6.1 Introduction

The preparation of low-dimensional supramolecular systems with controlled structure and optical dynamics is a topic of considerable current interest [1, 2]. Such systems may serve as artificial light-harvesters, in analogy to natural antenna complexes in photosynthetic systems [3–5], and as transport wires of electronic excitation energy. In addition, they may be used to create devices with tunable and strongly anisotropic optical properties, such as a strong circular dichroism based on a possible chirality in the supramolecular arrangement. In search of such new materials, the family of substituted 5,5′,6,6′-tetrachlorobenzimidacarbocyanine dyes (Figure 6.1) recently has stirred special interest [6]. This is due to the possibility to tune the morphology of the aggregates formed from these chromophores by (small) changes in their side chains and their environment. Thus, aggregates with planar, spherical, and cylindrical (tubular) morphologies have been prepared [7, 8]. These different shapes give rise to strong variations in the optical properties. These variations do not arise from changes in the electronic structure of the individual chromophores; the side chains and environment hardly affect the \( \pi \) system of a single chromophore [9]. Rather, these variations result from the influence of the side chains and the solvent on the packing of the dye molecules in the aggregates. By influencing the intermolecular interactions and the spatial arrangement of dipole orientations, the packing has a strong effect on the collective optical properties of the molecules within an aggregate.

Thus far it has turned out difficult to relate the changes in the optical properties directly to changes in the microscopic molecular arrangement. The reason is that, although changes in aggregate morphology can be readily observed using cryo-TEM
Structure, spectroscopy, and microscopic model of tubular carbocyanine dye aggregates

In Figure 6.1: Chemical structure of the 5,5',6,6'-tetrachlorobenzimidacarbocyanine dyes with their abbreviated names.

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>Counterion</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₅</td>
<td>C₂H₅</td>
<td>Cl⁻</td>
<td>TTBC</td>
</tr>
<tr>
<td>C₂H₅</td>
<td>(CH₂)₃SO₂⁻</td>
<td>Na⁺</td>
<td>TDBC</td>
</tr>
<tr>
<td>C₈H₁₇</td>
<td>(CH₂)₃COOH</td>
<td>Br⁻</td>
<td>C₈O₃</td>
</tr>
<tr>
<td>C₈H₁₇</td>
<td>(CH₂)₄COOH</td>
<td>Br⁻</td>
<td>C₈O₄</td>
</tr>
<tr>
<td>C₈H₁₇</td>
<td>(CH₂)₂SO₂⁻</td>
<td>Na⁺</td>
<td>C₈S₃</td>
</tr>
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[7, 8, 10], this technique lacks the spatial resolution to give insight into the aggregate structure at the molecular scale. It is the aim of this chapter to present the first detailed exploration of the relation between morphology, structure, and optical properties for one type of tetrachlorobenzimidacarbocyanine aggregates, namely for the tubular ones formed in the case of 1,1'-dioctyl and 3,3'-bis(3-sulfopropyl) substituents (abbreviated by C₈S₃ in Figure 6.1). The reason for our special interest in these tubular aggregates is that they closely resemble the rod elements in the light-harvesting chlorosomes of green bacteria [11–14] and exhibit a rigid wire structure that may be suitable for energy transport.

In order to appreciate the variation of morphologies and related optical properties, it is useful to briefly review recent studies on the aggregates of several of the derivatives of the 5,5',6,6'-tetrachlorobenzimidacarbocyanine chromophore shown in Figure 6.1. The frequently studied dye TDBC (1,1'-diethyl, 3,3'-bis(4-sulfobutyl) substituents) forms sheet-like aggregates [7] that reveal an absorption spectrum dominated by one intense sharp J band centered at 587 nm [15]. On the other hand, the dye C₈O₄ (1,1'-dioctyl and 3,3'-bis(4-carboxybutyl) substituents) forms stacks of bilayered ribbons, with an absorption spectrum that strongly resembles the one of TDBC, although the shape of the J band changes [7]. Finally, the dye C₈O₃, in which just a very small change occurs relative to C₈O₄, namely the 3,3'nitrogen substituents are changed from bis(4-carboxybutyl) to -bis(3-carboxypropyl), self-assembles into superhelical aggregates of tubular strands with a total thickness of a few tens of nanometers and hundreds of nanometers length. Each strand represents a double-wall tubule of total diameter 10–11 nm with a double-wall thickness of 4.0 ± 0.5 nm [7, 10]. We note in passing that double-wall cylindrical aggregates also occur as natural light-harvesting complexes [16]. The optical properties of the C₈O₃ aggregates are very rich: they exhibit four J-type absorption bands [10]. Moreover, it was shown that the addition of short-chain alcohols to a C₈O₃/water solution leads to the formation of thicker and longer superhelices [17], while addition of polyvinyl alcohol (PVA) causes dismantling...
of the superhelices into separate strands with a slightly increased thickness [10]. Alternatively, adding the anionic surfactant sodium dodecyl sulfate to a C8O3/water solution initially gives single-wall tubules, which in the course of several days are twisted into thick multilamellar tubes [8]. All these modifications in the aggregate morphology lead to changes in their optical properties, in particular in the number, positions, and relative strengths of the absorption bands.

The first observation of the C8O3 absorption spectra with two or three J bands was reported in Ref. [18] and, using a simple exciton model, could be directly related to a cylindrical morphology. The polarization of the various exciton transitions relative to the aggregate axis, as could be determined in a stretched polymer film, added support to the model and the assignment of the J bands. As the samples studied in Ref. [18] contained short-chain alcohols in the solution, the C8O3 aggregates were recently re-investigated, now revealing four J bands [10], once again underlining the strong effects of additives on the aggregation process. Aligning the helices in streaming solution showed that three of these bands are polarized parallel to the aggregate alignment and one perpendicular to it. The C8O3 superhelices also exhibit a pronounced CD spectrum [19–21].

In spite of all the previous work, no detailed structural model has been reported that explains the number, positions, polarization directions, and relative strengths of the absorption bands observed for the tubular tetrachlorobenzimidacarbocyanine aggregates. Generic exciton models have been used to explain the rough features of the linear absorption, linear dichroism, and pump-probe spectra [18, 22–24]. Although of interest, these models contained too much freedom to reveal detailed microscopic information, such as the packing of the molecules in the aggregate. This is in sharp contrast to the situation of the tubular aggregates that occur in the chlorosomes of green bacteria, for which the molecular arrangement is known rather well [13, 14] and many of the spectroscopic details have been described successfully using exciton theory [25, 26].

