{\text{em}}^{(\alpha)}(\{\nu_n\})|^2. \tag{5.19}
\]

We assume that the helical aggregates are isotropically distributed in the solution. In that case we may average this result over all equivalent directions \( \hat{e}_i \), leading to

\[
I^{(\alpha)}_{||} \propto \frac{1}{15} \sum_{\nu_\iota} \sum_{\{\nu_n\}}' (\omega_\alpha - \nu_\iota \omega_\iota)^3 \left[ 2 |\vec{\mu}_{\text{abs}}^{(\alpha)} \cdot \vec{\mu}_{\text{em}}^{(\alpha)}(\{\nu_n\})|^2 + |\vec{\mu}_{\text{abs}}^{(\alpha)}|^2 |\vec{\mu}_{\text{em}}^{(\alpha)}(\{\nu_n\})|^2 \right]. \tag{5.20}
\]

Similarly, the intensity of emitted light with polarization perpendicular to that of the exciting light is given by

\[
I^{(\alpha)}_{\perp} \propto \frac{1}{2} \sum_{\nu_\iota} \sum_{\{\nu_n\}}' (\omega_\alpha - \nu_\iota \omega_\iota)^3 |\hat{e}_i \cdot \vec{\mu}_{\text{abs}}^{(\alpha)}|^2 |\hat{e}_i \times \vec{\mu}_{\text{em}}^{(\alpha)}(\{\nu_n\})|^2. \tag{5.21}
\]

Averaging this result over all equivalent directions \( \hat{e}_i \) gives

\[
I^{(\alpha)}_{\perp} \propto \frac{1}{15} \sum_{\nu_\iota} \sum_{\{\nu_n\}}' (\omega_\alpha - \nu_\iota \omega_\iota)^3 \left[ 2 |\vec{\mu}_{\text{abs}}^{(\alpha)}|^2 |\vec{\mu}_{\text{em}}^{(\alpha)}(\{\nu_n\})|^2 - |\vec{\mu}_{\text{abs}}^{(\alpha)} \cdot \vec{\mu}_{\text{em}}^{(\alpha)}(\{\nu_n\})|^2 \right]. \tag{5.22}
\]
From eqs 5.20 and 5.22 we immediately find that the total intensity of emission from the $\alpha$-th exciton state,

$$I^{(\alpha)}_{\parallel} + 2I^{(\alpha)}_{\perp} \propto \frac{1}{3} \sum_{\nu_n} \sum_{\nu_t} ^{'} (\omega_\alpha - \nu_t \omega_0)^3 |\bar{\mu}_{\text{abs}}^{(\alpha)}|^2 |\bar{\mu}_{\text{em}}^{(\alpha)}(\{\nu_n\})|^2. \quad (5.23)$$

does not depend on the amount of depolarization of the emission. The anisotropy of the emission intensity, $I^{(\alpha)}_{\parallel} - I^{(\alpha)}_{\perp}$, depends on the amount of depolarization of the emitted light and is given by

$$I^{(\alpha)}_{\parallel} - I^{(\alpha)}_{\perp} \propto \frac{1}{15} \sum_{\nu_n} \sum_{\nu_t} ^{'} (\omega_\alpha - \nu_t \omega_0)^3 \left[3|\bar{\mu}_{\text{abs}}^{(\alpha)} \cdot \bar{\mu}_{\text{em}}^{(\alpha)}(\{\nu_n\})|^2 - |\bar{\mu}_{\text{abs}}^{(\alpha)}|^2 |\bar{\mu}_{\text{em}}^{(\alpha)}(\{\nu_n\})|^2 \right]. \quad (5.24)$$

Following ref 33, we define the polarization anisotropy of the $\alpha$-th exciton state, $r^{(\alpha)}$, by

$$r^{(\alpha)} \equiv \frac{I^{(\alpha)}_{\parallel} - I^{(\alpha)}_{\perp}}{I^{(\alpha)}_{\parallel} + 2I^{(\alpha)}_{\perp}}. \quad (5.25)$$

From eqs 5.23-5.25 we then find

$$r^{(\alpha)} = \frac{3}{5} \sum_{\nu_n} \sum_{\nu_t} ^{'} (\omega_\alpha - \nu_t \omega_0)^3 \frac{|\bar{\mu}_{\text{abs}}^{(\alpha)} \cdot \bar{\mu}_{\text{em}}^{(\alpha)}(\{\nu_n\})|^2}{|\bar{\mu}_{\text{abs}}^{(\alpha)}|^2 |\bar{\mu}_{\text{em}}^{(\alpha)}(\{\nu_n\})|^2} - \frac{1}{5}. \quad (5.26)$$

Due to transitions between exciton states, the polarization anisotropy changes in time. If $P_\alpha(t)$ are the exciton populations at time $t$, then the polarization anisotropy $r(t)$ is given by

$$r(t) = \sum_\alpha P_\alpha(t) \left[ \frac{3}{5} \sum_{\nu_n} \sum_{\nu_t} ^{'} (\omega_\alpha - \nu_t \omega_0)^3 \frac{|\bar{\mu}_{\text{abs}}^{(\alpha)} \cdot \bar{\mu}_{\text{em}}^{(\alpha)}(\{\nu_n\})|^2}{|\bar{\mu}_{\text{abs}}^{(\alpha)}|^2 |\bar{\mu}_{\text{em}}^{(\alpha)}(\{\nu_n\})|^2} - \frac{1}{5} \right], \quad (5.27)$$

which is eq 5.10 in the main text.

**References**


Chapter 6

Extreme sensitivity of circular dichroism to long-range excitonic couplings in helical supramolecular assemblies

Circular Dichroism (CD) spectroscopy is an ideal tool for studying the self-assembly of helical supramolecular assemblies, since it is very sensitive to extended excitonic couplings between chiral chromophores. In this chapter we show that the CD spectrum retains its high sensitivity to long-range interactions even in the presence of extreme disorder and strong interaction with vibrations, when excitations are essentially localized on individual molecules. We derive a universal expression for the first moment of the CD spectrum of helical assemblies in terms of a modulated sum over excitonic couplings, which is independent of the strength of the energetic disorder, the spatial correlation of the disorder, and the strength of the interaction with vibrations. This demonstrates that excitonic couplings can be directly extracted from experimental CD spectra, without having information about the energetic disorder and vibrational interactions. We apply our results to helical assemblies of functionalized chiral oligo(p-phenylenevinylene) molecules and show that existing theoretical values for the excitonic couplings should be adapted in order to obtain agreement with the experimental CD spectrum.

6.1 Introduction

Optical spectroscopy is a very useful tool for obtaining information about the structure of proteins, DNA, liquid crystal phases and (supra)molecular assemblies.¹–⁸ These systems have in common that they consist of electronically coupled units, leading to a delocalization of their photo-excitations (excitons). This delocalization affects their optical spectra and one may therefore attempt to extract the excitonic coupling strength between units using optical spectroscopy. Since this coupling depends on the distance between the units and their relative orientation, optical spectra contain information about the structure of the molecular system under investigation.

Circular dichroism (CD) measures the difference in absorption between left- and right-handed circularly polarized light and is particularly useful for studying molecular systems that involve chiral molecules. Most biological (macro)molecules are chiral and therefore CD spectroscopy is widely used to study biological systems.¹–⁴ For example, CD spectroscopy can be utilized to probe changes in the conformation of biological macromolecules and their interaction with other molecules. More recently, the application of CD spectroscopy has been extended to supramolecular chemistry⁷,⁸ in the study of the supramolecular self-assembly of chiral molecules, which can be used to construct well-organized functional nanomaterials.⁹–¹¹

A beautiful example is the self-assembly of helical OPV aggregates,¹²,¹³ which have been discussed extensively in previous chapters. Figure 1.3 shows the molecular structure of OPV4 and a schematic representation of the helical self-assembly. OPV molecules are chiral oligo(p-phenylene-vinylene) derivatives that are functionalized on one end with a ureidotriazine group. This end group enables a molecule to engage in four hydrogen bonds with another molecule. H-bonded pairs (dimers) are formed when OPV molecules are dissolved in dodecane solution at high temperature. Upon lowering the temperature, these dimers associate into small randomly ordered aggregates. Below a critical temperature, the randomly ordered assemblies attain a helical conformation, followed by a strong elongation upon further cooling. UV/vis absorption, fluorescence, and CD spectroscopy were used to identify and distinguish different stages in the self-assembly process of helical OPV aggregates as a function of temperature.¹³

The main signature of aggregation of OPV dimers is the appearance of a shoulder on the low-energy side of the absorption spectra¹³,¹⁴ whereas the transition into long helices leads to the emergence of a bisignate CD activity (Cotton effect) in the vicinity of the lowest molecular singlet transition, indicative of a left-handed helix.¹³,¹⁴ Fluorescence spectra of OPV are characterized by a clear vibronic progression due to a symmetric ring breathing/vinyl stretching mode with an energy of 0.17 eV (∼ 1400 cm⁻¹). Upon aggregation, the fluorescence spectra red-shift and show a reduction of the 0-0 emission intensity relative to the sideband emission.¹⁴ The absorption, fluorescence, and CD spectral line shapes of the helical OPV aggregates were successfully reproduced in ref 14 by employing the Holstein Hamiltonian with spatially correlated disorder.

Circular dichroism in helical assemblies stems entirely from the excitonic coupling between chiral molecules,³,⁴ making this technique very sensitive to this coupling, in contrast to absorption and fluorescence. In fact, it has been known for a long time that the specific signature of a Cotton effect in exciton-coupled dimers can be detected even at very large intermolecular
distances.\textsuperscript{15–18} For example, in porphyrin dimers covalently bound to an oligo-naphthalene scaffold, a Cotton effect was detected at an intermolecular distance as far as 7 nm.\textsuperscript{18} More recently, an even more dramatic demonstration of the sensitivity of the CD response to long-range interactions was given in ref 14: limiting the excitonic couplings in a helical OPV4 aggregate to the first six nearest neighbors (i.e. by setting the seventh and further nearest-neighbor couplings to zero) results in a surprising 30\% increase in the CD intensity, whereas there is no discernible effect on the absorption. But perhaps even more surprising is the fact that this happens while the exciton is localized by energetic disorder to only two OPV molecules. How can the CD response to such localized excitons be so sensitive to long-range excitonic interactions?

In this chapter we study this extreme sensitivity of the CD response to long-range excitonic couplings. Our analysis starts in section 6.2 with a study of CD in helical assemblies without interactions between excitations and vibrations (exciton-phonon interaction). Harada and coworkers showed that the magnitude of the CD response in disorder-free assemblies is directly related to a sum over all extended excitonic couplings.\textsuperscript{15} We will show that the magnitude of the CD response in the presence of energetic disorder decreases with increasing disorder strength, but that this magnitude is still proportional to exactly the same sum. This leads to the surprising conclusion that the sensitivity of CD to extended excitonic couplings is unaffected by disorder: even very strong localization of the exciton does not affect this sensitivity. Another important quantity characterizing the CD spectrum is its first spectral moment. This quantity is unaffected by energetic disorder and also proportional to the above sum over all extended excitonic couplings, as has been shown by Somsen \textit{et al.}\textsuperscript{19} and Burin \textit{et al.}\textsuperscript{20} Burin and coworkers neglected further than nearest-neighbor couplings in their analysis of exciton couplings in DNA hairpins.\textsuperscript{20} This is justified because of the relatively large angle between the base pairs comprising the DNA hairpins (\(\sim 36^\circ\)). We will show that long-range excitonic couplings can actually have a significant contribution in helical aggregates with smaller pitch angles and we will show that the CD first spectral moment is very sensitive to these long-range couplings.

In section 6.3, we will consider the realistic case of presence of exciton-phonon interaction and spatially correlated energetic disorder. We will show that the relation between the CD first spectral moment and the sum over all extended excitonic couplings is unaffected by the exciton-phonon interaction and the spatial correlation of the energetic disorder. This leads to the important conclusion that CD spectroscopy is indeed a very useful experimental tool for probing extended couplings, since information about these couplings can be extracted without the need to have information about the energetic disorder and the exciton-phonon interaction. We apply our results to the OPV4 helices and show that while inclusion of both correlated energetic disorder and exciton-phonon interaction is essential to describe the absorption and luminescence spectra,\textsuperscript{14} it has no influence at all on the sensitivity of the CD spectrum to long-range excitonic couplings. In section 6.4, we give a summary of our results and our main conclusions, and propose a method to extract excitonic couplings using CD spectroscopy on templated assemblies.
6.2 Helical assemblies with energetic disorder

In this section we study CD in helical assemblies with spatially uncorrelated energetic disorder without exciton-phonon interaction. We model the helical assemblies as linear chains consisting of \( N \) two-level chromophores with radially oriented transition dipoles. The exciton Hamiltonian of the system is given by

\[
H = \omega_{0-0} + D + \sum_{n} N \Delta_{n}|n\rangle\langle n| + \sum_{n=1}^{N} \sum_{m \neq n} J_{nm}|n\rangle\langle m|, \tag{6.1}
\]

where we have set \( \hbar = 1 \), and where \(|n\rangle\) denotes an electronic state in which chromophore \( n \) is electronically excited while all other chromophores remain in the electronic ground state. The energy needed for exciting a chromophore from its electronic ground state to its first optically allowed excited state is the transition energy. For the \( n \)-th chromophore the transition energy is given by \( \omega_{0-0} + D + \Delta_{n} \), where \( \omega_{0-0} \) is the gas-phase 0–0 transition energy and \( D \) is the gas-to-crystal shift due to non-resonant interactions. The randomly assigned transition energy offsets \( \Delta_{n} \) account for fluctuations in transition energies along the aggregates. These transition energies fluctuate due to thermally induced deformations within each chromophore (e.g. by bending and twisting) or due to randomness in the direct environment of the chromophores because of the presence of solvent molecules. To model the effect of this energetic disorder, we draw the transition energy offsets \( \Delta_{n} \) from a Gaussian distribution function with standard deviation \( \sigma \). The off-diagonal elements of \( H \) account for the exciton coupling between the \( n \)-th and \( m \)-th chromophore. We will study the case of dipole-dipole coupling, for which \( J_{nm} = J \cos[(n - m)\phi]/|n - m|^3 \), with \( J > 0 \) the excitonic coupling between nearest neighbors and \( \phi \) the pitch angle between the radially oriented transition dipole moments of consecutive chromophores. Because of the finite size of the molecules, however, excitonic couplings can often not be described by a simple dipole-dipole coupling. Therefore, we will also study the case of the excitonic couplings between chromophores in OPV4 aggregates, going beyond the dipole-dipole term. In fact, these excitonic couplings are obtained from ref 14 and they have been evaluated by combining a coupled cluster single and double (CCSD) approach to the INDO Hamiltonian on the basis of model geometric structures, see ref 21.

