Unraveling optical signatures of tubular aggregates altered with halogen exchange

In the field of self-assembly, the quest for gaining control over the supramolecular architecture without affecting the functionality of the individual molecular building blocks is intrinsically challenging. By using a combination of synthetic chemistry, cryogenic transmission electron microscopy, optical absorption measurements, and exciton theory, we demonstrate that halogen exchange in carbocyanine dye molecules allows for fine-tuning the diameter of the self-assembled nanotubes formed by these molecules, while hardly affecting the molecular packing determined by hydrophobic/hydrophilic interactions. The findings of this chapter open a unique way to study size effects on the optical properties and exciton dynamics of self-assembled systems under well-controlled conditions.

2.1. Introduction

Molecular self-assembly has proven to be a versatile tool in nanotechnology, as it allows for the autonomous and reproducible assembly of a wide variety of low-dimensional functional systems, extending in size from 10’s of nanometers to microns. A key challenge in the field of self-assembly is to control the shape and size of the final supramolecular structure with minimal changes of the molecular entities that provide the functionality essential for potential applications. As the structure of the final assembly is encoded in each individual building block, any modification becomes a highly non-trivial task that requires fine-tuning at the molecular level. It has been shown that tailoring non-covalent molecular interactions such as π-stacking, hydrogen bonding, halogen bonding, or hydrophobic/hydrophilic interactions provides powerful approaches in directing self-assembly. The coordinating nature of hydrophobic/hydrophilic interactions is of special interest, as it may be utilized to tune the supramolecular structure by solely changing the hydrophilic or hydrophobic side groups of the molecules without affecting their functional cores. Indeed, variations of size and composition of the amphiphilic substituents have been used to change between various structures, such as micelles and bilayers, which is often accompanied by changes in the molecular packing. In this chapter, we show that even more subtle modifications, namely just replacing a few halogen atoms, may be used to complement hydrophobic/hydrophilic interactions for fine control over the characteristic size of a self-assembled structure, while preserving the molecules’ functional properties and their supramolecular packing.
We demonstrate this control of self-assembly for a class of tubular molecular aggregates of amphiphilic carbocyanine molecules that recently have attracted considerable interest for their optical functionality. The close packing of the optically active carbocyanine molecules within the aggregates gives rise to efficient excitation energy transfer and collective optical effects caused by exciton states shared by many molecules. Changing the amphiphilic side groups results in a wide variety of different supramolecular structures, of which double-walled tubular structures with a diameter in the order of 10 nm have attracted the most attention. The strong interest in these tubular aggregates stems from their structural resemblance to the light-harvesting antennae of photosynthetic green sulfur bacteria, which are the most efficient photosynthetic organisms known. Also, the potential of the tubular aggregates as quasi-one-dimensional energy transport wires is of great interest. Previous attempts to control the diameter of tubular aggregates, including changing solvents or adding surfactants yielded only limited variations of the diameter and often completely changed the supramolecular architecture, thereby impeding systematic studies of the size effect on the optical functionality and energy transport.

In this chapter, we show how the diameter of the double-walled tubular system may be increased in a well-defined fashion (by 40% for the outer wall and 110% for the inner one) by replacing the four chlorine atoms in the original carbocyanine molecule by bromine atoms. By measurement and simulation of the absorption spectrum, we show that radial inflation of this tubular system is achieved without significantly altering the molecular packing. Besides extending the toolbox of controlling self-assembly, our results pave the road to greater flexibility in controlling of the diameter of tubular aggregates by, e.g., partial substitution of the halogen atoms. This would provide a model system to elucidate the effects of the inherent structural heterogeneity (namely variation of the aggregate radii) encountered in natural chlorosomes. Moreover, such systematic control also opens up unprecedented opportunities to study size effects on such important photonics properties as exciton dynamics—a crucial aspect of efficient energy transport—and polarization properties, both equally intriguing from theoretical and experimental points of view.

2.2. Experimental details

The dye molecule of interest in this study is the new cyanine dye derivative 3,3′-bis(2-sulfopropyl)-5,5′,6,6′-tetrabromo-1,1′-dioctylbenzimidacarbocyanine, or C8S3-Br, as opposed to its commercially available and much studied counterpart C8S3-Cl (Figure 2.1). The new molecules were produced in a four-step synthesis described in detail in Ref. 103.