In this chapter, we aim at reaching a similar level of understanding for tubular aggregates formed by one of the 5,5′,6,6′-tetrachlorobenzimidacarbocyanine derivatives. The dye we have studied is C8S3. The reason to study this derivative, instead of C8O3, is that in pure water these chromophores turn out to form isolated double-wall tubules, which are simpler to model than the complicated superhelical arrangements of tubules formed by C8O3. The absence of interactions between individual tubules obviously reduces the number of unknown parameters in the model. We report cryo-TEM data, as well as isotropic and polarized absorption spectra for C8S3 aggregates, and show that an exciton model based on wrapping a brick-layer structure [27–29] for the molecular arrangement on the inner and outer cylinder walls explains the observed spectra. As a result, for the first time a reliable microscopic picture is given of tubular carbocyanine aggregates.

The outline of this chapter is as follows. In Section 6.2 we briefly address the materials used and the sample preparation, as well as the methods to measure the spectra. In Section 6.3 we present the morphology of the C8S3 aggregates as revealed by cryo-TEM and the measured isotropic and polarized absorption spectra. Next, in Section 6.4 we first describe the structure obtained when rolling a bricklayer onto a cylinder wall, then present the exciton Hamiltonian on this structure, give general expressions of the various spectra of interest in terms of the eigenstates of this Hamiltonian, and finally address the incorporation of energetic disorder in the model. Explicit results of the ex-
citon model, in particular tuned to understanding the experimentally obtained spectra for C8S3 aggregates, are presented and discussed in Section 6.5. Finally, in Section 6.6 we present our conclusions.

### 6.2 Materials and methods

The synthesis, purification, and analytical characterization of the dye C8S3 and the other 5,5',6,6'-tetrachlorobenzimidacarbocyanine derivatives is described in detail in Ref. [6]. The dye C8S3 consisting of its betain salt was supplied by FEW Chemicals (Wolfen, Germany) and has been used as received. The molecular mass is 902.8 g/mol. The molar extinction coefficient in dimethyl sulfoxide (DMSO) was found to be $1.40 \times 10^5$ L/(mol·cm).

To form aggregates the dye was dissolved in doubly-distilled deionized water, forming 0.35 mM stock solutions. The samples for cryo-TEM were prepared at room temperature by placing a droplet (10 µL) of the stock solution on a hydrophilized perforated carbon filmed grid (60 s Plasma treatment at 8 W using a BALTEC MED 020 device). The excess fluid was blotted off to create an ultrathin layer (typical thickness of 100 nm) of the solution spanning the holes of the carbon film. The grids were immediately vitrified in liquid ethane at its freezing point ($-184^\circ$C) using a standard plunging device. Ultra-fast cooling is necessary for an artifact-free thermal fixation (vitrification) of the aqueous solution avoiding crystallization of the solvent or rearrangement of the assemblies. The vitrified samples were transferred under liquid nitrogen into a Philips CM12 transmission electron microscope using the Gatan cryoholder and -stage (Model 626). Microscopy was carried out at $-175^\circ$C sample temperature using the microscope’s low dose protocol at a primary magnification of 58300×. The defocus was chosen in all cases to be 0.9 µm, corresponding to a first zero of the phase contrast transfer function at 1.8 nm.

Spectroscopic experiments were performed at room temperature using white light, generated in a 2 mm sapphire plate by pumping with 120 fs 800 nm pulses originating from a 1 kHz Ti:sapphire laser system (Hurricane, Spectra Physics). The energy of the incident light and of the light transmitted through the sample was monitored via a polychromator by an OMA system (Princeton Instruments). The linear dichroism (LD) spectra were calculated as the difference between the absorption spectra measured for light polarized parallel and perpendicular to the direction of an aligning flow. The flow was created by a peristaltic pump (Cole-Parmer’s Masterflex), which pumped the aggregated dye solutions through a 100 µm thick and 1 cm wide fused silica cell. The measurement of the LD spectrum as a function of the flow rate revealed maximum alignment of the aggregates already at relatively low flow rates. For example, saturation of the alignment of pure C8O3 aggregates[10] is reached at a flow rate of about 0.5 cm$^3$/s or a flow velocity of 50 cm/s. The measurements presented here were performed for maximum alignment of the sample, i.e., at a flow rate of about 2 cm$^3$/s.

Fluorescence spectra were recorded using a luminescence spectrometer (Perkin Elmer LS50B). The fluorescence was detected in front face geometry, with excitation and emission slits set at 3 nm. In these experiments, the sample solution was placed in a 0.2 mm fused silica cell.
6.3 Experimental results

6.3.1 Morphology

A representative cryo-TEM micrograph of a fresh 0.35 mM C8S3 solution is shown in Figure 6.2(a). The micrograph clearly reveals tubular aggregates, which are slightly bent and typically several hundreds of nanometers long (bar is 50 nm). Figure 6.2(b) shows a section of such a tubular aggregate at larger magnification (bar is 20 nm), where its double walls are clearly observable. The wall thickness of about 4 nm strongly suggests a packing of dye molecules in a bilayer arrangement. This particular structure can be attributed to the amphiphilic nature of the dye molecule [7]. The strong dispersion forces between the chromophores lead to their stacking within each layer in a plane-to-plane orientation, whereas the attached octyl chains are intercalated between the layers to avoid contact with the surrounding aqueous medium due to the hydrophobic effect. In the electron micrographs, the chromophore layers appear as dark lines, while the interlayer formed by the hydrocarbon chains exhibits less contrast. Upon defocusing, Fresnel diffraction fringes appear at the edges of the tubules. From the calculated optical density profile, tubule diameters of $15.6 \pm 0.5$ nm and $10.8 \pm 0.5$ nm were obtained for the outer and inner chromophore layers, respectively. The tubules are highly monodisperse in diameter.

6.3.2 Linear absorption and fluorescence

In Figure 6.3 isotropic and polarized absorption spectra of the aggregated C8S3/water solution flowed through a 0.1 mm cell are plotted. In addition the dotted line presents the absorption spectrum of C8S3 monomers dissolved in ethanol. From the figure it is evident that the isotropic absorption spectrum of C8S3 aggregates is composed of five bands. We number them from 1 to 5 starting from the lowest energy. As is seen, bands 4 and 5 overlap with the vibronic subbands of the monomer absorption spectrum. Moreover, they exhibit no polarization behavior (this is seen more clearly in Figure 6.4 below). This combination of facts strongly suggest that bands 4 and 5 are
associated with non-aggregated molecules. Henceforth, we will therefore concentrate on bands 1, 2, and 3.

The bands 1, 2, and 3 are red-shifted relative to the monomer absorption spectrum and they are clearly polarized: bands 1 and 2 with maxima at 602 nm and 592 nm, respectively, represent transitions with dipole moments oriented parallel to the direction of alignment of the aggregates (presumably the tubule’s axis), while band 3, centered at 580 nm, corresponds to transitions with dipole moments oriented perpendicular to this axis. We also note that these three bands are narrow compared to the monomer spectrum. The above observations clearly suggest that transitions 1-3 should be associated with excitonic J bands of the C8S3 aggregates.