In what follows, we evaluate the absorption spectrum, \( A(\omega) \), and the circular dichroism spectrum, \( \text{CD}(\omega) \), for a helical assembly using the expressions

\[
A(\omega) = \langle \sum_{\alpha} d_{\alpha} \Gamma(\omega - \omega_{\alpha}(C)) \rangle_{C}, \tag{6.2}
\]

and

\[
\text{CD}(\omega) = \langle \sum_{\alpha} R_{\alpha} \Gamma(\omega - \omega_{\alpha}(C)) \rangle_{C}, \tag{6.3}
\]

respectively. Here \( \langle ... \rangle_{C} \) denotes an average over disorder configurations and \( \Gamma(\omega - \omega_{\alpha}) \) is a symmetric line-shape function centered about the energy of the \( \alpha \)-th eigenstate \( \omega_{\alpha} \) of the exciton Hamiltonian. For this line-shape function we use a Gaussian, with its standard deviation
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σ\(H\) representing the homogeneous line width and its integral normalized to one. Throughout this chapter we use \(σ\(H\) = 14 meV for calculating absorption and CD spectra. This value is small enough for all cases studied to guarantee that the spectral broadening is dominated by the energetic disorder, but large enough to obtain smooth spectra. For consistency, we will use the same value in our analysis of disorder-free helical aggregates. The dimensionless absorption and rotational line strengths in eqs 6.2 and 6.3 are given by

\[
d_\alpha = \frac{1}{\mu^2} \left| \sum_n \langle \psi(\alpha)|\hat{\mu}_n|G\rangle \right|^2, \tag{6.4}
\]

and

\[
R_\alpha = \frac{k_\lambda}{\mu^2} \sum_n \sum_{n'} \langle \psi(\alpha)|\hat{\mu}_n|G\rangle \times \langle G|\hat{\mu}_{n'}|\psi(\alpha)\rangle \cdot (r_n - r_{n'}). \tag{6.5}
\]

Here \(|\psi(\alpha)\rangle \equiv \sum_n c_n^{(\alpha)}|n\rangle\) is the wave function of the \(\alpha\)-th eigenstate (the coefficients \(c_n^{(\alpha)}\) can be chosen real) and \(|G\rangle\) is the ground state of the assembly in which all molecules are in their electronic ground state \(|g\rangle\). In addition, \(k_\lambda\) is equivalent to \(\omega_{\alpha-o}/c\), with \(c\) the speed of light, \(\mu\) is the transition dipole moment (tdm) of the individual chromophores, and \(\hat{\mu}_n\) is the molecular tdm operator. With the helical axis directed along the \(z\)-axis, the tdm operator of the \(n\)-th chromophore is

\[
\hat{\mu}_n = \mu (\cos(n\phi)\hat{e}_x - \sin(n\phi)\hat{e}_y)|n\rangle\langle g| + \text{H.c.}, \tag{6.6}
\]

with \(\hat{e}_x\) and \(\hat{e}_y\) the unit vectors in the \(x\)- and \(y\)-directions. This definition of the tdm operator corresponds to a left-handed (right-handed) helix for \(\phi > 0\) (\(\phi < 0\)). Inserting the wave function of the \(\alpha\)-th eigenstate into eqs 6.4 and 6.5 leads to expressions for the line strengths in terms of the wave-function coefficients \(c_n^{(\alpha)}\):

\[
d_\alpha = \sum_n \sum_{m} c_n^{(\alpha)} c_m^{(\alpha)} \cos[(n-m)\phi], \tag{6.7}
\]

and

\[
R_\alpha = \frac{k_\lambda}{\mu^2} \sum_n \sum_{m} c_n^{(\alpha)} c_m^{(\alpha)} (n-m) \sin[(n-m)\phi]. \tag{6.8}
\]

Figure 6.1 shows absorption (dotted lines) and CD (solid lines) spectra of a helical assembly containing \(N = 30\) chromophores with pitch angle \(\phi = 14^\circ\) and with the excitonic couplings as calculated in ref 14. This results in an exciton bandwidth of \(W = 150\) meV, with the exciton bandwidth \(W\) defined as the energy difference between the highest-energy and lowest-energy exciton state when energetic disorder is absent. Figure 6.1 shows spectra of disorder-free assemblies (a) and assemblies with strong energetic disorder (b), for the inclusion of all excitonic couplings (black lines) and for excitonic couplings truncated after \(N_{tr} = 1\) (red lines), \(N_{tr} = 6\) (green lines) and \(N_{tr} = 12\) (blue lines) nearest neighbors. In general, the absorption spectra are blue-shifted, which is characteristic for H-aggregates \((J > 0)\), and the corresponding CD spectra for the left-handed helix show the classic bisignate Cotton effect and cross zero at the peak of the absorption spectrum.
Extreme sensitivity of circular dichroism to long-range excitonic couplings in helical supramolecular assemblies

Figure 6.1: Calculated absorption (dotted lines) and CD (solid lines) spectra of a helical assembly containing $N = 30$ chromophores with pitch angle $\phi = 14^\circ$, for the calculated excitonic couplings of ref 14, leading to an exciton bandwidth of $W = 150$ meV for a disorder-free assembly. The homogeneous line width is set to $\sigma_H = 14$ meV and the average chromophore transition energy is $\omega_{0-0} + D = 2.53$ eV. Spectra are shown for (a) disorder-free assemblies and (b) assemblies with strong disorder $\sigma = 5W$, with inclusion of all excitonic couplings and with excitonic couplings truncated after $N_{tr}$ nearest neighbors. Note the different $x$- and $y$-scales in (a) and (b).
Figure 6.1 demonstrates that the magnitude of the CD response is very sensitive to extended excitonic couplings. With respect to the spectrum with all couplings included, truncating the extended excitonic coupling beyond $N_{tr} = 1$ and $N_{tr} = 12$ nearest neighbors results in a decrease of the CD intensity of about 70% and 20%, respectively, whereas truncating beyond $N_{tr} = 6$ nearest neighbors leads to an increase of about 35%. Amazingly, the magnitude of the CD response in assemblies with strong energetic disorder is just as sensitive to extended excitonic couplings as it is for disorder-free assemblies, despite the fact that strong localization of the excitonic states has taken place. In contrast to the CD spectra, the absorption spectra are far less sensitive to extended excitonic couplings. The absorption spectra of assemblies with strong energetic disorder are practically identical, while for disorder-free assemblies small differences in the blue-shift of the spectra are discernible, except for the $N_{tr} = 1$ spectrum, which has a much smaller blue-shift than the other absorption spectra.

For sufficiently long disorder-free assemblies, the only optically allowed states are the degenerate exciton states with wave vectors $k = \pm \pi \phi / 180$, with $k$ expressed in inverse units of the lattice spacing and $\phi$ expressed in degrees.\(^{22,23}\) The absorption spectrum is then very accurately described by

$$A(\omega)/N = \Gamma(\omega - \omega_{0-0} - D - J_\phi).$$  \hspace{1cm} (6.9)

Here $J_\phi$ is the spectral blue-shift given by

$$J_\phi = \frac{2}{N} \sum_{n=1}^{N} \sum_{s > 0} J_{n,n+s} \cos(s \phi),$$  \hspace{1cm} (6.10)

which is the excitonic contribution to the energy of the optically allowed degenerate exciton states with wave vectors $k = \pm \pi \phi / 180$. These exciton states are also the only states that contribute significantly to the CD spectrum. In that case we can derive an expression for the CD spectrum by using a procedure similar to that employed by Harada and coworkers,\(^{15}\) in which the Gaussian distribution function appearing in eq 6.3 is Taylor-expanded in the small deviations $(\omega_\alpha - J_\phi)/\sigma_H$. Using this procedure\(^6\) we find

$$\text{CD}(\omega) = 2 k_d d \left\{ \sum_n \sum_{s > 0} J_{n,n+s} \sin(s \phi) \right\} \frac{\omega - \omega_{0-0} - D - J_\phi}{\sigma_H^2} \Gamma(\omega - \omega_{0-0} - D - J_\phi).$$ \hspace{1cm} (6.11)

We numerically checked that eqs 6.9 and 6.11 describe the absorption and CD spectra for disorder-free assemblies very accurately if the assemblies are sufficiently long ($N > 100$). We note that eq 6.11 agrees with the expression derived by Didraga and coworkers for the special case of radially directed transition dipole moments.\(^{22}\)

A good measure for the magnitude of the CD response is the absolute value of the difference between the CD maximum and minimum, $|A_{CD}|$. For disorder-free assemblies, it follows from eq 6.11 that

$$|A_{CD}| = \frac{4 k_d d}{\sqrt{2\pi e \sigma_H^2}} \sum_n \sum_{s > 0} J_{n,n+s} \sin(s \phi).$$ \hspace{1cm} (6.12)

As is clear from this expression, $|A_{CD}|$ is proportional to an $s \sin(s \phi)$-modulated sum over couplings, which is responsible for the extreme sensitivity of CD to extended excitonic couplings.
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Figure 6.2: Calculated excitonic couplings $J_{n,n+s}$ from ref 14 for OPV4 aggregates as a function of the intermolecular distance $s$ in units of the lattice constant $d$. Shown in the inset are the cosine-modulated interactions responsible for the spectral shift of the absorption (red circles) and the much longer-range $s \sin(s\phi)$-modulated interactions responsible for the strength of the CD response (blue triangles).

This is illustrated in Figure 6.2, which shows the calculated excitonic couplings $J_{n,n+s}$ for OPV4 aggregates as a function of $s$, together with the cosine-modulated couplings (inset: red circles) and the much longer range $s \sin(s\phi)$-modulated couplings (inset: blue triangles). Figure 6.2 clearly demonstrates that the $s \sin(s\phi)$-modulated interaction sum that appears in eqs 6.11 and 6.12 is much more sensitive to extended interactions than the cosine-modulated sum $J_\phi$ that causes the spectral shift of the absorption spectrum. This makes CD spectroscopy particularly sensitive to long-range interactions, as was first pointed out by Harada and coworkers and later by others. For disorder-free assemblies, the sensitivity to extended excitonic couplings is interesting, but perhaps not so surprising, because the excitonic states are delocalized over the entire assembly. Energetic disorder has a localizing effect on excitations and one would expect that CD spectra become less sensitive to extended interactions with increasing disorder. However, Figure 6.1 shows that the CD spectrum is just as sensitive to extended excitonic couplings in the case of strong energetic disorder. This is illustrated further in Figure 6.3, which shows $|A_{CD}|$ as a function of the truncation distance $N_{tr}$ for an OPV helix consisting of $N = 30$ chromophores and a pitch angle of $\phi = 14^\circ$. We have also calculated $|A_{CD}|$ for a helix consisting of $N = 100$ chromophores with dipole-dipole coupling $J_{nm} = J \cos[(n - m)\phi]/|n - m|^3$ and the same pitch angle. The nearest-neighbor coupling was set to $J = 38$ meV, leading to a disorder-free bandwidth of $W = 150$ meV, equal to that of a disorder-free OPV helix. The solid lines in Figure 6.3 represent eq 6.12, which gives $|A_{CD}|$ for disorder-free assemblies, whereas the symbols correspond to $|A_{CD}|$ for $\sigma = W$ (red squares) and $\sigma = 5W$ (blue circles), determined from
6.2 Helical assemblies with energetic disorder

Figure 6.3: Magnitude of the CD response $|A_{CD}|$ as a function of $N_{tr}$ for a helical assembly with a pitch angle of $\phi = 14^\circ$, for the case of excitonic couplings as calculated in ref 14 for OPV4 ($N = 30$ chromophores) as well as for dipole-dipole excitonic couplings ($N = 100$). The solid lines correspond to eq 6.12 for the disorder-free case and a homogeneous line width $\sigma_H = 14$ meV. The symbols represent $|A_{CD}|$ as determined from numerically obtained spectra, normalized to match eq 6.12 at $N_{tr} = 30$, for $\sigma = W$ (red squares) and $\sigma = 5W$ (blue circles). The green triangles correspond to the normalized $|A_{CD}|$ obtained with the disordered Holstein model in section 6.3, with spatially correlated disorder, and with aggregate parameters $\omega_0 - 0 + D = 2.53$ eV, $\sigma = 85$ meV, $l_0 = 4.5$, $\omega_0 = 0.172$ eV and $\lambda^2 = 1.2$.

Numerically obtained spectra and normalized to match eq 6.12 at $N_{tr} = 30$. For both disorder strengths we find that $|A_{CD}|$ remains proportional to the $s \sin(s\phi)$-modulated interaction sum present in eq 6.12 and therefore remains highly sensitive to extended interactions, even in the presence of strong energetic disorder.

Although energetic disorder does not affect the extreme sensitivity of CD to extended excitonic couplings, it certainly has a dramatic effect on the magnitude of the CD response. Figure 6.1 shows that the CD maximum decreases by a factor of 1500 if the energetic disorder strength is increased from $\sigma = 0$ to $\sigma = 5W$. To illustrate this further, we show in Figure 6.4 $|A_{CD}|$ as a function of the ratio $\sigma/W$ of the inhomogeneous line width and the disorder-free exciton bandwidth. As indicated by the dash-dotted line, $|A_{CD}|$ is proportional to $\sigma^{-2}$ as long as the inhomogeneous broadening $\sigma$ is much larger than the homogeneous broadening $\sigma_H$. Figure 6.4 demonstrates that strong localization of the exciton due to energetic disorder causes a significant decrease in the magnitude of the CD response.

A very useful quantity to characterize the CD spectrum is its first spectral moment, which
Extreme sensitivity of circular dichroism to long-range excitonic couplings in helical supramolecular assemblies

Figure 6.4: Magnitude of the CD response $|A_{CD}|$ versus the ratio of the disorder strength and the exciton bandwidth, $\sigma/W$, for the case of excitonic couplings calculated for OPV4 in ref 14 as well as for the case of dipole-dipole excitonic couplings. If the inhomogeneous broadening $\sigma$ is much larger than the homogeneous broadening $\sigma_H$, $|A_{CD}|$ is proportional to $\sigma^{-2}$, as indicated by the dash-dotted line.

we define as

$$M^1_{CD} \equiv \frac{\int_0^\infty \omega CD(\omega)d\omega}{\int_0^\infty A(\omega)d\omega}. \quad (6.13)$$

Experimentally, normalization by the total absorption is convenient because this makes $M^1_{CD}$ an intensive quantity that does not depend on the magnitude of the transition dipole moments and the optical path length. Theoretically, we have $\int A(\omega)d\omega = N$. Somsen et al.$^{19}$ and Burin et al.$^{20}$ derived for the case at hand expressions for $M^1_{CD}$ that can be written as

$$M^1_{CD} = \frac{2k_l d}{N} \sum_n \sum_{s>0} J_n,n+s s \sin(s\phi). \quad (6.14)$$

Equation 6.14 shows that $M^1_{CD}$ depends only on an $s \sin(s\phi)$-modulated sum of couplings and not on the strength of the energetic disorder. Figure 6.5 shows $M^1_{CD}$ as a function of the truncation distance $N_t$ for the case of dipole-dipole coupling and with different pitch angles. We checked eq 6.14 against the first spectral moment obtained from numerically calculated CD spectra and found perfect agreement. Figure 6.5 demonstrates that $M^1_{CD}$ is quite sensitive to $N_t$, making it a very useful quantity for probing long-range excitonic interactions.