Exchanging chlorine with bromine slightly shifts the absorption peak of diluted molecules towards longer wavelengths, but introduces no other new features (Figure
Unraveling optical signatures of tubular aggregates

Figure 2.1 | Schematic representation of the effect of halogen exchange on the radius of the formed aggregates. Chemical structure of C8S3 (on the left) with the halogen substituents abbreviated as X = Cl (C8S3-Cl) and X = Br (C8S3-Br). The radius of the formed tubular aggregates (on the right) is increased by changing the halogen substituent from chlorine to bromine, as revealed by this work.

2.2a,b), which is in line with our electronic structure calculations (see Section 2.6.1). Addition of Milli-Q water to the methanolic C8S3-Br/Cl stock solutions at room temperature induces a spectral red-shift of about 75 nm (~2400 cm⁻¹) and narrowing of absorption bands, both features that are typical for J-type aggregation (Figure 2.2a,b).

The two sharp low-energy bands that both aggregate spectra have in common are broader for C8S3-Br than for C8S3-Cl. In addition, the high-energy flank of the C8S3-Br aggregate spectrum misses the peaks at ~560 nm and ~570 nm characteristic for the C8S3-Cl aggregate spectrum. Because the optical properties of molecular aggregates are governed by the interplay of all individual building blocks, the question arises what changes in the aggregate morphology induced by the halogen substitution are responsible for the observed spectral changes.

Experimental evidence for the aggregation of molecules into nanotubes, as schematically depicted in Figure 2.1, was found by cryo-TEM. Although thicker bundles of C8S3-Br were occasionally observed (see SI of Ref. 103), there was no apparent morphological relation with the isolated tubes. Therefore, the more abundant nanotubes will be the focus of this study.

The cryo-TEM micrograph in Figure 2.2d clearly reveals a double-walled structure of C8S3-Br aggregates, similar to the structure of the C8S3-Cl aggregates (Figure 2.2c). From the profile scans of the aggregates, the outer- and inner-wall diameters of C8S3-Br aggregates were obtained as 18.1 ± 0.2 nm and 11.2 ± 0.3 nm, respectively. This is in striking difference with C8S3-Cl aggregates, where these quantities are 13.1 ± 0.2 nm and 5.4 ± 0.1 nm, respectively. Accordingly, the wall-to-wall thickness
2.3. Theoretical modeling

It is important to understand whether the changes in the absorption spectra (Figure 2.2a,b) are due mainly to the changes in diameter, or whether they result from different molecular packing in both types of aggregates, which results in differences in excitonic interactions. Since the cryo-TEM micrographs lack sufficient signal and 3D analysis to enhance the signal to noise ratio requires prior information on the symmetry, we retrieve the molecular packing by simulating the absorption spectrum for model structures and determining the structural parameters by fitting the experimental spectrum.

As the basic framework, we use the Extended Herringbone (EHB) model, which successfully describes the optical transitions of the double-walled tubular aggregates of C8S3-Cl. Briefly (see Section 2.6.2 for more details), we consider the dye molecule
as a brick with length $a$ and thickness $d$. The transition dipole vector lies along the molecular axis defined by the polymethine bridge and it is aligned with the long side of the brick, as shown in Figure 2.3a and b. Within the EHB model, the bricks are initially stowed in the rectangular planar $x, y$-lattice with the long side $a$ oriented along the $y$-axis, and their thickness $d$ along the $x$-axis. The molecules are first rotated clockwise over an angle $\delta$ around their axis. Subsequently they are alternately rotated over an angle $\pm \beta$ in the plane of the molecule, i.e., the plane defined by the molecule’s axis and the angle $\delta$, as shown in Figure 2.3a. The lattice is then rolled onto a cylindrical surface over a chiral vector with length equal to the cylinder circumference and direction determined by its angle $\theta$ relative to the axis $x$ of the plane (Figure 2.3c). This results in a cylindrical aggregate structure with each unit cell containing two molecules, which in turn leads to four (two Davydov-split) optically dominant exciton transitions per cylinder. The inner and outer cylinders were modeled as spectroscopically independent entities (see Section 2.6.7 of this chapter, and Section 6 in the SI of Ref. 103 for justification), keeping the structural parameters similar for both cylinders, but varying the radii in accordance with the experimental values obtained from cryo-TEM measurements.