The LD spectrum, shown in Figure 6.4, clearly reflects the above polarization properties by featuring two positive peaks (1 and 2) and one negative dip (3). The small negative background in the spectral region 500–550 nm either results from an experi-
mental error or it indicates that some weakly allowed transitions with oriented transition dipole moments contribute to the absorption in this spectral region. Returning to Figure 6.3, we also note that the absorption for perpendicularly polarized light is still substantial over the spectral interval where parallel transitions are located and vice-versa. For instance, at around 600 nm the parallel-polarized transition is only reduced by approximately 70% in the perpendicular-polarized spectra. We will return to this in Section 6.5.

In Figure 6.5 the fluorescence spectra of C8S3 aggregates (top panel) and monomers (bottom panel) are presented, along with the corresponding isotropic absorption spectra. Because of the large overlap between the fluorescence and absorption spectra of the aggregates, the shape of the fluorescence spectrum is strongly influenced by reabsorption. Therefore, the fluorescence spectrum was corrected using the equation:

$$I(\lambda) = I_r(\lambda) \frac{-\ln \left[ 10^{-OD(\lambda)} \right]}{1 - 10^{-OD(\lambda)}}, \quad (6.1)$$

where $I(\lambda)$ is the real fluorescence, $I_r(\lambda)$ is the recorded fluorescence, and $OD(\lambda)$ is the optical density of the sample at wavelength $\lambda$.

The two fluorescence bands observed in Figure 6.5 clearly overlap with the absorption bands 1 and 2 of the aggregate. In addition a fluorescence shoulder in the vicin-
ity of 580 nm can be seen. The latter can be related either to the absorption band 3 or to a complicated lineshape of the fluorescence corresponding to band 2. Finally, a broad and weak fluorescence in the spectral region 540–560 nm may originate from non-aggregated molecules (cf. bottom panel of Figure 6.5).

The occurrence of two clear fluorescence peaks, overlapping with the two lowest-energy J bands, gives important information about the underlying origin of the absorption bands 1 and 2. If these two features would originate from excitonic transitions within the same exciton band (i.e., have a common ground state), intra-band exciton relaxation would lead to fast relaxation from state 2 to state 1 and no fluorescence associated with the high-energy absorption band 2 would be observed. Therefore, the two-peak structure of the fluorescence strongly suggests that we are dealing with two weakly coupled exciton manifolds.† Given the double-wall structure revealed by the cryo-TEM data discussed above, it is natural to assume that the bands 1 and 2 should be attributed to two exciton transitions on the inner and outer cylinder, respectively, which are weakly coupled. It is not clear a priori which transition can be associated with the inner cylinder and which one with the outer cylinder (see Section 6.5). The absence of a Stokes shift of the fluorescence peaks relative to the absorption peaks 1 and 2, indicates that these transitions are located at the bottom of the two exciton manifolds involved.

Finally, the weak coupling between the two cylinders, while not giving rise to the formation of one collective exciton band, does result in Förster energy transfer between both cylinders. This is evident from the intensity ratio of the two fluorescence peaks compared to this ratio for the absorption bands. Estimates for the interactions between both cylinders confirm the picture of weakly-coupled cylinders (cf. Section 6.4.2).

6.4 Model and theoretical considerations

6.4.1 Aggregate structure

While the cryo-TEM data give clear insight into the double-wall cylindrical structure of the C8S3 aggregates and the radii of the inner and outer cylinders, the resolution of this technique does not suffice to determine the molecular arrangement within the cylinders. The double-wall structure, however, resembles the planar bilayer structure formed by the closely related C8O4 derivative. Since it is well-accepted that in a planar geometry, cyanine dye molecules self-assemble in a brick-layer structure [27–29, 31–33], it is natural to model the molecular arrangement in the outer as well as the inner cylinder by wrapping a planar brick-layer lattice onto a cylindrical surface of appropriate radius.

Thus, our starting point is the brick-layer model depicted in Figure 6.6, with basis vectors $a_1$ and $a_2$ (see enlargement on lower right-hand side). Each unit cell (brick)

† We note that the observation of two fluorescence peaks at the same positions as the two lowest-energy absorption peaks is not a conclusive proof that we are dealing with two separate exciton bands. At room temperature, thermal equilibrium between the corresponding transitions could equally well give rise to two fluorescence peaks, even if both transitions occur in the same exciton band. A conclusive proof is provided by the observation [30] that pumping in the 602 nm band does not create bleaching of the 592 nm band. In addition, the estimate of the inter-wall interaction in the beginning of Section 6.4.2 lends independent theoretical support to the assumption of two weakly-coupled excitonic manifolds.
6.4 Model and theoretical considerations

is occupied by one C8S3 molecule, with its side-chains perpendicular to the plane of the lattice. The molecular transition dipole has magnitude $\mu$ and is oriented along the molecule’s long axis, which lies in the $a_1$ direction. The length $a$ and width $d$ of the unit cell agree with the length and thickness of the molecule, respectively. An important structural parameter is $s$, which indicates the shift between two adjacent lattice rows in the $a_1$ direction. This shift determines whether the dominant dipole-dipole interaction (the one between two neighboring molecules) is positive or negative, and thereby largely determines whether the aggregate appears as a J or an H aggregate [31]. For the purpose of calculating the intermolecular interactions, we will model the molecules by extended dipoles, i.e., two point charges separated by a distance $l$, as is indicated in the upper right-hand side of Figure 6.6 (see Section 6.4.2 for more details).

We may now wrap the planar brick-layer model onto a cylinder surface to obtain a structural model for the tubular aggregate. Many ways exist to do this, which may be uniquely characterized by the wrapping vector $C$, an example of which is indicated in Figure 6.6. The surface is rolled along the direction of this vector (i.e., the long ($z$) axis of the cylinder is perpendicular to $C$) and its begin and end points should be identified with each other after the rolling process. Hence, the length of $C$ equals the circumference, $C = 2\pi R$ ($R$ the cylinder’s radius). Of course, the consistency of the structure requires that after rolling the bricks at begin and end points exactly overlap,
which imposes the condition that $C$ is a lattice vector:

$$C = t_1 a_1 + t_2 a_2,$$

with $t_1$ and $t_2$ integers. Given the values of $a$, $d$, and $s$, this condition implies that $R$ and the angle $\theta$ between the $z$-axis and $a_1$ (this angle fixes the direction of $C$) cannot take arbitrary values, but may be taken from a discrete set only. Writing out Eq. (6.2) along the directions of $C$ and the $z$-axis, respectively, gives the two relations that define the allowed values for $R$ and $\theta$:

$$\begin{cases}
t_1 a \sin \theta + t_2 s \sin \theta + t_2 d \cos \theta = 2\pi R, \\
t_1 a \cos \theta + t_2 s \cos \theta - t_2 d \sin \theta = 0.
\end{cases}$$

We note that for the aggregates studied in this chapter, the discretization of $R$ takes place in very small steps, making it always possible to find a wrapping vector $C$ that (assuming $a$, $d$, and $s$ are fixed) gives a cylinder radius that agrees with the one observed in cryo-TEM within the experimental error.