In ref 20, Burin et al. used the experimentally determined CD first spectral moment to extract the exciton coupling between AT-AT and AT-TA base pairs in DNA hairpins and they found good agreement with the numerically calculated value. They assumed that the contribution of further than nearest-neighbor couplings are negligible. Our results clearly show that
6.2 Helical assemblies with energetic disorder

Figure 6.5: First spectral moment $M_{CD}^1$ of the CD spectrum as a function of $N_{tr}$ for the dipole-dipole interaction and $N = 100$ chromophores. Results are shown for different pitch angles.

these couplings can actually have a significant contribution. However, the angle between the AT base pairs in the DNA hairpins studied in ref 20 is about 36°. Figure 6.5 demonstrates that the CD first spectral moment is far less sensitive to further than nearest-neighbor interactions if the pitch angle is around 40°. Therefore, for this specific case no significant error is made if further than nearest-neighbor interactions are neglected. In general, however, long-range couplings will have to be taken into account.

The consideration of the first spectral moment also provides an explanation for the proportionalities to $\sigma^{-2}$ and the $s\sin(s\phi)$-modulated interaction sum of the magnitude $|A_{CD}|$ of the CD spectrum. In the strong-disorder limit, the CD spectral line shape is quite accurately described by the function $C(\omega - \omega_{0-0} - D) \exp[-(\omega - \omega_{0-0} - D)^2/2\sigma^2]$, where the constant $C$ determines the magnitude of the CD response. Since the relation $\int \omega \omega_{CD}(\omega) d\omega = N M_{CD}^1$ should be obeyed for any disorder strength, we find that $C \propto M_{CD}^1 \sigma^{-2}$ and hence $|A_{CD}|$ is proportional to $\sigma^{-2}$ and to the $s\sin(s\phi)$-modulated interaction sum.

We obtain further understanding of this result by considering the strong-disorder limit. Excitonic coupling then acts as a perturbation and we can apply perturbation theory to find the rotational line strengths. This procedure was followed in ref 4 for the case of an exciton-coupled dimer. We have extended this approach to helical $N$-mers, for which we refer to appendix A of this chapter. The final result for the rotational line strength of the $\alpha$-th eigenstate, which is strongly localized to the $\alpha$-th chromophore, is

$$R_\alpha \approx -k_3 d \sum_{n \neq \alpha} \frac{J_{\alpha \alpha}}{2(\Delta_n - \Delta_\alpha)} (n - \alpha) \sin[(n - \alpha)\phi],$$ (6.15)

which should be inserted in eq 6.3 to obtain the CD spectrum. In the average over all disorder
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configurations, each term in eq 6.15 becomes proportional to \(1/(\Delta_n - \Delta_\alpha)\), which is independent of the distance between the \(n\)-th and \(\alpha\)-th chromophore, \((n - \alpha)\). The rotational line strength is therefore proportional to the \(s\sin(s\phi)\)-modulated sum over all exciton couplings. Furthermore, on average the energy difference \(\Delta_n - \Delta_\alpha\) is of the order of \(\sigma\), leading to a scaling of the rotational line strengths with \(\sigma^{-1}\). Since in addition inhomogeneous broadening spreads the absorption of light over an energy range that scales with \(\sigma\), the CD intensity becomes indeed proportional to \(\sigma^{-2}\).

6.3 Helical assemblies with exciton-phonon interaction and correlated disorder

In this section we study the dependence of CD on extended excitonic couplings in the presence of spatially correlated disorder and exciton-phonon interaction, which are both important in describing realistic systems. Organic materials, such as OPV helices, are soft in the sense that the electronic excitations are accompanied by significant nuclear rearrangements in the participating chromophores. In comparison with the model discussed in the previous section, the photophysics of OPV helices is therefore much more complicated. We will investigate how the interaction of excitons with intermolecular vibrations (exciton-phonon interaction) affects the findings of the previous section.

The general model used to account for the photophysics of OPV4 helices is the disordered Holstein model, which has been discussed extensively in chapter 4. In short, the disordered Holstein Hamiltonian includes excitonic coupling between chromophores (OPV molecules), exciton-phonon interaction, and disorder in the transition energies. Like in ref 14, we assume that the transition energies of the two OPV molecules within each H-bonded pair are equal. Because the interstrand excitonic couplings are relatively weak as compared to the intrastrand couplings, we can then use the single-strand approximation (SSA). This approximation treats each H-bonded pair as a single chromophore, enabling us to double the maximum aggregate length that can be studied numerically. For analyzing absorption and CD spectra the SSA is particularly useful because the analysis requires full diagonalization of the Holstein Hamiltonian, which is very time consuming for long double-stranded aggregates.

Under the SSA, we thus model the OPV helices as a linear chain of \(N\) two-level chromophores with an electronic ground state \(|g\rangle\) and an energetically lowest-lying excited state \(|e\rangle\). For the \(n\)-th chromophore the transition energy is \(\omega_{0-0} + D + \Delta_n\). As in ref 14, we assume spatially correlated disorder and the covariance between two randomly assigned transition energy offsets \(\Delta_n\) and \(\Delta_m\) is given by \(\langle\Delta_n\Delta_m\rangle_c = \sigma^2 \exp(-|n - m|/l_0)\). Here, \(\sigma\) is again the standard deviation of the Gaussian distribution function representing the disorder strength and \(l_0\) is the spatial correlation length in dimensionless units of the lattice spacing. This form was originally used by Knapp in a study of the line shapes of \(J\)-aggregates. In ref 14 a good agreement with the experimental spectra was obtained with \(\omega_{0-0} + D = 2.53\) eV, \(\sigma = 85\) meV, and \(l_0 = 4.5\), and we adopt these values here.

The exciton-phonon coupling arises from coupling of each OPV chromophore to a high-
energy intramolecular symmetric ring breathing/vinyl stretching vibrational mode with frequency \(\omega_0 = 0.172\) eV (1400 cm\(^{-1}\)) and Huang-Rhys factor \(\lambda^2\). The Huang-Rhys factor is a measure for the shift in the equilibrium configuration of the ground and excited state nuclear arrangements. We use a Huang-Rhys factor of \(\lambda^2 = 1.2\). This value, together with the cubic frequency dependence of the emission rate, yields roughly equal single-molecule 0–0 and 0–1 emission peak intensities, as is found for OPV4 molecules in solution. This vibrational mode is responsible for the formation of exciton-polarons, which are also called neutral polarons.

To represent the eigenstates of the disordered Holstein Hamiltonian we use the two-particle approximation. Within this approximation, the \(\alpha\)-th eigenstate of the Hamiltonian is given by

\[
|\psi^{(\alpha)}\rangle = \sum_{n, \tilde{\nu}} c_{n, \tilde{\nu}}^{(\alpha)} |n, \tilde{\nu}\rangle + \sum_{n, \tilde{\nu}, n', \nu'} c_{n, \tilde{\nu}, n', \nu'}^{(\alpha)} |n, \tilde{\nu}; n', \nu'\rangle,
\]

where the coefficients \(c_{n, \tilde{\nu}}^{(\alpha)}\) and \(c_{n, \tilde{\nu}, n', \nu'}^{(\alpha)}\) can be chosen real. The first term of this expansion represents the one-particle states. A one-particle state \(|n, \tilde{\nu}\rangle\) consists of a vibronic (both electronic and vibrational) excitation at chromophore \(n\) containing \(\tilde{\nu}\) vibrational quanta in the shifted excited-state nuclear potential. All other chromophores remain electronically and vibrationally unexcited. The second term represents the two-particle states. In addition to a vibronic excitation at chromophore \(n\), a two-particle state \(|n, \tilde{\nu}; n', \nu'\rangle\) has a vibrational excitation at chromophore \(n'\) containing \(\nu'\) vibrational quanta in the ground state nuclear potential (\(\nu' \geq 1\)).

A schematic representation of the two excitation types is shown in Figure 1.10. Inserting the wave function of the \(\alpha\)-th eigenstate into eqs 6.4 and 6.5 leads to expressions for the line strengths in terms of the multiparticle coefficients:

\[
d_\alpha = \sum_{n, n'} \sum_{\tilde{\nu}, \tilde{\nu}'} c_{n, \tilde{\nu}}^{(\alpha)} c_{n', \tilde{\nu}'}^{(\alpha)} f_{0\tilde{\nu}} f_{0\tilde{\nu}'} \cos[(n - n')\phi],
\]

and

\[
R_\alpha = k_\lambda d \sum_{n, n'} \sum_{\tilde{\nu}, \tilde{\nu}'} c_{n, \tilde{\nu}}^{(\alpha)} c_{n', \tilde{\nu}'}^{(\alpha)} f_{0\tilde{\nu}} f_{0\tilde{\nu}'} (n - n') \sin[(n - n')\phi].
\]

Here, \(f_{\nu\nu'} \equiv \langle \tilde{\nu}|\nu\rangle\) is the overlap between the harmonic-oscillator eigenfunction with \(\tilde{\nu}\) vibrational quanta in the shifted excited-state nuclear potential and the eigenfunction with \(\nu\) vibrational quanta in the ground-state nuclear potential. Equations 6.17 and 6.18 show that one-particle coefficients contribute directly to the line strengths. Two-particle coefficients contribute only indirectly through normalization of the wave function. The contribution of two-particle states is more evident in emission, enabling the evaluation of the polaron radius from the circularly polarized emission.

Remarkably, it turns out that the expression eq 6.14 for the CD first spectral moment is also valid for the disordered Holstein Hamiltonian with any type of spatial correlation of the disorder. The proof of this result can be found in appendix B of this chapter and it generalizes the result of Somsen et al. and Burin et al. by including exciton-phonon interaction. We thus come to the important conclusion that the first spectral moment of the CD spectrum is unaffected by the inclusion of both correlated energetic disorder and exciton-phonon interaction.
and depends only on excitonic couplings. Indeed, we find perfect agreement between the first spectral moment obtained from our calculations and eq 6.14. The normalized magnitude of the CD response $|A_{\text{CD}}|$ as a function of $N_{\text{tr}}$ is included in Figure 6.3 of the previous section (green triangles) and falls on top of the results obtained without inclusion of exciton-phonon interaction and spatial correlation of the energetic disorder. These results show that for realistic systems, including exciton-phonon interaction and spatially correlated disorder, the CD spectrum is a very accurate probe of long-range excitonic couplings and that information about these couplings can be extracted without having information about the exciton-phonon coupling strength and the strength and type of disorder. Of course, CD does not yield unique information on couplings and therefore the structure of complex assemblies of chromophores cannot uniquely be determined from the CD spectrum.

Figure 6.6 shows the experimental absorption (a) and absorption dissymmetry (b), $g_{\text{abs}}(\omega) \equiv \text{CD}(\omega)/A(\omega)$, for OPV4 helices formed in solution at $T = 278$ K, as compared to theoretical predictions, based on the excitonic couplings of ref 14. In contrast to the CD spectrum, $g_{\text{abs}}(\omega)$ is an intensive quantity that does not depend on the magnitude of the transition dipole moment and the optical path length. It represents the net degree of circular polarization normalized to the total absorption. In ref 14, it was reported that the calculated $A(\omega)$ and $g_{\text{abs}}(\omega)$ including all excitonic couplings (black solid lines) reproduce the experimental line shapes quite well, but that the magnitude of $g_{\text{abs}}(\omega)$ is about 30% smaller in comparison to experiment. The best result for $g_{\text{abs}}(\omega)$ was obtained for a truncation distance of $N_{\text{tr}} = 6$ units, which is shown in Figure 6.6 as well (green line). We note that the excitonic couplings of ref 14 have been calculated without accounting for dielectric screening effects. Such effects are expected to reduce the excitonic couplings at large distance, which could explain the fact that the best agreement was obtained by omitting couplings beyond $N_{\text{tr}} = 6$.

We have also displayed in Figure 6.6 the results for a truncation distance of the coupling of $N_{\text{tr}} = 1$ (red line) and $N_{\text{tr}} = 12$ (blue line). Clearly, $N_{\text{tr}}$ has a considerable influence on $g_{\text{abs}}(\omega)$. On the other hand, apart from $N_{\text{tr}} = 1$, the truncation distance has virtually no influence on the absorption spectrum. Figure 6.6b shows that the worst agreement with the experimental CD spectrum is obtained if only nearest-neighbor couplings ($N_{\text{tr}} = 1$) are included. This result demonstrates the importance of extended excitonic couplings for CD. Furthermore, for $N_{\text{tr}} = 6$ the magnitude of $g_{\text{abs}}(\omega)$ increases by 30% with respect to the results for $N_{\text{tr}} = \infty$, whereas in going from $N_{\text{tr}} = 6$ to $N_{\text{tr}} = 12$ the magnitude of $g_{\text{abs}}(\omega)$ drops by about 40%. In fact, the inset of Figure 6.6b shows that the difference between the maximum and the minimum of $g_{\text{abs}}(\omega)$ has essentially the same dependence on truncation distance $N_{\text{tr}}$ as the CD first spectral moment $M_{\text{CD}}^1$. The present analysis demonstrates that our results can be used to judge predictions for the exciton couplings, which are intimately related to the structure of the helical assemblies and to dielectric screening effects.

Since the CD first spectral moment $M_{\text{CD}}^1$ and magnitude are scaling with the $s \sin(s\phi)$-modulated interaction sum, they depend also on the number of chromophores in the helical assembly. We display in Figure 6.7 the absorption (a) and absorption dissymmetry (b) for aggregates of different lengths $N$. The aggregate length clearly has a considerable influence on $g_{\text{abs}}(\omega)$, whereas the absorption spectra for $N = 6$ and $N = 10$ have nearly converged to the $N = 30$ spectrum. The slow convergence of the CD spectrum with size in comparison to
Figure 6.6: Symbols: experimental absorption (a) and absorption dissymmetry (b) versus energy for OPV4 aggregates formed in dodecane solution at $T = 278$ K (black dots, from ref 14). Solid black lines: theoretical prediction, based on the exciton couplings from ref 14, for aggregates consisting of $N = 30$ chromophores. The aggregate parameters are $\omega_0 - 0 + D = 2.53$ eV, $\sigma = 85$ meV, $l_0 = 4.5$, $\omega_0 = 0.172$ eV and $\lambda^2 = 1.2$. Red, green and blue lines: excitonic couplings truncated beyond $N_{tr} = 1$, $N_{tr} = 6$, and $N_{tr} = 12$ units, respectively. Inset: first spectral moment $M_{CD}^1$ (solid line) and the normalized difference between the maximum and minimum of $g_{abs}(\omega)$ (symbols) as a function of truncation distance $N_{tr}$ for $N = 30$. The latter is normalized to match $M_{CD}^1$ at $N_{tr} = 30$. 
Figure 6.7: The same as in Figure 6.6 but now the dependence on aggregate lengths $N$ is investigated, taking into account all excitonic couplings, $N_{tr} = \infty$. The black lines are identical to the black lines in Figure 6.6. Inset: first spectral moment $M^1_{CD}$ and the normalized difference between the maximum and minimum of $g_{abs}(\omega)$ as a function of aggregate length $N$ for $N_{tr} = \infty$. The latter is normalized to match $M^1_{CD}$ at $N = 30$. 
the absorption spectra was also found by Didraga et al. in their analysis of helical cylindrical assemblies. The inset of Figure 6.7b shows how $M_{\text{CD}}^1$ changes as a function of aggregate length $N$. The largest change of $M_{\text{CD}}^1$ occurs between 2 and 10 chromophores, while $M_{\text{CD}}^1$ has converged for about 20 or more chromophores. These results are of importance for the analysis of the aggregation process of helices by measuring the CD activity. For aggregation with a high degree of cooperativity the growth of the assembly is very rapid, so that one can safely assume that in the analysis of CD spectra $N$ is very large. This is the case for the self-assembly of OPV aggregates. However, in the case of non-cooperative, isodesmic aggregation, the growth of the assemblies is more gradual and short assemblies will coexist with longer assemblies. In that case, taking into account the dependence of the CD activity on the assembly length becomes crucial in the analysis of CD spectra.