The lattice constants of the EHB model were taken identical to those for the C8S3-Cl case (see Section 2.6.6), while the free parameters $\beta, \delta$, and $\theta$ that provide the best fit
to the measured absorption spectrum for the C8S3-Br aggregate are given in Table 2.1, along with the original parameters of C8S3-Cl for comparison. Simulation of the absorption spectrum with these structural model parameters (see Section 2.6.4 for the details) indeed gives a good reproduction of the experimental spectrum (Figure 2.4a). In our modeling, the lowest-energy peak near 600 nm is associated with the inner wall absorption (in close analogy to C8S3-Cl), while the higher-energy band has contributions from both walls. This spectral assignment of the inner and outer cylinder was verified in oxidation experiments in which the absorption of the outer cylinder was impaired by silver nanoclusters (see SI of Ref. 103). From Table 2.1, it appears that the molecular packing is essentially preserved upon the Cl → Br exchange, leaving the increase in the radii as the most important factor that changes the absorption spectrum, specifically the loss of the high-energy structure. In other words, the observed optical changes arise from an enhanced overlap of the excitonic transitions caused solely by the increase of the tube radius and not by changing the optical properties of the individual dyes or the packing of molecules within the supramolecular assembly.

### Table 2.1 | Summary of structural model parameters for the inner and outer walls of C8S3-Br used in the calculation of spectra (Figure 2.4).

The values are compared to the model of C8S3-Cl from Ref. 8. The parameters β and δ define the molecular orientation in the local frame, while the parameter θ defines the aggregate lattice rolling.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Inner (C8S3-Br)</th>
<th>Outer (C8S3-Br)</th>
<th>Inner (C8S3-Cl)</th>
<th>Outer (C8S3-Cl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R (nm)</td>
<td>6.50</td>
<td>8.61</td>
<td>3.55</td>
<td>6.47</td>
</tr>
<tr>
<td>β (°)</td>
<td>23.1</td>
<td>22.3</td>
<td>23.6</td>
<td>23.1</td>
</tr>
<tr>
<td>δ (°)</td>
<td>25.5</td>
<td>26.0</td>
<td>25.6</td>
<td>28.0</td>
</tr>
<tr>
<td>θ (°)</td>
<td>55.5</td>
<td>49.4</td>
<td>53.7</td>
<td>53.4</td>
</tr>
<tr>
<td>N₂</td>
<td>3</td>
<td>1</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>γ (°)</td>
<td>86.8</td>
<td>101.4</td>
<td>36.5</td>
<td>33.4</td>
</tr>
<tr>
<td>h (nm)</td>
<td>0.082</td>
<td>0.021</td>
<td>0.296</td>
<td>0.055</td>
</tr>
</tbody>
</table>

Further validation of the theoretical model is given by the reasonable agreement of the theoretical and experimental LD spectra for flow-aligned C8S3-Br aggregates, shown on Figure 2.4b. The theoretical LD spectrum was determined as described in Section 2.6.5. In close analogy to C8S3-Cl aggregates, theory predicts that the two low-energy peaks are polarized parallel to the aggregate axis and therefore will show up as positive peaks in the LD spectrum. In contrast, the high-energy tail is predominantly polarized orthogonal to the axis, such that a negative LD signal is expected. The experimental and theoretical spectra show qualitative agreement, where all features are reproduced, i.e., a low-energy peak around 603 nm, a shoulder at 594 nm corresponding to a peak at 592 nm in the theoretical spectrum, and a negative dip at the tail below ~580 nm.

The modeling of the absorption spectra was performed in the homogeneous limit,
i.e., all the molecular transition energies were assumed to be the same. As shown above, this suffices to describe the absorption spectra and also explains the polarization properties of the spectral peaks, even though in reality some amount of disorder will occur in the transition energies and intermolecular resonance interactions. As has been shown by Bloemsma et al.,\textsuperscript{104} in tubular aggregates, such disorder leads to rather weak localization of the excitonic states, which explains the effectiveness of homogeneous models. Allowing for static Gaussian disorder in the transition energies\textsuperscript{40,49} and assuming that this disorder solely determines the lowest energy aggregate band width, we find the maximum value (standard deviation) of the disorder to amount to 180 cm\textsuperscript{-1}. See Chapter 3 for more details on the effect of disorder in these aggregates.

### 2.4. The influence of the tube radius on the absorption spectrum

Above, the large spectral difference between C8S3-Cl and C8S3-Br (Figure 2.2a,b) was attributed to the change in radii of the inner and outer walls. This interpretation is further substantiated by phenomenologically examining the influence of the cylinder radii on the optical spectra. We modeled 12 cylinders based on the EHB lattice of the inner wall of C8S3-Cl (parameters in Table 2.1) by only varying the length of the rolling vector resulting in radii from 2.4 nm to 8.9 nm. For convenience of comparison (and in contrast to the fit in Figure 2.4), all spectral transitions were broadened by identical Lorentzian lineshapes of 120 cm\textsuperscript{-1} FWHM. The obtained spectra (Figure 2.5) reveal congestion of the peaks when going from the smallest cylinder with four well separated peaks to the largest cylinder with three peaks with little separation. Two peaks, the large one at 600 nm and the small one at 570 nm,
correspond to the doublet of transitions polarized parallel to the tube axis with their positions essentially independent of the radii. With increasing radius, the doublet of peaks with perpendicular polarization moves down in energy towards the parallel peaks, reflecting the fact that upon decreasing the cylinder curvature, the energy separation between corresponding parallel and perpendicular transitions decreases. Consequently, with increasing cylinder radius, the high-energy peaks merge with the lower-energy ones and the spectral structure gets lost. In experiment, this effect is further enhanced by a stronger broadening of the higher-energy exciton peaks due to intraband relaxation, an effect not accounted for in Figure 2.5.