In principle the above description completes the general construction of the molecular arrangement in a cylindrical aggregate. In Chapter 3 we have argued that an arbitrary cylindrical aggregate may be modeled as a perpendicular stack of equidistant rings, each containing a fixed number of equidistant molecules ($N_2$) and each next ring rotated with respect to the previous one over a helical angle $\gamma$. This stack-of-rings representation has the big advantage that, in the case of homogeneous aggregates, it allows for a classification of the exciton eigenstates into independent one-dimensional problems, each characterized by a discrete transverse wave number $k_2$. In terms of this wave number, simple selection rules may be derived for the optically allowed exciton bands and their polarization directions (see Section 6.4.2 for some details).

Motivated by these advantages, we will map the cylindrical aggregate defined by the wrapping vector $C$ on a stack-of-rings representation. We will denote by $N_2$ the number of lattice points intersected by $C$ (not double counting the first and last one). $N_2$ is given by the greatest common divisor of $t_1$ and $t_2$: in the example of Figure 6.6, $N_2 = 4$. We now define a new basis vector $a_2' = C/N_2$. The other new basis vector $a_1'$ is then uniquely found from the following conditions: the unit cell must have the same area ($a_1' \times a_2' = a_1 \times a_2$), $a_1'$ should reach a lattice point ($a_1' = p_1 a_1 + p_2 a_2$ with $p_1$ and $p_2$ integers), and the projection of $a_1'$ on $a_2'$ should be smaller than $|a_2'|$. In the new basis ($a_1', a_2'$), the vector $a_2'$ defines the basis vector along rings of $N_2$ equidistant molecules, while $a_1'$ defines the direction along helices linking the set of equidistant rings.

Hence, we have mapped the wrapped surface on a stack of rings. The distance and helical angle between two adjacent rings is given by $h = a_1' \cdot z = adN_2/(2\pi R)$ and $\gamma = a_1' \cdot C/(2\pi R^2)$, respectively. In this representation, each molecule in the cylinder is indicated by the vector $n = (n_1, n_2)$ giving the decomposition on the basis ($a_1', a_2'$).

Assuming that the total cylinder has a length of $N_1$ rings, we have $n_1 = 1, 2, \ldots, N_1$, while $n_2 = 1, 2, \ldots, N_2$. Explicitly, the $x$, $y$, and $z$ components of the molecular position vectors and transition dipole moments are given by the three-dimensional vectors:

$$r_n = \left\{ R \cos [n_1 \gamma + n_2 \phi_2], R \sin [n_1 \gamma + n_2 \phi_2], n_1 h \right\}$$

and $\mu_n = \mu \hat{e}_n$, with $\hat{e}_n$ the unit vector

$$\hat{e}_n = \left\{ -\sin \theta \sin [n_1 \gamma + n_2 \phi_2], \sin \theta \cos [n_1 \gamma + n_2 \phi_2], \cos \theta \right\},$$
6.4 Model and theoretical considerations

with $\phi_2 = 2\pi / N_2$.

6.4.2 Exciton Hamiltonian, eigenstates, and spectra

We will model the optically active electronic states of the tubular aggregates using a Frenkel exciton Hamiltonian. In this Hamiltonian, we will neglect the possibility of exciton formation between the inner and the outer cylinder, i.e., for the purpose of calculating the coherent exciton states, we will consider the cylinders as electronically decoupled. This is motivated from the experimental observations on the fluorescence spectrum described at the end of Section 6.3. To give further support to this picture, we note that the dipole-dipole interaction between a molecule in the inner cylinder and one in the outer cylinder (taking dipoles of 11.4 Debye, cf. Section 6.5) has the maximum value (for parallel orientation and minimal distance) of 45 cm$^{-1}$, which is small compared to the observed linewidth of 150 cm$^{-1}$ of the absorption bands. This suggests that, indeed, exciton transfer between both cylinders happens via an incoherent Förster mechanism. This transfer will be the topic of a forthcoming study. For the purpose of calculating linear optical spectra, however, this transfer is not of relevance and we will simply model the spectra of the C8S3 tubules as the sum of spectra generated independently by the inner and outer cylinder.

In this section, we will thus consider the Frenkel exciton Hamiltonian and the formal results for its states and spectra for a single cylinder with the molecular positions and transition dipoles as described in Section 6.4.1. Setting $\hbar = 1$, this Hamiltonian reads

$$H_0 = \sum_n \omega_n b_n^\dagger b_n + \sum'_{n,m} J(n - m) b_n^\dagger b_m,$$

(6.6)

where $b_n^\dagger$ and $b_n$ denote the Pauli operators for creation and annihilation of an excitation on molecule $n$, respectively [34–36]. Here, the first term describes the molecular excitation energies, where in principle we allow for disorder in the molecular transition frequencies. The second term accounts for the excitation transfer interaction $J(n - m)$, where the prime on the summation excludes the term with $n = m$. We have assumed that this interaction follows the symmetry of the lattice, so that it only depends on the relative positions of the molecules. $J(n - m)$ will be modeled by the interaction between the extended transition dipoles of the molecules $n$ and $m$: each dipole is represented as two point charges, $-Q$ and $Q$ separated by a distance $l$ (Figure 6.6) and the four interactions between the charges of the molecules involved give the value for $J(n - m)$. Explicitly, we obtain:

$$J(n - m) = A \frac{\mu^2}{l^2} \left[ \frac{1}{r_{+n+}^{+n+}} - \frac{1}{r_{+n+}^{+n+}} - \frac{1}{r_{+n+}^{+n+}} + \frac{1}{r_{+n+}^{+n+}} \right],$$

(6.7)

where we used $\mu = Ql$ and defined

$$r_{+n+}^{+n+} = |r_{nm} \pm l(\hat{e}_n - \hat{e}_m)|/2|,$$

(6.8)

$$r_{+n+}^{+n+} = |r_{nm} - l(\hat{e}_n + \hat{e}_m)|/2|,$$

(6.9)

$$r_{+n+}^{+n+} = |r_{nm} + l(\hat{e}_n + \hat{e}_m)|/2|,$$

(6.10)
with \( \mathbf{r}_{nm} = \mathbf{r}_{n} - \mathbf{r}_{m} \). The vectors \( \mathbf{r}_{n} \) and \( \hat{\mathbf{e}}_{n} \) are given by Eqs. (6.4) and (6.5), respectively. Finally, \( A = 5.04 \text{ cm}^{-1} \text{ nm}^3/\text{Debye}^2 \).