### 6.4 Conclusions and outlook

We have studied circular dichroism (CD) in supramolecular helical assemblies with long-range excitonic couplings, with and without energetic disorder, spatial correlation of this disorder, and exciton-phonon interaction. We have found that the magnitude of the CD response and the first moment of the CD spectrum are extremely sensitive to extended excitonic couplings, such that even for the fast decaying dipole-dipole coupling the CD intensity has only converged after including the tenth nearest-neighbor coupling. We have derived an expression for the first CD spectral moment in terms of a modulated sum over extended excitonic couplings, which is unaffected by energetic disorder, spatial correlation of this disorder, and exciton-phonon interaction. This leads to the remarkable conclusion that information about excitonic couplings can be extracted from experimental CD spectra without the need to have information about the energetic disorder and the exciton-phonon interaction.

We have studied absorption and CD spectra of helical OPV4 aggregates using the disordered Holstein Hamiltonian with correlated disorder and excitonic couplings calculated with quantum-chemical techniques. Long-range excitonic couplings have almost no influence on the absorption spectrum, but change the CD spectrum dramatically. Including only nearest-neighbor couplings leads to a CD activity that is a factor of four too small as compared to experiment, while taking into account couplings up to the sixth nearest neighbor leads to good agreement. With the results of the present work, we can fully rationalize this extreme sensitivity to long-range excitonic couplings. Including all extended couplings leads to a CD activity that is about 30% too low, which we attribute to absence of dielectric screening effects in the quantum-chemical calculations. This demonstrates how the results of the present work can be used in judging predictions for excitonic couplings, giving insight into the structure of the helical assemblies and into dielectric screening effects.

Due to the extreme sensitivity to extended excitonic couplings, the assembly length also sensitively affects the CD spectrum. For example, the CD first spectral moment of OPV4 aggregates increases by more than a factor of five if the aggregate length is increased from two to ten chromophores. This property can be very useful to extract extended excitonic couplings from experiment if one can accurately control the length of the helical assemblies. One of
the most promising methods for creating helical $N$-mers with well-defined length $N$ employs single-stranded DNA (ss-DNA) as a template for naphthalene- and oligophenylenevinylene-based chromophores functionalized with diamino-triazine head groups for hydrogen bonding. With this method one can obtain stable $N$-mers of any length. Measurement of the CD first spectral moment for each length in principle allows for the determination of the excitonic coupling between each pair of chromophores in the $N$-mer. Analysis of the experimental CD spectra can thus clarify the nature of extended couplings in helical assemblies, allowing for careful testing of dielectric screening effects as well as more sophisticated models that go beyond pairwise couplings.

Appendix A: Rotational line strength in strongly-disordered $N$-mers

We model the helical assemblies as linear chains consisting of $N$ two-level chromophores with radially oriented transition dipoles. Without exciton-phonon coupling the exciton Hamiltonian of the system is given by

$$H = \sum_{n} \epsilon_{n} |n\rangle \langle n| + \sum_{n,m=1}^{N} J_{nm} |n\rangle \langle m|.$$  (6.19)

For the $n$-th chromophore the transition energy is given by $\epsilon_{n} = \epsilon_{0} + \Delta_{n}$, where $\epsilon_{0} = \hbar \omega_{0} - 0 + D$ is the average transition energy and $\Delta_{n}$ are random transition energy offsets to account for disorder. The exciton coupling caused by the off-diagonal elements $J_{nm}$ has a delocalizing effect on excitations, which we can treat as a perturbation in the case of strong disorder ($\Delta_{n} \gg J_{nm}$). The zeroth-order exciton states are then localized on separate chromophores.

Using perturbation theory we may write the perturbed ground state as

$$|G\rangle = |g\rangle - \sum_{n=1}^{N} \sum_{m>n} J_{nm} \frac{\epsilon_{n} - \epsilon_{m}}{\epsilon_{n} + \epsilon_{m}} |nm\rangle,$$  (6.20)

where $|nm\rangle$ is the unperturbed state in which chromophore $n$ and $m$ are electronically excited while all other molecules remain in the ground state, and $|g\rangle$ is the unperturbed ground state. The perturbed exciton states are given by

$$|\psi^{(\alpha)}\rangle = |\alpha\rangle - \sum_{n \neq \alpha} \frac{J_{\alpha n}}{\epsilon_{n} - \epsilon_{\alpha}} |n\rangle,$$  (6.21)

where $|\alpha\rangle$ is the state where chromophore $\alpha$ is excited and all the other chromophores are unexcited. The rotational line strength for a transition from the ground state to the $\alpha$-th exciton state is given by

$$R_{\alpha} = \text{Im}(\vec{p}^{0} \cdot \vec{m}^{0\alpha}).$$  (6.22)
Here $\hat{\mu}^{\alpha 0}$ is the electric dipole moment for the transition from the $\alpha$-th exciton state to the ground state and $\hat{m}^{0\alpha}$ is the magnetic dipole moment for the reverse transition. For the perturbed transition $|\psi^{(\alpha)}\rangle \rightarrow |G\rangle$, $\hat{\mu}^{\alpha 0}$ is given by
\[
\vec{\mu}^{\alpha 0} \equiv \langle G|\hat{\mu}|\psi^{(\alpha)}\rangle = \vec{\mu}_\alpha - \sum_{n\neq \alpha} \frac{2\epsilon_n J_{n\alpha}}{\epsilon_n^2 - \epsilon_\alpha^2} \vec{\epsilon}_n.
\] (6.23)

Similarly, $\hat{m}^{0\alpha}$ is given by
\[
\vec{m}^{0\alpha} \equiv \langle \psi^{(\alpha)}|\hat{m}|G\rangle = \frac{i}{2\hbar c} \left[ \epsilon_\alpha \vec{r}_\alpha \times \vec{\mu}_\alpha - \sum_{n\neq \alpha} \frac{2\epsilon_n \epsilon_\alpha J_{n\alpha}}{\epsilon_n^2 - \epsilon_\alpha^2} \vec{r}_n \times \vec{\mu}_n \right],
\] (6.24)
where we assumed that $\hbar \omega_0 \gg D$. The rotational line strength is therefore
\[
R_\alpha = -\sum_{n\neq \alpha} \frac{\epsilon_n \epsilon_\alpha J_{n\alpha}}{\hbar c (\epsilon_n^2 - \epsilon_\alpha^2)} \left[ (\vec{\mu}_n \times \vec{\mu}_\alpha) \cdot (\vec{r}_n - \vec{r}_\alpha) \right].
\] (6.25)

For a helical assembly, the molecular dipole moments are given by eq 6.6, leading to the expression
\[
R_\alpha = -\frac{d}{\hbar c} \sum_{n\neq \alpha} \frac{\epsilon_n \epsilon_\alpha J_{n\alpha}}{\epsilon_n^2 - \epsilon_\alpha^2} (n - \alpha) \sin[(n - \alpha)\phi].
\] (6.26)
where $d$ is the distance between consecutive chromophores. Since in general $\epsilon_0 \gg \Delta_n$, we can write the last expression as
\[
R_\alpha \approx -k_\lambda d \frac{\epsilon_n \epsilon_\alpha J_{n\alpha}}{2(\Delta_n - \Delta_\alpha)} (n - \alpha) \sin[(n - \alpha)\phi],
\] (6.27)
where $k_\lambda = \epsilon_0 / \hbar c$.

**Appendix B: CD first spectral moment**

The CD first spectral moment is defined as
\[
\int_0^\infty \omega \text{CD}(\omega) d\omega \equiv \int_0^\infty \omega \sum_\alpha R_\alpha \delta(\omega - \omega_\alpha) d\omega
= \sum_\alpha R_\alpha \int_0^\infty \omega \delta(\omega - \omega_\alpha) d\omega = \sum_\alpha R_\alpha \omega_\alpha
\] (6.28)

We will prove that the CD first spectral moment depends only on excitonic couplings and that it is independent of (correlated) energetic disorder and exciton-phonon coupling. Using eq 6.18, we can write $\sum_\alpha R_\alpha \omega_\alpha$ at the right-hand site of eq 6.28 as
\[
\sum_\alpha R_\alpha \omega_\alpha = k_\lambda d \sum_\alpha \sum_n \sum_{n'} \sum_{\nu} \sum_{\nu'} \omega_\alpha c_{n,\nu}^{(\alpha)} c_{n',\nu'}^{(\alpha)} f_{\nu 0} f_{\nu' 0} (n - n') \sin[(n - n')\phi].
\] (6.29)
Here $c_{n,\tilde{p}}^{(\alpha)}$ and $c_{n',\tilde{p}'}^{(\alpha)}$ can be chosen real and we can write this expression as

$$\sum_{\alpha} R_{\alpha} \omega_{\alpha} = k_{\lambda} d \sum_{\alpha} \sum_{n} \sum_{n'} \sum_{\tilde{p}} \sum_{\tilde{p}'} \omega_{\alpha} \langle n, \tilde{p} | \psi^{(\alpha)} \rangle \langle \psi^{(\alpha)} | n', \tilde{p}' \rangle f_{\tilde{p}0} f_{\tilde{p}'0} (n - n') \sin[(n - n') \phi].$$

(6.30)

Using the Schrodinger equation, $H \psi^{(\alpha)} = \omega_{\alpha} \psi^{(\alpha)}$, we find

$$\sum_{\alpha} R_{\alpha} \omega_{\alpha} = k_{\lambda} d \sum_{\alpha} \sum_{n} \sum_{n'} \sum_{\tilde{p}} \sum_{\tilde{p}'} \langle n, \tilde{p} | H | n', \tilde{p}' \rangle \langle \psi^{(\alpha)} | n', \tilde{p}' \rangle f_{\tilde{p}0} f_{\tilde{p}'0} (n - n') \sin[(n - n') \phi].$$

(6.31)

By applying the closure relation, $1 \equiv \sum_{\alpha} |\psi^{(\alpha)}\rangle \langle \psi^{(\alpha)}|$, we can further simplify this expression to

$$\sum_{\alpha} R_{\alpha} \omega_{\alpha} = k_{\lambda} d \sum_{\alpha} \sum_{n} \sum_{n'} \sum_{\tilde{p}} \sum_{\tilde{p}'} \langle n, \tilde{p} | H | n', \tilde{p}' \rangle f_{\tilde{p}0} f_{\tilde{p}'0} (n - n') \sin[(n - n') \phi].$$

(6.32)

The matrix element in the last expression is given by

$$\langle n, \tilde{p} | H | n', \tilde{p}' \rangle = (\omega_{0-0} + D + \Delta_{n} + \tilde{p} \omega_{0}) \delta_{nn'} \delta_{\tilde{p}\tilde{p}'} + J_{nn'} f_{\tilde{p}0} f_{\tilde{p}'0}.$$

(6.33)

Due to the factor $(n - n') \sin[(n - n') \phi]$, the diagonal elements do not contribute, and we find

$$\sum_{\alpha} R_{\alpha} \omega_{\alpha} = k_{\lambda} d \sum_{\alpha} \sum_{n} \sum_{n'} \sum_{\tilde{p}} \sum_{\tilde{p}'} J_{nn'} f_{\tilde{p}0}^2 f_{\tilde{p}'0}^2 (n - n') \sin[(n - n') \phi].$$

(6.34)

The Franck-Condon factors are given by $f_{\tilde{p}0}^2 \equiv \lambda^{2\tilde{p}} \exp(-\lambda^2/\tilde{p})$. Summing over $\tilde{p}$ and $\tilde{p}'$ finally results in

$$\sum_{\alpha} R_{\alpha} \omega_{\alpha} = k_{\lambda} d \sum_{\alpha} \sum_{n} \sum_{n'} J_{nn'} (n - n') \sin[(n - n') \phi].$$

(6.35)

From this expression we conclude that the CD first spectral moment depends only on the off-diagonal elements of the Hamiltonian $H$ and is thus independent of (correlated) energetic disorder. In addition, the CD first spectral moment is independent of exciton-phonon coupling. We note that eq 6.18 shows that only one-particle states contribute directly to the rotational line strength and that expanding the basis set to three- or higher-order particle states does not affect our derivation. Therefore, our derivation is not only valid within the two-particle approximation, which would limit its applicability to the weak and intermediate coupling regime, but is in fact valid for arbitrary strength of the exciton-phonon interaction.

References


Extreme sensitivity of circular dichroism to long-range excitonic couplings in helical supramolecular assemblies


Chapter 7

Circular dichroism of self-assembling helical aggregates

Circular dichroism (CD) spectroscopy is an ideal tool for monitoring the self-assembly of helical supramolecular polymers in solution. By fitting the experimental CD data with an appropriate thermodynamic model one can gain insight in the self-assembly mechanism of the supramolecular polymers. Two assumptions are commonly made to relate a thermodynamic model with the experimental CD data, namely that the magnitude of the CD response of helical assemblies scales linearly with their length and that it scales linearly with the mean helicity of an aggregate. However, we found in the previous chapter that CD in helical assemblies is extremely sensitive to long-range excitonic interactions and that the magnitude of the CD response scales only linearly with the aggregate length beyond a certain length. Furthermore, we will show in this chapter that there is no simple linear relationship between the magnitude of the CD response and the mean helicity of an aggregate, and that the CD intensity is weaker if an aggregate with a fixed degree of helicity contains many small helical sequences than if it contains one long helical sequence. We have examined the consequences of these findings for the interpretation of CD data of supramolecular polymers that self-assemble via an isodesmic polymerization, of assemblies that exhibit a helical transition in the limit of a high degree of polymerization, and of the helical assemblies of chiral oligo(p-phenylene-vinylene) derivatives, for which the polymerization transition coincides with a cooperative helical transition. From our analysis we conclude that a direct application of thermodynamic models is appropriate for interpreting experimental CD data provided that the helical transition is sufficiently cooperative.*

*Manuscript in preparation
7.1 Introduction

Supramolecular self-assembly is a very promising strategy for engineering functional nanomaterials with widespread applications. Examples include supramolecular polymers with excellent mechanical properties,\textsuperscript{1,2} biologically active supramolecular nanostructures with applications in regenerative medicine,\textsuperscript{3,4} and aggregates that consist of $\pi$-conjugated molecular building blocks to be used in supramolecular electronics.\textsuperscript{5,6} In supramolecular electronics, self-assembly provides a way to combine the advantages of the easy processing of conjugated polymers with the structural order of molecular crystals. The central idea is that specifically designed $\pi$-conjugated molecules self-assemble under suitable circumstances into ordered linear arrangements, such that the overlap of the $\pi$-orbitals allows for the transport of excitations (electrons, holes and excitons) along the stacking direction. These ‘nanowires’ have potential applications in optoelectronic devices in the 5-100 nm size range.\textsuperscript{5,6} Applications for supramolecular assemblies based on $\pi$-conjugated molecules require a high degree of control over the position of the molecules. In order to achieve this control, it is a necessity to acquire a deeper insight in the self-assembly mechanisms of supramolecular systems.