The exciton eigenstates of the general Hamiltonian Eq. (6.6) take the form

\[
| q \rangle = \sum_{n} \varphi_{q}(n) b_{n}^{\dagger} | g \rangle ,
\]  

(6.11)

where \( | g \rangle \) denotes the state with all molecules in their ground state, \( q \) is a general quantum label, and the \( \varphi_{q}(n) \) denote the eigenvectors of the \( N \times N \) matrix spanned by the Hamiltonian within the one-exciton subspace (\( N = N_{1}N_{2} \)). The corresponding eigenvalues \( E_{q} \) give the energy of the state with label \( q \).

The general expressions for the absorption and linear dichroism spectra in terms of these eigenvectors and eigenvalues are obtained through standard derivations. We will use the formal expressions for these spectra given in Chapter 5. Without further derivation, we repeat the expressions. For the absorption spectrum taken in an isotropic sample we have

\[
A(\omega) = \sum_{q} O_{q} \delta(\omega - E_{q}) ,
\]  

(6.12)

with the oscillator strengths

\[
O_{q} = \left\langle \sum_{n} \varphi_{q}(n) \mathbf{\mu}_{n} \cdot \mathbf{e} \right\rangle^{2} = \sum_{n,m} \varphi_{q}(n) \varphi_{q}^{*}(m) \langle (\mathbf{\mu}_{n} \cdot \mathbf{e}) (\mathbf{\mu}_{m} \cdot \mathbf{e}) \rangle .
\]  

(6.13)

Here \( \langle \ldots \rangle \) represents the isotropic average over the orientations of the cylinder with respect to the polarization vector \( \mathbf{e} \) of the exciting light, and \( * \) indicates complex conjugation. The spectrum is a series of peaks at exciton eigenfrequencies, with weights given by the oscillator strengths. Furthermore, assuming that the cylinders are perfectly aligned along their \( z \)-axes, the linear dichroism spectrum is given by:

\[
LD(\omega) = \sum_{q} L_{q} \delta(\omega - E_{k}) ,
\]  

(6.14)

with

\[
L_{q} = \sum_{n,m} \varphi_{q}(n) \varphi_{q}^{*}(m) \left[ (\mathbf{\mu}_{n} \cdot \mathbf{z}) (\mathbf{\mu}_{m} \cdot \mathbf{z}) - \langle (\mathbf{\mu}_{n} \cdot \mathbf{e}_{\perp}) (\mathbf{\mu}_{m} \cdot \mathbf{e}_{\perp}) \rangle \right] ,
\]  

(6.15)

where in the last term \( \langle \ldots \rangle \) denotes the average of the polarization vector \( \mathbf{e}_{\perp} \) over all orientations within the \( xy \) plane of the cylinders.

In the general case of disordered aggregates, the expressions for the spectra Eqs. (6.12) and (6.14) have to be averaged over the disorder realizations and their calculation in general requires a fully numerical analysis. This is mostly done through a brute-force simulation of disorder realizations followed by numerical diagonalization of the thus generated random exciton Hamiltonians. A numerically less expensive alternative is using the coherent potential approximation (CPA) [37, 38], which generally gives very good results for linear absorption spectra (see, e.g., Refs. [31, 39, 40]). As a full simulation of cylindrical aggregates involves diagonalizing large matrices (since
each C8S3 cylinder contains thousands of molecules), we have used the CPA to calculate spectra that account for disorder; several results will be presented in Section 6.5. More details of these calculations and the excellent agreement of the CPA results with numerically simulated absorption and LD spectra for cylindrical aggregates, were presented in Chapter 5.

To end this section, we address the exciton states and spectra in the absence of disorder, i.e., \( \omega_n = \omega_0 \) for all \( n \). The motivation to consider this limit is that it allows for analytical solutions of the exciton states and thus provides simple insights into the type of spectra that may be expected. This limit thus offers important guidance to fit experimental spectra (cf. Section 6.5).

In the homogeneous case, the label \( q \) may be replaced by a two-dimensional label \( k = (k_1, k_2) \) [Chapters 3 and 5]. The cylindrical symmetry dictates a Bloch form for the dependence of the exciton wave function \( \sim \exp \left[ ik_2 \phi_2 n_2 \right] \), with the transverse quantum number \( k_2 = 0, \pm 1, \ldots, \pm (N_2/2 - 1), N_2/2 \) on the position \( n_2 \) of the molecule in its ring. This may be used to break down the cylinder’s exciton Hamiltonian into \( N_2 \) independent effective Hamiltonians for linear systems of length \( N_1 \) [Chapter 3]. Only transitions from the cylinder’s ground state to states with \( k_2 = 0 \) or \( k_2 = \pm 1 \) may show up in the absorption or linear dichroism spectra. Transitions to the \( k_2 = 0 \) band are always polarized along the long (z) axis of the cylinder and will give rise to positive peaks in the LD spectrum. Transitions to the \( k_2 = \pm 1 \) bands (which are degenerate) are polarized perpendicular to the z axis and lead to negative peaks in the LD spectrum.

If we are dealing with long cylinders, the effective one-dimensional Hamiltonians that result from the decomposition into \( k_2 \) bands may be diagonalized by imposing periodic boundary conditions, i.e., by identifying top and bottom of the cylinder with each other. The eigenstates are then given by

\[
\varphi_k(n) = \frac{1}{\sqrt{N}} \exp \left[ i(k_1 \phi_1 + k_2 \phi_2) \right],
\]

with \( \phi_1 = 2\pi/N_1 \) and \( k_1 = 0, \pm 1, \ldots, \pm (N_1/2 - 1), N_1/2 \). The corresponding eigenenergy is given by

\[
E_k = \omega_0 + \sum_n' J(n) \cos(k_1 \phi_1 + k_2 \phi_2),
\]

where \( J(n) \) is the interaction Eq. (6.7) for two molecules separated by a relative position vector \( n \) and the prime on the summation excludes the term with \( n = 0 \). The summations over \( n \) must be made in a way consistent with the periodic boundary conditions. In particular, the summation over \( n_1 \) extends over \( -N_1/2 + 1, -N_1/2 + 2, \ldots, N_1/2 - 1, N_1/2 \).

As has been shown in Chapter 3, if we impose periodic boundary conditions only three states contribute to the absorption and LD spectrum. These are the states \((k_1, k_2) = (0, 0)\), polarized along the z axis and having energy

\[
E_0 = \omega_0 + \sum_n' J(n),
\]

\footnote{The upper boundary holds in case \( N_2 \) is even. If it is odd, \( k_2 = 0, \pm 1, \ldots, \pm (N_2 - 1)/2 \).}
and the degenerate states \((k_1,k_2) = (\pm N_1 \gamma/2\pi, \pm 1)\), which are polarized perpendicular to the \(z\) axis and have energy

\[
E_h = \omega_0 + \sum_n' J(n) \cos[\gamma n_1 + \phi_2 n_2].
\]  

(6.19)

The fact that only three dipole-allowed transitions occur leads to very simple spectra (cf. Chapter 3):

\[
A(\omega) = N \mu^2 \frac{2}{3} \left[ \cos^2 \theta \delta(\omega - E_0) + \sin^2 \theta \delta(\omega - E_h) \right]
\]  

(6.20)

and

\[
LD(\omega) = N \mu^2 \left[ \cos^2 \theta \delta(\omega - E_0) - \frac{1}{2} \sin^2 \theta \delta(\omega - E_h) \right].
\]  

(6.21)

The only numerical step involved in calculating these spectra are the summations in Eqs. (6.18) and (6.19).

We end this section by noting that, as we have seen in Chapter 4, alternative analytical expressions for the exciton wave functions may be obtained that do account for a finite cylinder length and open boundary conditions. Since the cylinders considered here are very long, we will not pursue that alternative route.

6.5 Numerical results and comparison to experiment

We will now use the model presented in Section 6.4 to analyze the experimental spectra reported in Section 6.3.2. Here, our main goal will be to see whether the wrapped brick-layer model may in principle explain the type of spectra that were measured and, if so, what structural model parameters for inner and outer cylinders give a good reproduction of the experimental spectra.

As argued in Section 6.3.2, three exciton bands (1-3) seem to dominate the aggregate spectra, the ones at 602 nm and 592 nm polarized along the cylinder’s long axis and the one at 580 nm polarized perpendicular to it. We will use the model results Eqs. (6.20) and (6.21) as guidance to perform the analysis, where it should be kept in mind that the inner and outer cylinder both contribute an absorption and LD spectrum of this type (one parallel and one perpendicular peak) to the total spectrum. This leads one to tentatively identify the two parallel bands with the parallel transitions of the inner and outer cylinder, respectively, while the single rather broad perpendicular band observed at 580 nm may result from the fact that the perpendicular transitions of both cylinders happen to be very close in energy. In recent experiments on the optical properties of aggregates of the dye C8O3, also two low-energy absorption bands were observed with parallel polarization [10]. The higher-energy one of these (corresponding to our transition 2) showed a much stronger sensitivity to changes in the solvent than the lowest-energy band. The same observation was made for the fluorescence bands associated with these two transitions [10]. This strongly suggests that the lowest (highest) parallel transition should be associated with the inner (outer) cylinder. The similarity of the dye C8O3 to the dye C8S3 considered here, as well as the similar morphology of both aggregates [10], suggests that this assignment may be transferred to
the C8S3 aggregates. We therefore attribute band 1 (at 602 nm) to an exciton transition in the inner cylinder and band 2 (at 592 nm) to a transition in the outer cylinder.

We now turn to the description of the various system parameters that are either fixed (known from other sources) or free for fitting purposes. To start with, we discuss the structural parameters, \( R, a, d, s, \) and \( \theta \). The cylinder radii were determined from the cryo-TEM experiments reported in Section 6.3.1: \( R = 7.8 \) nm for the outer cylinder and \( R = 5.4 \) nm for the inner one. We will accept these values as basically fixed, realizing that small deviations (well within the experimental error, \textit{vide infra}) will be necessary in order to accommodate the discrete character of \( R \) imposed by the underlying brick-layer lattice (see Section 6.4.1). The unit cell dimensions match the size of the chromophore and are fixed at \( a = 2.0 \) nm [27, 28] and \( d = 0.4 \) nm [27]. The two remaining structural parameters, \( s \) and \( \theta \), are not known a priori and will be used as free fit parameters.

The other system parameters are the energetic ones \( \omega_0, Q, \) and \( l \). For the former we use \( \omega_0 = 18868 \) cm\(^{-1} \), which agrees with a single-molecule 0-0 transition at 530 nm (cf. Figure 6.5). The parameters \( Q \) and \( l \) together describe the extended dipole that mediates the intermolecular transfer interactions \( J(n - m) \). We take a separation between the charges of \( l = 0.7 \) nm and a charge \( Q = 0.34e \) (with \( e \) the electron charge). These values were obtained from semi-empirical calculations [41] and are in good agreement with the ones obtained for similar dye molecules [28, 42]. Combined, these parameters give a single-molecule transition dipole moment of \( \mu = 11.4 \) Debye.

We are thus left with two free parameters, \( s \) and \( \theta \), to fit the experimental results. Although one does not expect very different values for these parameters for the inner and outer cylinder, the larger curvature of the inner one may lead to small discrepancies. For each cylinder, we have to fit the position of the parallel transition as well as the separation between the parallel and the perpendicular one. Having two independent free parameters per cylinder allows us to do this. Moreover, the ratio of oscillator strengths in the three observed absorption and LD bands should be reproduced, for which no extra free parameters are available.

As we will explain in some detail at the end of this section, the position \( E_0 \) of the parallel transition is almost independent of \( \theta \), due to the fact the cylinders exhibit a small curvature on the scale of a few lattice unit cells. As this position strongly depends on \( s \) through the nearest-neighbor interaction, \( s \) may be obtained from fitting it to experiment. On the other hand, we will also show that the detuning \( E_h - E_0 \) between the parallel and the perpendicular transitions of a given cylinder strongly depends on \( \theta \), implying that this quantity may be used to determine \( \theta \) once \( s \) has been obtained.