Optical spectroscopy is an extremely useful tool for monitoring the supramolecular self-assembly of $\pi$-conjugated molecules.\textsuperscript{7,8} A beautiful example are helical assemblies based on chiral oligo($p$-phenylene-vinylene) derivatives (OPV),\textsuperscript{9,10} which have received considerable attention in recent years due to their excellent optoelectronic properties.\textsuperscript{11–18} OPV molecules are functionalized on one end with an ureidotriazine group that enables a molecule to form a dimer with another molecule via quadruple hydrogen bonding. These H-bonded pairs (dimers) form when OPV molecules are dissolved in an apolar solution of alkanes at high temperature. Upon lowering the temperature these H-bonded pairs link together, forming small randomly ordered aggregates. Below a critical temperature, these randomly ordered aggregates attain a helical conformation and strong elongation sets in upon further decrease of the temperature. A combination of spectroscopic techniques, in particular UV/vis absorption, fluorescence and circular dichroism (CD), was used to identify and distinguish these different phases in the self-assembly process.\textsuperscript{10} The formation of small randomly ordered aggregates is detected by the gradual appearance of a shoulder at the low-energy side of the absorption spectra, whereas the helical ordering and the subsequent strong elongation are identified by the emergence of a strong bisignate CD activity. From a fit of the CD data to an appropriate thermodynamic model, viz. the nucleation-growth model,\textsuperscript{19} it was concluded that the self-assembly process is highly cooperative and that the solvent plays an active role in the supramolecular self-assembly.\textsuperscript{10}

In chapter 2 we applied the helical aggregation theory introduced in ref 20 and 21 to interpret the experimental CD data of OPV4. This theory, of which the nucleation-growth model is a mathematically more accessible version, is a combination of equilibrium polymerization and a model for the helix-coil transition, and has been successfully applied earlier to describe the helical transition in supramolecular polymers of chiral discotic molecules.\textsuperscript{20,21} The interpretation of CD data with thermodynamic models like the nucleation-growth model and the helical aggregation theory is based on the assumption that the magnitude of the CD response scales linearly with the length of the helical assemblies. We have shown in the previous chapter that CD is extremely sensitive to long-range excitonic couplings in helical supramolecular assemblies and that the
7.2 Circular dichroism in helical assemblies

In this section we study circular dichroism (CD) in helical assemblies with long-range excitonic couplings. We will show that the magnitude of the CD response of helical assemblies scales with a modulated sum over all extended excitonic couplings and that this scaling is found for disorder-free aggregates as well as for disordered aggregates. This observation was one of the main conclusions of the previous chapter and it implies that the magnitude of the CD response does not scale linearly with the assembly length, as we will demonstrate in this section.

To study circular dichroism in helical aggregates, we model the helical assemblies as linear chains of $N$ two-level chromophores with radially oriented transition dipoles. The exciton magnitude of the CD response is proportional to a modulated sum over excitonic couplings between chromophores at all distances. Most surprising was the conclusion that the presence of strong energetic disorder and exciton-phonon coupling, both leading to strong localization of the excitations, does not influence this result. Since the magnitude of the CD response scales with this modulated sum over all extended excitonic couplings, it does not scale linearly with the aggregate length, especially not when the aggregates are small. Moreover, the interpretation of CD measurements with the helical aggregation theory assumes that the magnitude of the CD response scales linearly with the mean helicity of the assemblies. Within the helical aggregation theory, aggregates are not necessarily completely helical, but can consist of both helically ordered and randomly ordered domains. Only the helically ordered domains will result in the emergence of CD activity. To our knowledge it has never been investigated how the distribution of helically ordered domains over the aggregate and the average length of these helical sequences affect the magnitude of the CD response.

In this chapter we examine the validity of the afore-mentioned assumptions and the possible consequences for the interpretation of CD measurements. We first introduce in section 7.2 the exciton Hamiltonian for studying CD in helical assemblies. We give expressions for the CD spectrum and its first spectral moment. For parameters representative for MPOV4 aggregates we investigate the dependence of the CD spectrum and its first spectral moment on the aggregate length. In section 7.3 we will devise a simple model to predict the temperature-dependent CD intensity for helical assemblies that form via isodesmic polymerization. This model takes into account the non-linear scaling of the magnitude of the CD response with the aggregate size and enables us to study deviations from a direct prediction of the thermodynamic model for isodesmic polymerization. In section 7.4 we study how the distribution of helically ordered domains over the aggregate and the average length of these helical sequences affect the magnitude of the CD response. We will see that the magnitude of the CD response does not scale linearly with the mean helicity of an individual aggregate and we will apply our findings to aggregates that exhibit a helical transition when the mean aggregate size is large. In section 7.5 we combine the helical aggregation theory with the disordered Holstein model to calculate the temperature-dependent CD spectra of self-assembling OPV4 aggregates. We conclude in section 7.6 with a short summary and the main conclusions.
Hamiltonian of the system is given by

\[
H = \omega_{0-0} + D + \sum_n \Delta_n |n\rangle \langle n| + \sum_{n=1}^{N} \sum_{m \neq n} J_{nm} |n\rangle \langle m|,
\]  

(7.1)

where we have set \(\hbar = 1\), and where \(|n\rangle\) denotes an electronic state in which chromophore \(n\) is electronically excited while all other chromophores remain in the electronic ground state. The energy needed for exciting a chromophore from its electronic ground state to its first optically allowed excited state is the transition energy. For the \(n\)-th chromophore the transition energy is given by \(\omega_{0-0} + D + \Delta_n\), with \(\omega_{0-0}\) the gas-phase 0–0 transition energy and \(D\) the gas-to-crystal shift due to non-resonant interactions. The randomly assigned transition energy offsets \(\Delta_n\) account for energetic disorder in the transition energies. Energetic disorder is present due to thermally induced deformations within each chromophore (e.g. by bending and twisting) or due to randomness in the direct environment of the chromophores because of the presence of solvent molecules. To model the effect of this energetic disorder, we draw the transition energy offsets \(\Delta_n\) from a Gaussian distribution function with standard deviation \(\sigma\). The off-diagonal elements of \(H\) account for the excitonic coupling between the \(n\)-th and \(m\)-th chromophore. We will consider the case of dipole-dipole coupling, for which \(J_{nm} = J \cos(\phi_{nm})/|n - m|^3\), with \(J > 0\) the excitonic coupling between nearest neighbors and \(\phi_{nm}\) the angle between the radially oriented transition dipole moments of chromophores \(n\) and \(m\). For a perfectly helical aggregate \(\phi_{nm}\) equals \((n - m)\phi\), with \(\phi\) the pitch angle of the helix.

The circular dichroism spectrum, \(\text{CD}(\omega)\), is evaluated using the expression

\[
\text{CD}(\omega) = \langle \sum_\alpha R_\alpha \Gamma(\omega - \omega_\alpha(C)) \rangle_C.
\]

(7.2)

Here \(\langle ... \rangle_C\) denotes an average over disorder configurations and \(\Gamma(\omega - \omega_\alpha)\) is a symmetric line-shape function centered around the energy of the \(\alpha\)-th eigenstate \(\omega_\alpha\) of the exciton Hamiltonian. We use a Gaussian for this line-shape function, with its standard deviation \(\sigma_H\) representing the homogeneous line width and its integral normalized to one. Unless stated otherwise, we use \(\sigma_H = 14\) meV throughout this chapter for calculating CD spectra. This value is small enough for all cases studied to guarantee that the spectral broadening is dominated by the energetic disorder, but large enough to obtain smooth spectra. The dimensionless rotational line strength in eq 7.2 is given by\(^{22,23}\)

\[
R_\alpha = \frac{k_\lambda}{\mu^2} \sum_n \sum_m \langle \psi^{(\alpha)} | \hat{\mu}_n | G \rangle \times \langle G | \hat{\mu}_m | \psi^{(\alpha)} \rangle \cdot (r_n - r_m).
\]

(7.3)

Here \(|\psi^{(\alpha)}\rangle = \sum_n c_n^{(\alpha)} |n\rangle\) is the wave function of the \(\alpha\)-th eigenstate (the coefficients \(c_n^{(\alpha)}\) can be chosen real) and \(|G\rangle\) is the ground state of the assembly in which all molecules are in their electronic ground state \(|g\rangle\). Additionally, \(k_\lambda \equiv \omega_{0-0}/c\), with \(c\) the speed of light, \(\mu\) is the transition dipole moment (tdm) of the individual chromophores, and \(\hat{\mu}_n\) is the molecular tdm operator. With the aggregate axis directed along the \(z\)-axis, the tdm operator of the \(n\)-th chromophore is

\[
\hat{\mu}_n = \mu (\cos(\phi_n) \hat{e}_x - \sin(\phi_n) \hat{e}_y) |n\rangle \langle g| + \text{H.c.},
\]

(7.4)
7.2 Circular dichroism in helical assemblies

with \( \hat{e}_x \) and \( \hat{e}_y \) the unit vectors in the x- and y-directions, and \( \phi_n \) the angle between the direction of the tdm of the \( n \)-th chromophore and \( \hat{e}_x \). For a perfectly helical aggregate \( \phi_n \) equals \( n\phi \) and the definition of the tdm operator corresponds then to a left-handed (right-handed) helix for \( \phi > 0 \) (\( \phi < 0 \)). Inserting the wave function of the \( \alpha \)-th eigenstate into eq 7.3 leads to an expression for the rotational line strength in terms of the wave-function coefficients \( c^{(a)}_n \):

\[
R_\alpha = k_\lambda d \sum_n \sum_m c^{(a)}_n c^{(a)}_m (n - m) \sin(\phi_{nm}).
\] (7.5)

For sufficiently long disorder-free assemblies that are perfectly helical, the only optically allowed states that contribute significantly to the CD spectrum are the degenerate exciton states with wave vectors \( k = \pm \pi \phi/180 \), with \( \phi \) expressed in degrees.\(^{24,25}\) The energy of these degenerate exciton states is \( \omega_0 - D + J_\phi \), where \( J_\phi \) is the spectral blue-shift given by

\[
J_\phi = \frac{1}{N} \sum_{n=1}^{N} \sum_{s>0} J_{n,n+s} \cos(s\phi).
\] (7.6)

We can derive an expression for the CD spectrum by using a procedure similar to that utilized by Harada and coworkers,\(^{26}\) in which the Gaussian distribution function appearing in eq 7.2 is Taylor-expanded in the small deviations \( (\omega_\alpha - J_\phi) / \sigma_H \). Using this procedure\(^{27}\) we find

\[
\text{CD}(\omega) = 2k_\lambda d \left\{ \sum_n \sum_{s>0} J_{n,n+s} \sin(s\phi) \right\} \frac{\omega - \omega_0 - D - J_\phi}{\sigma_H^2} \Gamma(\omega - \omega_0 - D - J_\phi). \] (7.7)

We note that this expression agrees with that derived by Didraga and coworkers for the special case of radially directed transition dipole moments.\(^{25}\) The absolute value of the difference between the CD maximum and minimum, \( |A_{\text{CD}}| \), is a good measure for the magnitude of the CD response. It follows from eq 7.7 that for disorder-free assemblies

\[
|A_{\text{CD}}| = \frac{2k_\lambda d \sqrt{2\pi}\sigma_H^2}{c^2} \sum_n \sum_m J_{nm}(n - m) \sin(\phi_{nm}). \] (7.8)

This expression clearly shows that \( |A_{\text{CD}}| \) is proportional to a modulated sum over all couplings \( J_{nm} \), which is responsible for the extreme sensitivity of the CD to extended couplings. The linear factor \( (n - m) \) makes CD spectroscopy particularly sensitive to long-range interactions, as was first pointed out by Harada and coworkers\(^{26}\) and later by others.\(^{28-30}\)

In the previous chapter we have shown that \( |A_{\text{CD}}| \) is proportional to the same sum over all couplings in the case of energetic disorder. We obtained this result by using the CD first spectral moment, which we define here as

\[
M_{\text{CD}}^1 \equiv \int_0^\infty \omega \text{CD}(\omega) d\omega / N.
\] (7.9)

For helical aggregates, Somsen \textit{et al.}\(^{31}\) and Burin \textit{et al.}\(^{32}\) derived expressions for \( M_{\text{CD}}^1 \) that can be written as

\[
M_{\text{CD}}^1(N) = \frac{k_\lambda d}{N} \sum_n \sum_m J_{nm}(n - m) \sin(\phi_{nm}). \] (7.10)
Equation 7.10 shows that $M_{\text{CD}}^1(N)$ depends only on a modulated sum over all couplings and not on the strength of the energetic disorder. In the case of strong energetic disorder, the CD spectral line shape is quite accurately described by the function $C(\omega - \omega_0 - D) \exp[-(\omega - \omega_0 - D)^2/2\sigma^2]$, where the constant $C$ determines the magnitude of the CD response. Since the relation $\int \omega \text{CD}(\omega) d\omega = N M_{\text{CD}}^1(N)$ should be obeyed for any disorder strength, we find that $C \propto M_{\text{CD}}^1(N)$ and hence $|A_{\text{CD}}|$ is proportional to the modulated sum over all excitonic couplings.

Since the magnitude of the CD response scales with a modulated sum over all excitonic couplings, it must depend also on the number of chromophores in the helical assembly. Figure 7.1 shows CD spectra for different aggregate lengths, ranging from 2 to 30 chromophoric units, with a helical pitch angle of $\phi = 15^\circ$. In the calculations, the aggregate parameters are set to $\omega_0 + D = 2.53$ eV and $\sigma = 85$ meV, and we used dipole-dipole excitonic couplings with a nearest-neighbor coupling of $J = 38$ meV, resulting in a free exciton bandwidth of $W = 150$ meV. With this set of parameters, the average chromophore transition energy, the disorder strength and the free exciton bandwidth equal that of the OPV4 aggregates studied in section 7.5. Figure 7.1 clearly demonstrates that the aggregate length has a considerable influence on the magnitude of the CD response, which scales only linearly with the aggregate length if $N$ is larger than about 20. The inset of Figure 7.1 shows that the difference between the maximum and minimum of the CD spectra has essentially the same dependence on the aggregate size as the CD first spectral moment $M_{\text{CD}}^1(N)$. We note that $M_{\text{CD}}^1(N)$ does no longer weakly oscillate with $N$ as in Figure 6.7. This can be attributed to the much faster diminution of the dipole-dipole excitonic couplings as opposed to the couplings of OPV4. Figure 7.2 shows the CD first spectral moment $M_{\text{CD}}^1(N)$ as a function of aggregate length $N$ for several helical pitch angles $\phi$, demonstrating that $M_{\text{CD}}^1(N)$ converges slower to the result for $N = \infty$ for smaller pitch angles. This shows that the non-linear scaling of the magnitude of the CD response with the aggregate size is more important for aggregates with a large helical pitch.