These properties greatly help in establishing relations between structure and spectra and simplify finding values for \( s \) and \( \theta \) that give a good match between positions, oscillator strengths, and polarization directions of the exciton transitions in the model with the bands 1-3 found in the experiment of Figure 6.4. Figure 6.7 gives the model absorption and LD spectra for such a favorable choice of parameters: \( s = 0.242a \) and \( \theta = 43.0^\circ \) for the outer cylinder and \( s = 0.252a \) and \( \theta = 47.4^\circ \) for the inner one. The finite linewidths in this figure were obtained by convoluting the theoretical stick spectra Eqs. (6.20) and (6.21) with a Lorentzian lineshape with full width at half maximum of 150 cm\(^{-1} \) (homogeneous broadening) and transforming to a wavelength scale: \( A(\lambda) = A(\omega)d\omega/d\lambda \) and analogous for the LD. The stick spectra account for all dipole-dipole interactions within each cylinder.
Figure 6.7: Calculated absorption (solid) and LD (dashed) spectra for a homogeneous system of two noninteracting concentric cylindrical aggregates in the infinite-length limit, with model parameters as given in Table 6.1. The spectra were calculated by convoluting the stick spectra Eqs. (6.20) and (6.21) with Lorentzians of FWHM = 150 cm$^{-1}$. The sticks shown give the LD strength of the underlying exciton transitions, with solid (dashed) sticks associated with the outer (inner) cylinder. Positive sticks result from states with $k_2 = 0$ and negative ones from those with $k_2 = \pm 1$.

Comparing Figs. 6.4 and 6.7, we observe that the general features of the experimental absorption and LD spectra are explained rather well by the simple homogeneous double-wall cylinder model. The main discrepancy is related to band 3, whose width is underestimated in the model result. It is clear from the stick spectra that, indeed, this band results from close lying perpendicular transitions in the inner and the outer cylinder. The LD dip associated with these transitions, while occurring at the correct frequency, is somewhat overestimated by the homogeneous model. Nevertheless, it is clear that this simple model captures the main features of the spectra, giving support to the structural model and parameters.

For convenience, a summary of the model parameters used is given in Table 6.1, where we also give the fine-tuned values for the cylinder radii of $R = 7.833$ nm and $R = 5.455$ nm that conform with the discreteness condition Eq. (6.3). Within the experimental errors, these values indeed show excellent agreement with the cryo-TEM results of Section 6.3.1. The number of molecules $N_2$ per ring is 5 in the outer cylinder and 2 in the inner one. These numbers are so low, because of the low commensurability of the coordinates $t_1$ and $t_2$ of the rolling vector $C$; the values for the interring separation $h$ are correspondingly small (0.081 nm and 0.047 nm, respectively). As a consequence, the $N_2$ numbers, while useful for theoretical analysis, do not give intuitive insight into the typical number of molecules one encounters when going around the cylinder’s circumference once. This intuition is easier to obtain from the number of molecules on the cylinder surfaces per nm length of the cylinder, given by $2\pi R/\alpha d = N_2/h$. These numbers are 62 for the outer cylinder and 43 for the inner one.

The purely homogeneous model considered thus far, while giving very reasonable results, oversimplifies reality. In general the linewidth of aggregate spectra obtains important contributions from static disorder, which also localizes the exciton wave functions on parts of the cylinder surface. The opposite extreme of the purely homogeneous
Table 6.1: Summary of model parameters that generate the spectra in Figure 6.7, where disorder is neglected and stick spectra are convoluted with Lorentzians of FWHM 150 cm\(^{-1}\). The same parameters, except that \(\omega_0\) is changed to 19194 cm\(^{-1}\), generate Figure 6.8, where diagonal disorder of standard deviation 670 cm\(^{-1}\) is used to generate spectral linewidths.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>inner cylinder</th>
<th>outer cylinder</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R)</td>
<td>5.455 nm</td>
<td>7.833 nm</td>
</tr>
<tr>
<td>(a)</td>
<td>2.0 nm</td>
<td>2.0 nm</td>
</tr>
<tr>
<td>(d)</td>
<td>0.4 nm</td>
<td>0.4 nm</td>
</tr>
<tr>
<td>(s)</td>
<td>0.488 nm</td>
<td>0.508 nm</td>
</tr>
<tr>
<td>(\theta)</td>
<td>47.4(^\circ)</td>
<td>43.0(^\circ)</td>
</tr>
<tr>
<td>(\omega_0)</td>
<td>18868 cm(^{-1})</td>
<td>18868 cm(^{-1})</td>
</tr>
<tr>
<td>(l)</td>
<td>0.7 nm</td>
<td>0.7 nm</td>
</tr>
<tr>
<td>(Q)</td>
<td>0.34e</td>
<td>0.34e</td>
</tr>
</tbody>
</table>

Figure 6.8: As Figure 6.7, except that now the linewidths derive from static diagonal disorder of standard deviation \(\sigma = 670\) cm\(^{-1}\). The spectra were obtained using the coherent potential approximation (CPA) in the limit of long cylinders.

broadening considered above is a model in which the exciton linewidth solely derives from static disorder. To consider this situation, we calculated the absorption and LD spectra allowing for diagonal disorder. Here \(\omega_n = \omega_0 + \epsilon_n\), with the \(\epsilon_n\) chosen independently from a Gaussian distribution with standard deviation 670 cm\(^{-1}\). The model parameters were kept identical to those in Table 6.1, except that the average molecular transition frequency was shifted to 19194 cm\(^{-1}\) (521 nm) to compensate for the disorder-induced shift of the band-edge exciton transitions. We note that the disorder strength is small compared to the exciton band width of about 4000 cm\(^{-1}\) for both the inner and outer cylinder, implying that the exciton states are still considerably delocalized. This is confirmed by calculating the inverse participation ratio [43, 44], which indicates that the exciton states contributing to the maxima of the parallel absorption peaks are shared by several tens (30–40) of molecules.

The spectra resulting from the model with diagonal disorder, calculated using the CPA, are shown in Figure 6.8. We observe the same general features of the spectra as
for the homogeneous case, but the disorder creates a better resemblance of the line-
shape to the measured spectra in Figure 6.4. We see in particular that band 3 obtains
a larger disorder-induced width than bands 1 and 2, which agrees with the experi-
ment; also the LD dip related to band 3 now agrees much better with experiment.
Overall, the model with static diagonal disorder generates a remarkable similarity to
experiment. A remaining discrepancy is that the experimental spectra in Figure 6.3
show substantial absorption for perpendicularly polarized light in the interval where
parallel transitions are located and vice versa, while the theoretical spectra for both
polarizations (not shown) do not reveal this effect. This may be explained either from
the fact that the cylinders are not perfectly oriented in the polarization dependent ex-
periments, or from a deformation of the cylinder’s circumference from a perfect circle.
The lowest-symmetry deformation (of wavelength $2\pi R$) mixes the states in the paral-
lel and perpendicular bands of each cylinder and thus leads to transfer of polarization
from one band to the other (cf. Refs. [45, 46]). Using an analysis similar to Ref. [46],
we have estimated that small deformations of this type (of the order of several percent)
may explain the experimental observations.

At the end this section, we return in more detail to the role of the free parameters $s$ and $\theta$ on the position of the parallel and perpendicular transitions for homogeneous
aggregates. As mentioned above, this provides insight into the relation between struc-
ture and spectrum and simplifies finding fit parameters.