### 7.3 Isodesmic self-assembly of helical aggregates

In the case of isodesmic polymerization, the fraction of molecules in the aggregated state, $\eta$, is related to the number-averaged mean aggregate size, $\langle N \rangle_n$, through the equality (see chapter 2)

$$\eta = \frac{\sum_{N=1}^{\infty} N \rho(N)}{\sum_{N=1}^{\infty} \rho(N)} = 1 - \langle N \rangle_n^{-2},$$

where $\rho(N) \propto (1 - \langle N \rangle_n^{-1})^N$ is the dimensionless size distribution of aggregates with length $N$. In chapter 2 we have shown that at a fixed concentration of the aggregating molecules in solution, the temperature dependence of the mean aggregate size is given by

$$\langle N \rangle_n \approx \frac{1}{2} + \frac{1}{2} \sqrt{1 + \hat{\gamma} \exp \left( \frac{h_p(T - T_p)}{k_B T_p^2} \right)},$$
Figure 7.1: Calculated CD spectra of a helical assembly with a pitch angle of $\phi = 15^\circ$ for the case of dipole-dipole excitonic couplings. The nearest-neighbor excitonic coupling is $J = 38 \text{ meV}$, resulting in an exciton bandwidth of $W = 150 \text{ meV}$, the average chromophore transition energy is $\omega_{0-0} + D = 2.53 \text{ eV}$ and the disorder strength is $\sigma = 85 \text{ meV}$. Spectra are shown for different aggregate lengths $N$. Inset: first spectral moment $M_{CD}^1(N)$ and the difference between the maximum and minimum of the CD, $|A_{CD}|$, as a function of aggregate length $N$, both normalized such that they converge to 1 for $N \gg 1$.

where $\gamma \equiv 4(2 - \sqrt{2}) \approx 2.34$ is a numerical constant, $T_p$ the polymerization temperature at which half of the material is in the aggregated state, and $h_p$ is the enthalpy of the formation of a single bond at $T = T_p$. Note that at the polymerization temperature, the solution consists mainly of monomers and dimers, since $\langle N \rangle_n = \sqrt{2}$ if $\eta = \frac{1}{2}$.

A bisignate CD activity emerges if the aggregates formed are helical. The magnitude of the CD response is directly correlated with the fraction of material absorbed in helical assemblies. The temperature dependence of $\eta$ is therefore experimentally accessible by probing the CD intensity at an appropriate wavelength as a function of temperature. One may obtain information about the thermodynamics of the isodesmic self-assembly by extracting the bond enthalpy $h_p$ and the polymerization temperature $T_p$ from fitting eq 7.11 to the experimentally magnitude of the CD response as a function of temperature. However, this procedure assumes that this magnitude scales linearly with the aggregate length. Our analysis in the previous section demonstrates that the magnitude of the CD response is proportional to an $s \sin(s\phi)$-modulated sum of all extended couplings and scales only linearly with aggregate length beyond a certain aggregate size. Since around the polymerization temperature the solution contains mainly monomers and dimers, we expect that this procedure of interpreting experimental CD data leads to an incorrect estimate of the the bond enthalpy $h_p$ and the polymerization temperature $T_p$.

The polymerization curves obtained with CD spectroscopy may be predicted by taking into
account the length dependence of the magnitude of the CD response. To that end we use the CD first spectral moment $M_{1CD}^1(N)$ as a measure for the magnitude of the CD response. This polymerization curve $\eta_{CD}(T)$ is then predicted by

$$\eta_{CD}(T) = \frac{\sum_{N=1}^{\infty} N \rho(N) M_{1CD}^1(N)}{\sum_{N=1}^{\infty} \rho(N) N_{c}} \simeq \eta(T) - \frac{\sum_{N=1}^{N_c} N \rho(N)(1 - M_{1CD}^1(N)/M_{1CD}^1(N_c))}{\sum_{N=1}^{\infty} \rho(N)},$$

(7.13)

where $N_c$ is the aggregate length beyond which the CD first spectral moment can be assumed to be equal to its value at $N = \infty$. We assume dipole-dipole excitonic coupling between the chromophores in the aggregates and we set $N_c = 100$, which is sufficiently long for all pitch angles under consideration. By assuming that the magnitude of the CD response scales with $M_{1CD}^1(N)$ we neglect small deviations from this scaling due to spectral shifts of the CD spectrum and energetic disorder, see Figure 7.1. The spectral shift of the CD spectrum and effects of energetic disorder depend on the specific details of the system under consideration. Since we want to keep the discussion as general as possible, we take into account only the scaling of the magnitude of the CD response with $M_{1CD}^1(N)$.

Figure 7.3 shows $\eta_{CD}(T)$ for various helical pitch angles as a universal function of $-h_p(T - T_p)/k_B T_p^2$ (non-solid colored lines). These curves deviate strongly from eq 7.11 (black solid line). We observe that the curves deviate more strongly when the helical pitch angle is smaller. This is due to the slower convergence of $M_{1CD}^1(N)$ for smaller angles, see Figure 7.2. If we directly use eq 7.11 to fit the polymerization curves as predicted by eq 7.13, we obtain lower values for $T_p$ and $h_p$ than the actual values. To illustrate this we have taken $T_p = 300$ K and $h_p = -50$ kJ · mol$^{-1}$, which are realistic values for a supramolecular polymer that self-assembles upon cooling. Table 7.1 shows the values of $T_p$ and $h_p$ obtained by fitting eq 7.11 to the polymerization curves given by eq 7.13 for various pitch angles. The results clearly
7.4 Helical transitions in the long-chain limit

Figure 7.3: Fraction of molecules absorbed in helical assemblies \( \eta \) as a universal function of \(-h_p(T - T_p)/k_B T_p^2\) (black solid line). The non-solid colored lines represent the polymerization curves predicted by eq 7.13 for various helical pitch angles. A dipole-dipole excitonic coupling is assumed between chromophores. The top x-axis corresponds to a temperature-scale based on \( T_p = 300 \text{ K} \) and \( h_p = -50 \text{ kJ mol}^{-1} \), which are realistic values for a supramolecular polymer that self-assembles upon cooling.

Demonstrate that directly employing eq 7.11 to interpret the experimental CD data leads to incorrect estimates of the bond enthalpies \( h_p \) and the polymerization temperatures \( T_p \) when the helical aggregates form via an isodesmic polymerization mechanism.

Many helical structures self-assemble via a non-isodesmic cooperative growth mechanism, in which the length rapidly grows as soon as nucleation has started. However, there are examples of helical supramolecular polymers that form via an isodesmic pathway. The lack of cooperativity in the formation of these helices is probably due to a large helical pitch. Precisely the CD polymerization curves of self-assembling helices with a large helical pitch, which implies a small pitch angle, are most susceptible to an erroneous interpretation of the experimental data.

7.4 Helical transitions in the long-chain limit

The helical self-assembly of supramolecular polymers in solution can be described by a theoretical model that is a combination of equilibrium polymerization theory and a theory for the helix-coil transition. This theoretical model was outlined in chapter 2. It enables us to calculate the size distribution of aggregates \( \rho(N) \) as a function of temperature. In addition, the model provides information about the conformational states of individual aggregates as a function
Table 7.1: Values of \( T_p \) and \( h_p \) obtained by direct fitting of eq 7.11 to the polymerization curves given by eq 7.13 for various pitch angles \( \phi \).

<table>
<thead>
<tr>
<th>( \phi )</th>
<th>( T_p ) [K]</th>
<th>( h_p ) [kJ mol(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5°</td>
<td>255</td>
<td>-23</td>
</tr>
<tr>
<td>10°</td>
<td>265</td>
<td>-27</td>
</tr>
<tr>
<td>15°</td>
<td>270</td>
<td>-29</td>
</tr>
<tr>
<td>20°</td>
<td>274</td>
<td>-31</td>
</tr>
<tr>
<td>30°</td>
<td>280</td>
<td>-33</td>
</tr>
<tr>
<td>40°</td>
<td>283</td>
<td>-34</td>
</tr>
</tbody>
</table>

of temperature via the single-aggregate partition function \( Q(N) \). A conformational state is specified by the state of the bonds between neighboring molecules within an aggregate. In the high-energy/low-entropy bonded state two neighboring molecules are locked in a helical arrangement, where the helical sense is fixed by the chiral nature of the molecules involved. The molecules do not have fixed orientations relative to each other if the bond is in the low-energy/high-entropy state. For simplicity we refer to the former as the helical bond, and to the latter as the non-helical bond.

The helical aggregation theory indicates the existence of two regimes: one in which the polymerization transition and helical transition coincide, and another regime in which they do not.\(^{21,35}\) In the next section we consider the helical self-assembly of OPV4 aggregates, which can be classified as belonging to the former regime. Here, we consider the latter regime. More specifically, we assume that the helical transition occurs when the mean aggregate size is very large, \( \langle N \rangle_n \gg 1 \). Under this condition, the mean fraction of helical bonds \( \langle \theta \rangle_w \) does not depend on specific details of the aggregate ends and the mean aggregate size. In that case the expression for \( \langle \theta \rangle_w \) reduces to\(^{20,36}\) (see chapter 2)

\[
\langle \theta \rangle_w \approx \frac{1}{2} + \frac{s - 1}{2\sqrt{(s - 1)^2 + 4\sigma_C s}} = -\frac{1}{N - 1} \frac{\partial \ln Q(N)}{\partial \ln s}. \tag{7.14}
\]

Here, \( s = \exp(-P) \) and \( \sigma_C = \exp(-2R) \) are the so-called Zimm-Bragg parameters.\(^{36}\) Conformational frustration occurs when a molecule is involved in two types of bonding with its direct neighbors and a free energy penalty \( R \geq 0 \) is introduced for those molecules. The parameter \( 0 \leq \sigma_C \leq 1 \) is therefore a measure for the cooperativity of the crossover from a non-helical to a helical conformation. This crossover becomes sharper when the value of \( \sigma_C \) becomes smaller. Moreover, the smaller the value of \( \sigma_C \), the longer the mean length of helical sequences along the aggregate at a fixed average degree of helicity. The free-energy difference associated with the formation of a helical bond from a non-helical bonds is denoted by \( P \). A helical bond is more favorable than a non-helical one if \( P < 0 \) while for \( P > 0 \) the opposite is true. The temperature dependence of \( P \) can be made explicit by means of a Taylor expansion around a reference temperature \( T_h \) (defined below)

\[
P(T) \approx -\frac{h_h(T - T_h)}{k_B T_h^2}. \tag{7.15}
\]
7.4 Helical transitions in the long-chain limit

Here, $h_h$ represents the enthalpy of the formation of a helical bond from a non-helical one. If we arbitrarily define the helical transition to occur at the point when half of the bonds are helical, then it follows that in the limit $\langle N \rangle_n \gg 1$ this transition occurs when $P = 0$ ($s = 1$). Therefore, $T_h$ is defined as the helical transition temperature of an infinitely long aggregate. Equation 7.14 was successfully used in fitting the experimental results obtained from a solution of chiral discotic molecules and it was concluded that the helical transition in these supramolecular polymers is highly cooperative.

In the definition of the mean helicity according to eq 7.14 we count the number of helical bonds ($\partial \ln Q(N)/\partial \ln s$) and compare it to the maximum number of helical bonds, $N - 1$. Employing eq 7.14 to interpret the experimental CD data thus assumes that the magnitude of the CD response scales linearly with the number of helical bonds. Figure 7.4 shows calculated CD spectra of an assembly containing $N = 25$ chromophores with dipole-dipole excitonic coupling. The nearest-neighbor coupling is set to $J = 38$ meV, resulting in an exciton bandwidth of $W \approx 150$ meV, and we have taken $\omega_{0-0} + D = 2.53$ eV. Furthermore, we neglect energetic disorder ($\sigma = 0$) and the homogeneous line width is set to $\sigma_H = 85$ meV. Since these parameters are in principle different for each system under investigation, we have chosen to employ values that are similar to those used for OPV4 assemblies. Calculated spectra are shown for the same fraction of helical bonds, $\langle \theta \rangle_w = 2/3$, but for different configurational states of the aggregate. To calculate these spectra we have fixed the angle between consecutive molecules to $\phi = 15^\circ$ if a bond is helical (h), whereas a random angle has been assigned to each non-helical (n) bond. We have carried out an average over $10^4$ aggregates. The black line in Figure 7.4 represents the CD spectrum of an aggregate that is entirely helical, whereas the other spectra correspond to aggregates with a fraction $\langle \theta \rangle_w = 2/3$ of helical bonds. We observe that only the intensity of the spectrum of the aggregate that contains one long helically ordered region (red line) is about 2/3 of the CD intensity of the entirely helical aggregate. Figure 7.4 thus clearly demonstrates that the magnitude of the CD response does not scale linearly with the number of helical bonds. Moreover, we observe that the smaller the helical sequences along the aggregate, the lower the relative CD intensity as compared to other configurational states with the same fraction of helical bonds.

The helical transition curves obtained with CD spectroscopy can be predicted by taking into account all possible configurational states at a certain temperature in our calculations of CD spectra. Since the single-aggregate partition function $Q(N)$ contains information about the conformational states of individual aggregates as a function of temperature, we can calculate the CD spectra through

$$\langle \text{CD}_N(\omega) \rangle_{\text{conf}} = \frac{1}{Q(N)} \sum_{\{s\}} \text{CD}_N(\omega) e^{-H(\{s\})},$$

(7.16)

where the summation over $\{s\} \equiv \{s_1, ..., s_{N-1}\}$ involves all possible conformations and $H(\{s\})$ is the dimensionless Ising-like Hamiltonian that describes the conformational state of an aggregate of length $N$, see chapter 2. The Boltzmann factor $e^{-H(\{s\})}$ depends on temperature through the temperature dependence of $P$ and gives the relative probability that a certain configurational state of the aggregate occurs. Equation 7.2 can be used to calculate the CD
Figure 7.4: Calculated CD spectra of a helical assembly consisting of \( N = 25 \) chromophores for the case of dipole-dipole excitonic couplings. Spectra are shown for different configurational states, where \( (h_x n_y)_z \) denotes a configurational state that consist of \( z \) repeat units, with each unit consisting of \( x \) consecutive helical bonds (h) followed by \( y \) consecutive non-helical bonds (n). The fraction of helical bonds is the same for each configurational state, \( \langle \theta \rangle_w = 2/3 \). For a helical bond, the angle between consecutive chromophores is fixed to \( \phi = 15^\circ \), whereas a random angle is assigned to a non-helical bond. Aggregate parameters are \( J = 38 \) meV for the nearest-neighbor excitonic coupling, \( \omega_{0-0} + D = 2.53 \) eV, and \( \sigma_H = 85 \) meV (energetic disorder is neglected, \( \sigma = 0 \)).

spectrum of a certain configurational state. For calculating a CD spectrum we use an aggregate consisting of \( N = 100 \) chromophores with dipole-dipole excitonic coupling. To avoid calculating the CD spectra of all possible configurational states we use a Monte-Carlo procedure based on single spin-flip sampling to carry out the configurational averaging. Starting from a random configuration, an equilibration time of \( 40N \) Monte-Carlo steps proved sufficient for all temperatures studied. After equilibration we perform \( 10^4 \) measurements and \( 20N \) Monte-Carlo steps are taken in between consecutive measurements. With this procedure we obtain a CD spectrum for each temperature.