Let us first consider the position of the parallel transition, which in the model is ob-
tained as $E_0$ defined in Eq. (6.18). Owing to the fact that the cylinders’ circumferences
are much larger than the molecular dimensions, the curvature of the surface in the local
surroundings of a molecule is small, even for the inner cylinder. As the interactions to
nearest-neighbors in the local environment of a molecule contribute most to the sum-
mation in Eq. (6.18), we conclude that the position of the parallel band should hardly
depend on the fact that the brick-layer lattice is wrapped, i.e., it hardly depends on the
angle $\theta$. Rather it depends on the planar geometry of the underlying brick-layer lattice,
which is determined by $a$ and $d$ (both fixed) and $s$ (free). In fact, it is well-known that
the position of the absorption band of two-dimensional $J$ and $H$ aggregates sensitively
depsends on $s$, as it has a strong influence on (even the sign of) the nearest-neighbor
interactions [31]. Thus, if $a$ and $d$ are given, the position of the parallel band may be
used to find the value for $s$. We note that the detuning of 10 nm for the two parallel
transitions cannot be explained from a difference in curvature of the inner and outer
cylinders and requires accepting different $s$ values.

While the position of the parallel transition hardly depends on $\theta$, the situation is
different for the perpendicular transition. This is clear from the fact that this transition
is associated with the wave vector $k = (\pm N_2 \gamma / 2\pi, \pm 1)$, which depends on $N_2$ and on
the helical angle $\gamma$, which in turn both depend on $\theta$ (cf. Section 6.4.1). Using only the
dominant interaction in the summations in Eqs. (6.18) and (6.19), which usually is the
one between two neighboring molecules connected by the lattice vector $a_2$ in the brick-
layer lattice, allows us to estimate the detuning between the perpendicular and parallel
transitions of the individual cylinders. We thus restrict ourselves to $j = j(n_1, n_2)$ with
\[ n_1 a_1' + n_2 a_2' = a_2. \]
Projecting the latter identity on the $C$ direction and dividing by $R$, yields:
\[ n_1 \gamma + n_2 \phi_2 = \frac{s \sin \theta + d \cos \theta}{R}, \] (6.22)
where the left-hand side is exactly the argument of the cos in Eq. (6.19). From this, we find

\[ E_h - E_0 = 8J \sin^2 \left( \frac{s \sin \theta + d \cos \theta}{2R} \right). \]  

(6.23)

If \( n_1 \) or \( n_2 \) equals 0, i.e., if \( a_2 \) happens to coincide with one of the new lattice vectors, the pre-factor 8 should be replaced by 4. The interesting aspect of Eq. (6.23) is that it is a monotonic function of \( \theta \) over the interval \([0, \arctan (s/d)]\) with a value of \( 8J \sin^2 (d/2R) \) at \( \theta = 0 \) and a maximum value of \( 8J \sin^2 (\sqrt{s^2 + d^2}/2R) \) at \( \theta = \arctan (s/d) \). Above, when fitting the experimental spectra using the homogeneous model, we have used this property to perform an efficient search for the optimal \( \theta \) values.

### 6.6 Conclusions

In this chapter, using a combination of cryo-TEM, optical spectroscopy, and theoretical techniques, we have built a microscopic model for the tubular self-assembled aggregates of C8S3 dye molecules in water. The wall of the tubules possesses a double-layer structure, which is a consequence of the amphiphilic nature of the dye molecule. Cryo-TEM reveals diameters of 10.8 ± 0.5 nm and 15.6 ± 0.5 nm for the constituting inner and outer chromophore layers, respectively. In our theoretical analysis, both layers are modeled as brick-layer lattices wrapped on a cylindrical surface. Each unit cell of the lattice is occupied by one molecule. The collective excitations of the molecules, resulting from intermolecular dipole-dipole interactions, are described within a Frenkel exciton model. This microscopic model for the aggregate’s structure and collective excitations explains all experimental observations and allows us to determine the structural parameters \( s \) (lattice shift) and \( \theta \) (wrapping angle) that have thus far not been determined by other means (cf. Table 6.1).

The model leads to two dominant exciton bands for each cylinder, one polarized parallel to the cylinder’s axis, and one perpendicular to it. We have shown that the position of the parallel band may be used to determine \( s \) from experiment, while the detuning between the parallel and the perpendicular band is sensitive to \( \theta \). Our final model results, which include the effect of diagonal disorder, show a good agreement with experiment, in which three exciton bands can be discerned: two parallel ones, one deriving from each layer, and one broader perpendicular one, which derives from overlapping transitions in both layers. The delocalization area of the optically dominant exciton wave functions is estimated to be several tens of molecules, which, not surprisingly, is smaller than the low-temperature value of about 100 molecules obtained from pump-probe experiments [22, 24].

As noted in Section 6.1, the morphology and spectral properties of the substituted 5,5′,6,6′-tetrachlorobenzimidacarbocyanine dye aggregates depends on the particular attached side groups as well as the solvent. Within the class of tubular aggregates, however, generic features seem to exist, in particular the occurrence of two lowest-energy parallel J bands and one higher energy perpendicular band. Exact positions and strengths of these transitions are influenced by the choice of side groups and solvent. This suggests that all these aggregates have the same basic structure, however, with changes in the values of the structural parameters. For instance, the addition of
methanol during aggregation of C8S3 in aqueous solution gives rise to different tubular aggregates. In a forthcoming publication, a systematic study of the effect of preparation conditions on the aggregates’ morphology and spectroscopy will be presented. There we will also address the CD spectrum. This spectrum seems ideal to further pinpoint the chiral structure of the aggregates and test our model. Experiments reveal, however, that the CD spectrum is extremely sensitive to sample preparation (even to the sample’s concentration). At the same time, the calculated CD spectra sensitively depend on the model parameters. In fact, it turns out that within the range of parameters that give good fits for the absorption and LD spectra, the experimental variety of CD spectra may be covered completely.

A most interesting perspective of the tubular tetrachlorobenzimidacarbocyanine aggregates is the possibility to use them as nanometer scale wires for energy transport. Obtaining more insight into this aspect requires investigating the exciton dynamics. This will be done in a forthcoming publication, in which we will present results of time-resolved fluorescence and pump-probe spectroscopy, as well as calculations of the dynamics based on the same structural model as presented above. These studies should also cast light on the contribution of intraband and interband exciton relaxation to the width of the absorption peak 3 (the perpendicular transitions). The best calculated spectrum (Figure 6.8) still overestimates the height of this peak and seems to underestimate its width (cf. Figure 6.3). The lack of a detailed description of relaxation in our present model may well be the cause of this discrepancy.
References