The black lines in Figure 7.5a-d represent the mean helicity \( \langle \theta \rangle_w \) for several values of the cooperativity parameter \( \sigma_C \) as a universal function of \( -h_b(T - T_h)/k_B T_h^2 \), whereas the green and red lines represent the helical transition curves calculated by means of eq 7.16 for pitch angles \( \phi = 5^\circ \) and \( \phi = 10^\circ \), respectively. The other aggregate parameters are the same as above. We have taken the difference between the CD maximum and minimum as a measure for the magnitude of the CD response and the transition curves obtained are normalized to one at low temperature. Figure 7.5 demonstrates that deviations from eq 7.14 occur only for helical transitions with a very low cooperativity, \( \sigma_C \geq 10^{-1} \). This observation can be understood by looking at the configurational states of the aggregate at the helical transition.
temperature, where $\langle \theta \rangle_w = 1/2$. The average length of a helical sequence along the aggregate at the helical transition temperature is $\sigma_{c}\frac{1}{2}$. For transitions with low cooperativity, these helical sequences are very small and the resulting CD intensity is therefore less than half of the maximally attainable CD intensity of an entirely helical aggregate. To show the helical transition curves in Figure 7.5 on a realistic temperature scale (see top x-axis), we have taken $T_h = 300$ K and $h_h = -50$ kJ mol$^{-1}$, which are realistic values for a supramolecular polymer that features a helical transition upon cooling.

### 7.5 Application to self-assembling OPV4 helices

In chapter 2 we applied the helical aggregation theory to the specific case of OPV4 aggregates. We estimated the model parameters by comparing the normalized CD intensities at $\lambda = 466$ nm to the theoretical weight-averaged fraction of helical bonds. The model parameters obtained are shown in Table 2.1. For these parameters the agreement between the predictions of the helical self-assembly theory and the CD data is good, except at very low temperatures, where OPV helices are thought to form bundles. The model parameters in Table 2.1 enable us to determine both the size distribution of aggregates $\rho(N)$ and the single aggregate partition function $Q(N)$ as a function of temperature. This information can be used to calculate the CD spectra of self-assembling OPV aggregates at different stages in the self-assembly.

The procedure we follow here to calculate temperature-dependent CD spectra is similar to that shown in Figure 3.2 for the calculation of temperature-dependent photoluminescence spectra. We use $\rho(N)$ to define a probability distribution $P(N)$, which is discussed in more details below. This distribution determines how much the circular dichroism from aggregates with length $N$ contributes to the total CD spectrum. Next, we take a large number of aggregates according to the distribution $P(N)$ and for each aggregate we generate an energetic disorder configuration. To obtain the CD spectrum of each aggregate, we employ a quantum-mechanical model to calculate the circular dichroism from each configurational state and we average over all configurational states by utilizing $Q(N)$. In the following we will give a more detailed discussion of our procedure for calculating temperature-dependent CD spectra.

We start by concentrating on the CD spectrum of a single aggregate with length $N$. The general model we use to account for the CD spectral line shape of OPV helices is the disordered Holstein model (eq 4.1), which has been discussed extensively in the previous chapters. Compared to the exciton Hamiltonian given by eq 7.1, the disordered Holstein Hamiltonian contains a contribution accounting for the exciton-phonon coupling that arises from coupling of each OPV chromophore to a high-energy intramolecular symmetric ring breathing/vinyl stretching vibrational mode with frequency $\omega_0 = 0.172$ eV ($1400$ cm$^{-1}$) and Huang-Rhys factor $\lambda^2$. The Huang-Rhys factor is a measure for the shift in the equilibrium configuration of the ground and excited state nuclear arrangements. We use a Huang-Rhys factor of $\lambda^2 = 1.2$. This value, together with the cubic frequency dependence of the emission rate, yields roughly equal single-molecule 0–0 and 0–1 emission peak intensities, as is found for OPV4 molecules in solution.

Concerning the excitonic contributions to the disordered Holstein Hamiltonian, we assume spatially correlated disorder with a covariance between two randomly assigned transition energy
Figure 7.5: Mean helicity $\langle \theta \rangle_w$ for several values of $\sigma_C$ (a-d) as a universal function of $-h_h(T - T_h)/k_B T_h^2$ (black lines). The green and red lines represent the helical transition curves of an aggregate consisting of $N = 100$ chromophores with helical pitch angles $\phi = 5^\circ$ and $\phi = 10^\circ$, respectively. These curves are obtained by calculating CD spectra by means of eq 7.16. We have taken $\omega_{0-0} + D = 2.53$ eV and a dipole-dipole excitonic coupling between chromophores, with the nearest-neighbor coupling set to $J = 38$ meV. Energetic disorder is neglected ($\sigma = 0$) and the homogeneous line width is set to $\sigma_H = 85$ meV. At each temperature we have taken the difference between the CD maximum and minimum as a measure for the magnitude for the CD response. The top $x$-axis corresponds to a temperature scale based on $T_h = 300$ K and $h_h = -50$ kJ mol$^{-1}$, which are realistic values for a supramolecular polymer that features a helical transition upon cooling.
offsets $\Delta_n$ and $\Delta_m$ given by $\langle \Delta_n \Delta_m \rangle_C = \sigma^2 \exp(-|n - m|/\ell_0)$. Here, $\sigma$ is the standard deviation of the Gaussian distribution function representing the disorder strength and $\ell_0$ is the spatial correlation length in dimensionless units of the lattice spacing. In ref 17 a good agreement with the experimental spectra was obtained with $\omega_{0-0} + D = 2.53$ eV, $\sigma = 85$ meV, and $\ell_0 = 4.5$, and we adopt these values here. For the pitch angle in the OPV helices we take $\phi = 14^\circ$ and we obtain the excitonic couplings from ref 17, resulting in a free exciton bandwidth of $W = 150$ meV.

In the previous chapter we used the two-particle approximation to represent the eigenstates of the disordered Holstein Hamiltonian.38,39 Within this approximation, the $\alpha$-th eigenstate of the Hamiltonian is expanded as

$$|\psi^{(\alpha)}\rangle = \sum_{n,\nu} c^{(\alpha)}_{n,\nu} |n, \nu\rangle + \sum_{n,\nu} \sum_{n',\nu'} c^{(\alpha)}_{n,\nu,n',\nu'} |n, \nu; n', \nu'\rangle,$$

(7.17)

where the coefficients $c^{(\alpha)}_{n,\nu}$ and $c^{(\alpha)}_{n,\nu,n',\nu'}$ can be chosen real. The first term of this expansion represents the one-particle states. A one-particle state $|n, \nu\rangle$ consists of a vibronic (both electronic and vibrational) excitation at chromophore $n$ containing $\nu$ vibrational quanta in the shifted excited-state nuclear potential. For such a state, all other chromophores remain electronically and vibrationally unexcited. The second term represents the two-particle states. In addition to a vibronic excitation at chromophore $n$, a two-particle state $|n, \nu; n', \nu'\rangle$ has a vibrational excitation at chromophore $n'$ containing $\nu'$ vibrational quanta in the ground state nuclear potential ($\nu' \geq 1$). A schematic representation of the two excitation types is shown in Figure 1.10. Inserting the wave function of the $\alpha$-th eigenstate into eq 7.3 leads to an expression for the rotational line strength in terms of the multiparticle coefficients:

$$R_\alpha = k_\lambda d \sum_{n,\nu,\nu'} c^{(\alpha)}_{n,\nu} c^{(\alpha)}_{n',\nu'} f_{\nu\nu} f_{\nu'0} (n - n') \sin(\phi_{mn'}).$$

(7.18)

Here, $f_{\nu\nu} \equiv \langle \nu | \nu\rangle$ is the overlap between the harmonic-oscillator eigenfunction with $\nu$ vibrational quanta in the shifted excited nuclear potential and the eigenfunction with $\nu$ vibrational quanta in the ground state nuclear potential. Equation 7.18 shows that one-particle coefficients contribute directly to the line strength. Two-particle coefficients contribute only indirectly through normalization of the wave function. Taking into account two-particle states is important to describe the in emission spectra, enabling, e.g., the evaluation of the polaron radius from the circularly polarized emission.17 However, in absorption the one-particle basis set produces essentially the same spectral line shapes as obtained with the two-particle basis set.17 Two-particle effects are suppressed when $\sigma/W$ is sufficiently large and the spectra are sufficiently broad,40 which is the case here. Therefore, we will employ the one-particle approximation, using only the first term in eq 7.17.

Like in the previous section, we obtain the CD spectrum $CD_N(\omega)$ of a single aggregate with length $N$ by performing the average eq 7.16 over all conformational states of the aggregate. For each conformational state, we fix the angle between consecutive molecules to the pitch angle $\phi = 14^\circ$ if the bond is helical whereas, just like above, a random angle is assigned to each non-helical bond. Since it is practically unfeasible to perform a diagonalization of the
Hamiltonian for each conformational state, we only perform the diagonalization for the perfectly helical aggregate. We then assume that the introduction of non-helical bonds with a random angle does not influence the excitonic couplings, but only randomizes angles appearing in eq 7.18. We have checked this approximation by repeating the analysis of the previous section, where diagonalization of the Hamiltonian for each conformational state was feasible, using this approximation. In this check we found no discernible deviations from the results presented in Figure 7.5.

We have to carry out an additional averaging over all aggregate lengths $N$ to obtain the total CD spectrum. Each chromophore in an aggregate can absorb a photon and therefore the absorption cross section of an aggregate is proportional to its length. This means that each spectrum of aggregates with length $N$ should be weighed by the probability distribution

$$P(N) = N \rho(N) / \sum_{N=1}^{\infty} N \rho(N).$$

Hence, the total CD spectrum is obtained as

$$\text{CD}(\omega) = \sum_{N=1}^{\infty} P(N) \text{CD}_N(\omega) / N,$$

where we have divided by $N$ because our definition of $\text{CD}_N(\omega)$ already takes into account that the absorption cross section of an aggregate is proportional to its length. In the numerical evaluation of the sum in eq 7.20 we take $10^4$ aggregates with $N \geq 3$ according to the distribution $P(N)$ of eq 7.19. To evaluate the CD spectrum of a single aggregate we consider in our calculations each aggregate that consists of more than $N = 20$ chromophores as an aggregate with size $N = 20$. This approximation is reasonable since the CD spectrum of an aggregate has practically converged for $N > 20$, see Figure 6.7. In addition we need to take into account energetic disorder. For that purpose we generate a disorder configuration for the chromophore transition energies for each aggregate. We then carry out the conformational averaging in eq 7.16 by a Monte-Carlo procedure based on single spin-flip sampling. Starting from a random configuration, an equilibration time of $40N$ Monte-Carlo steps proved sufficient for all temperatures studied. After equilibration we perform 1000 measurements, where $20N$ Monte-Carlo steps are taken between consecutive measurements. With this procedure we obtain a CD spectrum for each temperature.

Figure 7.6a shows calculated CD spectra of self-assembling OPV4 aggregates at different temperatures. The intensity of the CD spectra increases upon lowering the temperature due to the formation of helical assemblies. Figure 7.6b shows the CD intensity of the calculated spectra at $\lambda = 466$ nm as a function of temperature (red symbols). The CD curve obtained is normalized to one at $T = 270$ K and follows almost exactly the mean helicity as predicted by direct application of the helical aggregation theory (blue solid line). We may thus conclude that for OPV it is indeed justified to assume that the magnitude of the CD response scales linearly with both the length of helical assemblies and the mean helicity of an aggregate, and that direct application of the helical aggregation theory for interpreting the optical data is appropriate. We
7.6 Conclusions

Circular dichroism (CD) spectroscopy is an ideal tool for monitoring the self-assembly of helical supramolecular polymers in solution. The experimental CD data gathered may be fitted to an appropriate thermodynamic model to gain insight in the self-assembly mechanism of the supramolecular polymers. Two assumptions are commonly made to relate a thermodynamic model with the experimental CD data, namely that the magnitude of the CD response of helical assemblies scales linearly with their length and that it scales linearly with the mean helicity of an aggregate. In the present chapter, we have checked these assumptions. In the previous chapter, we found that CD in helical assemblies is extremely sensitive to long-range excitonic interactions. As a result of this, the magnitude of the CD response scales only linearly with aggregate length beyond a certain length. Furthermore, there is no simple linear relationship between the magnitude of the CD response and the mean helicity of an aggregate. We found that the CD intensity is weaker if an aggregate with a fixed degree of helicity contains many small helical sequences than if it contains one long helical sequence.

attribute this to the high cooperativity \( (\sigma_C \approx 6 \cdot 10^{-6}, \text{ see Table 2.1}) \) of the helical self-assembly of OPV aggregates. As we have seen already in the previous section, a high cooperativity is essential for the direct application of thermodynamic models to interpret experimental CD data.

Figure 7.6: (a) Calculated CD spectra at different temperatures. Aggregate parameters are \( \omega_0 + D = 2.53 \text{ eV}, \sigma = 85 \text{ meV}, l_0 = 4.5, \omega_0 = 0.172 \text{ eV} \) and \( \lambda^2 = 1.2 \). The parameters for the helical aggregation theory are taken from Table 2.1. (b) Solid blue line: calculated mean fraction of helical bonds versus temperature, as predicted by the helical aggregation theory. Red symbols: CD intensity at a wavelength of \( \lambda = 466 \text{ nm} \) as a function of temperature, obtained from the calculated spectra.
We have developed a simple model that predicts the temperature-dependent CD intensity for helical assemblies forming via isodesmic polymerization. This model takes into account the non-linear scaling of the magnitude of the CD response with the aggregate size. From a comparison of our simple model with the direct prediction of the thermodynamic model for isodesmic polymerization we conclude that the direct application of the thermodynamic model results in an erroneous interpretation of experimental data, since it gives estimates of the polymerization temperature and the bond enthalpy that are too low.

The self-assembly of supramolecular polymers that exhibit a helical transition can be described with the helical aggregation theory introduced in ref 20 and 21. We studied the helical transition in the limit of a large degree of polymerization. For that we calculated the CD intensity as a function of temperature by taking into account all possible configurational states of the aggregate. We compared our results to the mean helicity as predicted by a direct application of the helical aggregation theory and we found that the direct application of helical aggregation theory yields an estimate of the helical transition temperature that is too low when the helical transition is weakly cooperative.

We applied the helical aggregation theory to the specific case of OPV4 in chapter 2, where good agreement was found between the experimental CD data and the theoretically predicted mean helicity. In this chapter we have combined the helical aggregation theory with the disordered Holstein model. The combined theory allows us to calculate the CD spectra at various temperatures. We have compared the calculated CD intensity as a function of temperature to the mean helicity as predicted by the helical aggregation theory. No significant deviations were found, which we attribute to the high cooperativity of the helical self-assembly of OPV aggregates. We conclude that a direct application of thermodynamic models is appropriate to interpret experimental CD data provided that the helical transition is sufficiently cooperative.

References


Chapter 8

Conclusions and outlook

The main goal of the work described in this thesis has been to acquire a better understanding of the optical properties of self-assembling aggregates by confronting fundamental and phenomenological modeling with experimental data. This requires a good insight in the underlying physics of exciton-polarons in supramolecular assemblies and the relation between their optical response and supramolecular structure. For that purpose, helical stacks of chiral oligo-\textit{p}-phenylene-vinylene (OPV) derivatives have received special attention. This supramolecular system has been studied by experimentalists with numerous spectroscopic techniques, where the helicity makes it possible to obtain valuable information using polarized light. Moreover, the well-defined helical structure of this system is ideal for testing theoretical models of energy transport. In the following we will summarize our main conclusions and we will give directions for future studies.

The optical properties of OPV aggregates, in particular absorption, fluorescence, circular dichroism (CD) and the time-dependent polarization anisotropy, can be understood with a fundamental Hamiltonian for the excitons that includes energetic site disorder, excitonic coupling and exciton-phonon coupling. For describing the optical properties of these aggregates at different temperatures it is essential to take into account the size distribution of the aggregates and the stacking disorder as well. It proved possible to include these ingredients with an increasing extent of complexity when required.

Energetic site disorder has a localizing effect on optical excitations and has been taken into account phenomenologically by assuming a Gaussian distribution for the chromophore transition energies (chapter 3 and further). The degree of disorder is revealed mainly in the width of the spectra, whereas the presumed correlation in the disorder turns out to be essential for determining the intensity of the 0–0 emission relative to the sideband emission (chapter 4). Moreover, along with the size distribution of aggregates, energetic disorder turns out to be essential for understanding the red-shift of the fluorescence with decreasing temperature (chapter 3).

The inclusion of stacking disorder is essential for understanding the temperature-dependent magnitude of the CD response (chapter 2 and 7). Stacking disorder affects both the excitonic coupling and the orientation of the molecular transition dipole moments. The latter is crucial as the sudden helical ordering of the molecular transition dipole moments upon cooling leads
to a strong increase of the magnitude of the CD response (chapter 2 and 7). We modeled the temperature-dependent fluorescence under the simplifying assumption that the nearest-neighbor coupling is zero for non-helical bonds (chapter 3). Although this assumption is adequate in this context it is not fundamentally correct because the interaction between chromophores extends further than nearest-neighbors only. In fact, we found that extended excitonic couplings cannot be neglected in quantifying the magnitude of the CD response (chapter 6).

The vibronic progression in the optical spectra of OPV aggregates can be understood within the framework of the disordered Holstein Hamiltonian, which takes into account exciton-phonon coupling as well. This Hamiltonian makes it possible to identify all vibronic peaks in the experimental spectra (chapter 4). By comparison to experiment, all free parameters could be evaluated: the degree of disorder and the correlation therein are determined from the width of the absorption and the relative height of the 0–0 emission, respectively, whereas a fixed (average) aggregate length accounts for the experimental Stokes shift. This aggregate length can be interpreted as the average distance traveled by the exciton until its radiative decay. Our analysis of the steady-state spectra suggests that exciton migration in helical OPV aggregates is an incoherent diffusive process between small coherent domains (chapter 4). Further insight in the dynamics was obtained from our analysis of the experimental time-dependent polarization anisotropy, which could be explained by assuming that transitions between exciton states are induced by coupling of the exciton to low-energy acoustic phonons in the solvent (chapter 5).

We conclude that our goal to explain the optical properties of OPV aggregates has been reached to a fair extent, although some practical choices had to be made when necessary. Providing a full and quantitative explanation of the optical spectra at all temperatures is still a challenge. To achieve both a quantitative description and a more fundamental understanding of the spectra, several issues need to be addressed.

Although energetic site disorder is essential for understanding the optical properties of OPV assemblies, its origin and exact form (for example Gaussian or Lorentzian) remains unknown. If energetic disorder arises from low-energy intramolecular vibrations then the determination of this disorder might be resolved by combining molecular dynamics simulations with quantum-chemical methods to study the fluctuations in the chromophore transition energies.

The spectral line shape of the emission at low temperature is still not completely understood, showing a discrepancy between the experimental and theoretical spectra at the low-energy side. We attributed this to emission from very deep trap sites, which is not included in our modeling so far. Emission from deep trap sites could be included by taking into account the actual relaxation dynamics of the excitons, instead of assuming a Boltzmann distribution for the emitting exciton states. However, such an approach is hampered at the moment by computational limitations, as these calculations require very large basis sets.

Computational limitations also limit our understanding of the optical spectra at higher temperatures, when it is necessary to take into account the stacking disorder. This requires not only sampling over energetic disorder configurations but also over many configurational states, which is computationally expensive. Even more important for a good understanding of the high-temperature spectra is a better insight in the relation between the molecular structure and the corresponding optical spectra. For example, it remains unclear whether the appearance of a shoulder on the low-energy side of the absorption spectrum originates from aggregation or
planarization of the OPV molecules.

The nature of extended excitonic couplings in helical assemblies may be clarified further by analyzing the CD activity of DNA-templated chromophores. DNA-templated self-assembly makes it possible to create helical $N$-mers with a well-defined length. The excitonic coupling between each pair of chromophores within the $N$-mer can then be evaluated by measuring the first spectral moment of the CD spectrum for each template length. This procedure would allow for careful testing of dielectric screening effects as well as more sophisticated models that go beyond pairwise interactions.

Although this thesis concerns the optical properties of self-assembling aggregates, the charge-transport properties of such aggregates are also of major importance for applications in optoelectronic devices. Many attempts to describe charged-polaron motion in organic materials are based on perturbation theory and are limited to the case of a very narrow electronic bandwidth (compared to the nuclear relaxation energy). Our theory for the dynamics of exciton-polarons in OPV aggregates treats excitonic coupling and exciton-phonon coupling on equal footing. We suggest that a similar approach may be followed for studying charged-polaron transport in supramolecular assemblies and organic crystals.
Summary

Exciton-polarons in self-assembling helical aggregates: relating optical properties to supramolecular structure

Supramolecular self-assembly is a very promising bottom-up approach for constructing functional nanomaterials with optoelectronic applications, because it combines the easy processing typical of π-conjugated polymers with the high structural order typical of crystals of π-conjugated small molecules. Since applications for supramolecular assemblies based on π-conjugated molecules require a high degree of control over the position of the molecules, a deep insight in the self-assembly mechanisms of supramolecular systems is a necessity. Optical spectroscopy is an extremely useful tool for monitoring the supramolecular self-assembly of π-conjugated molecules, because optical spectra contain valuable information about the structure of the supramolecular system under investigation. A good understanding of the relation between the optical properties of supramolecular assemblies and their structure is therefore essential for a proper interpretation of the spectroscopic data.

The main goal of this thesis is to obtain a better insight in the relation between the optical properties of self-assembling aggregates and their supramolecular structure. Essential for the understanding of the optical response of supramolecular aggregates is the concept of a Frenkel exciton. In a Frenkel exciton, the electron and hole composing the exciton are located on the same molecule. Due to the soft nature of many organic materials, the presence of an exciton induces a significant rearrangement of the nuclei in the participating molecules. Frenkel excitons in these aggregates are therefore composite particles involving electronic as well as vibronic degrees of freedom. A central theme of this thesis is to obtain a proper understanding of the optical properties of these so-called exciton-polarons. For that purpose, helical stacks of chiral oligo-p-phenylene-vinylene (OPV) derivatives have received special attention. This supramolecular system has been studied by experimentalists with numerous spectroscopic techniques, where the helicity makes it possible to obtain valuable information using polarized light. Moreover, this system is ideal for testing theoretical models of energy transport, because of its well-defined helical structure.

An outline of an existing statistical mechanical theory for the helical self-assembly of supramolecular aggregates is given in chapter 2. The theory is a combination of the standard theory of linear self-assembly and a simple two-state model for the helicity of the bonds between the molecules in the aggregates. This two-state model is based on the Zimm-Bragg theory for the helical transition in conventional polymers and can be mapped onto the well-known Ising
model. The helical aggregation theory is applied to the self-assembly of OPV aggregates and quantitative agreement is found with the experimentally observed circular dichroism intensities.

The helical self-assembly of supramolecular aggregates can be monitored by photoluminescence spectroscopy. In order to provide the interpretation of measured spectroscopic data with a firm theoretical basis, a theory for the photoluminescence of self-assembling supramolecular aggregates is developed in chapter 3. This theory is a combination of the helical aggregation theory, taking into account the influence of mass action and conformational transitions during the self-assembly, and a quantum-mechanical tight-binding model for the optical excitations. Although the quantum-mechanical model does not take into account the coupling of the exciton to the high-energy vibrational mode that causes the clear vibronic progression in the experimental photoluminescence of OPV aggregates, the combined theory does provide a qualitative understanding of the red-shift of the main peak in the experimental photoluminescence and its decreasing intensity upon aggregation.

The photoluminescence of helical OPV assemblies at low temperature, where the assemblies are long and perfectly helical, is studied in chapter 4 by employing the disordered Holstein Hamiltonian. This Hamiltonian includes not only excitonic coupling and energetic disorder, but also the strong coupling of the exciton to the high-energy vibrational mode responsible for the vibronic progression in the photoluminescence and absorption. The dependence of the Stokes shift, the emission line widths, and the ratio of the 0-0 and 0-1 emission peaks in the photoluminescence on aggregate size and disorder are studied. It is demonstrated that the ratio of the 0-0 and 0-1 emission peaks is a reliable probe for energetic disorder and the coherence length of the emitting exciton. Insight in the dynamics of excitons in the helical OPV stacks is acquired by comparing the results obtained to the steady-state experimental absorption and emission spectra, suggesting that exciton migration in these stacks is an incoherent diffusive process between small coherent domains.

In chapter 5 a theory is developed to describe the dynamics of exciton-polarons in helical OPV assemblies. Within this theory, the dynamics of exciton-polarons is described by a Pauli master equation for the exciton populations, where the transitions between the weakly delocalized exciton states are assumed to arise from the weak coupling of the exciton-polarons to low-energy phonons of the solvent and/or the assembly. The theory is able to reproduce the experimental polarization anisotropy in helical OPV aggregates and predicts that exciton-polarons migrate significantly slower with increasing strength of the coupling of the excitons to the nuclear framework over which they travel. Furthermore, it is demonstrated that time-dependent emission spectra exhibit a dynamic Stokes shift and a diminishing 0-0 emission intensity with respect to the sideband emission after initial high-energy excitation, due to relaxation of the exciton-polaron to energetically lower-lying excited states.

Circular dichroism (CD) in supramolecular helical assemblies with long-range excitonic couplings is discussed in chapter 6. Long-range excitonic couplings have almost no influence on absorption, but have a dramatic effect on the magnitude of the CD response. It is found that the magnitude of the CD response retains its extreme sensitivity to long-range excitonic couplings even in the presence of strong energetic disorder and strong exciton-phonon coupling, when excitons are essentially localized on individual molecules. Furthermore, a universal expression for the first moment of the CD spectrum of helical assemblies is derived in terms of a modulated
sum over excitonic couplings, which is independent of the strength of the energetic disorder, the spatial correlation of the disorder, and the strength of the exciton-phonon coupling. This demonstrates that excitonic couplings may be extracted directly from experimental CD spectra, without having information about the energetic disorder and the exciton-phonon coupling. Application of these results to helical OPV assemblies points out that existing theoretical values for the excitonic couplings should be adjusted to obtain agreement with the experimental CD spectrum.

Insight in the self-assembly mechanism of supramolecular polymers can be obtained by fitting experimental CD data with an appropriate thermodynamical model. To relate a thermodynamical model with the experimental CD data it is commonly presumed that the magnitude of the CD response of helical assemblies scales linearly with their length and that it scales linearly with the mean helicity of an aggregate. In chapter 7 it is shown that the magnitude of the CD response scales only linearly with the aggregate length beyond a certain length and that there is no simple linear relationship between the magnitude of the CD response and the mean helicity of the aggregate. Analysis of the consequences of these findings for the interpretation of experimental CD data leads to the conclusion that direct application of thermodynamical models is only appropriate if the helical self-assembly is sufficiently cooperative. This condition is met for helical OPV assemblies, but possibly not for other assemblies.

Finally, in chapter 8 the main conclusions of the thesis are summarized and directions are proposed for future studies.
List of publications

*Circular dichroism of self-assembling helical aggregates*
L. van Dijk, P. van der Schoot, F. C. Spano, P. A. Bobbert
Manuscript in preparation.

*Dynamics of exciton-polarons in helical supramolecular assemblies*
L. van Dijk, F. C. Spano, P. A. Bobbert
Manuscript in preparation.

*Magnetic properties of Fe nanolines fabricated by atom lithography*
Manuscript submitted.

*Extreme sensitivity of circular dichroism to long-range excitonic interactions in helical supramolecular assemblies*
L. van Dijk, P. A. Bobbert, F. C. Spano
*Journal of Physical Chemistry B* 2010, 114, 817-825.

*Theoretical study of fluorescence of self-assembling helical supramolecular aggregates*
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*Optical spectra and Stokes shift in double-stranded helical supramolecular assemblies*
L. van Dijk, P. A. Bobbert, F. C. Spano
Photoluminescence spectra of self-assembling helical supramolecular assemblies: a theoretical study
L. van Dijk, S. P. Kersten, P. Jonkheijm, P. van der Schoot, P. A. Bobbert

Focused ion beam machined nanostructures depth profiled by macrochannelling ion beam analysis
S. M. Orbons, L. van Dijk, M. Bozkurt, P. N. Johnston, P. Reichart, D. N. Jamieson

Macrochannelling: Characterization of nanostructures by ion beam analysis
L. van Dijk, M. Bozkurt, A. Alves, P. N. Johnston, T. J. Davis, P. Reichart, D. N. Jamieson
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Leon
Leon van Dijk is born on September 24th, 1981 in Helmond. After finishing secondary school at the Zwijsen College in Veghel he started in 1999 the study Applied Physics at the Eindhoven University of Technology (TU/e). During his studies he carried out an internship in the Theoretical Atomic Physics and Quantum Electronics group under supervision of prof.dr. B.J. Verhaar and dr.ir. E.G.M. van Kempen in which he investigated whether magnetically detunable three-body Feshbach resonances could exist. He has carried out an international research internship at the Royal Melbourne Institute of Technology and the Micro-Analytical Research Center of the University of Melbourne, Australia, which concerned the characterization of nanostructures with ion beam analysis and was supervised by prof.dr. P.N. Johnston and prof.dr. D.N. Jamieson. His M.Sc. research work was carried out in the Atomic Physics and Quantum Electronics group under supervision of dr.ir. S.J.J.M.F. Kokkelmans and dr.ir. B. Marcelis, which concerned a theoretical study of three- and four-body collisions in ultracold boson-fermion mixtures. In May 2006, he started with his Ph.D. research under supervision of dr. P.A. Bobbert and prof.dr. M.A.J. Michels in the Theory of Polymers and Soft Matter group at the faculty of Applied Physics, TU/e. The most important results of this Ph.D. research are presented in this thesis.