Figure 2.5 | The influence of the tube radius on the absorption spectrum for a single tube with the EHB lattice. Structural parameters are identical to the inner wall of C8S3-Cl aggregate. Red and black lines correspond to the spectral components polarized parallel and perpendicular to the tube’s axis, respectively. The spectral differences between R=3.5 nm and R=6.5 nm catch the essential differences between the spectra for the inner walls of C8S3-Cl and C8S3-Br.
2.5. Conclusions

In conclusion, we have shown that a very moderate chemical modification through the exchange of four halogen atoms in the chromophore of an amphiphilic carbocyanine dye leads to well-defined changes in the final supramolecular assembly without altering the underlying molecular architecture. This allowed us to study the effect of purely radial growth on the collective optical properties of the supramolecular structure. In a broader perspective, our results demonstrate that a combination of halogen exchange and amphiphilically driven self-assembly opens up unprecedented opportunities in controlling the supramolecular structure to a fine degree for systems, where modifications of other molecular moieties and/or changes of the immediate environment (solvent, pH, external fields) are not feasible as is the case in, e.g., many biological systems or for medical applications. In addition, we believe that the presented design principle can be transferred to structurally related molecules that are known to form other supramolecular architectures, such as single-walled tubes,\textsuperscript{105} twisted bundles\textsuperscript{64} or vesicles.\textsuperscript{64,98} Nonetheless, the exact underlying mechanism of how halogen exchange affects the aggregation behavior is yet to be understood. Our results suggest that the size of the halogen substituents and/or the ability to form halogen bonds play an important role. For instance, fluorine, unlike bromine or chlorine, is known to hardly form halogen bonds and may even lead to intermolecular repulsion,\textsuperscript{77} which would impede the formation of molecular aggregates. We tested this concept experimentally by synthesizing the C8S3-F molecule and indeed found a poor degree of aggregation under normal conditions (see SI of Ref. \textsuperscript{103}). Based on our results, it is envisioned that further studies of partial replacement of only a few halogen atoms will shed light on the effect of different halogen substituents on the aggregation behavior. This would open great perspectives for fine-tuning size effects for optical functionality and for optimization of tubular aggregates for specific applications as for instance artificial light-harvesting systems.

Author contributions

B.K., A.S.B., and V.R.J. contributed equally to this work. V.R.J. performed the organic synthesis supervised by A.J.M. B.K. and L.E.F. performed the cryo-TEM experiments. B.K. performed the aggregate self-assembling and the optical experiments; the analysis was supervised by M.S.P. A.S.B. performed the theoretical modeling and interpreted the optical spectra supervised by T.L.C.J. and J.K.
2.6. Appendix: Theoretical calculations and modeling

2.6.1. Electronic structure calculations

Quantum chemical electronic structure calculations of C8S3-F, C8S3-Cl, and C8S3-Br were performed with the Orca software package (version 3.0.3) using the 6-311++G(d,p) basis set and the B3LYP exchange correlation functional. For these calculations the hydrophilic sulfur tails –(CH\(_2\))\(_3\)SO\(^+\) were substituted by methyl groups and the hydrophobic tails –(CH\(_2\))\(_7\)CH\(_3\) were substituted by propyl groups to facilitate calculation speed and eliminate differences due to the long floppy tails.

Below, we give the transition energies, oscillator strengths, and transition dipole moments of the S\(_0\) → S\(_1\) transition in the gas phase obtained from the time-dependent density functional theory calculations for C8S3-F, C8S3-Cl, and C8S3-Br. The transition energies, oscillator strengths, and transition dipole moments do not change significantly when going from Cl– to Br–substituted C8S3 molecules, as can be seen from Table 2.2. The values of the transition dipole moments are close to 11.4 D from Ref. 21 that takes into account the solvent shift and is in good agreement with the experimental absorption spectrum.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition energy (cm(^{-1}))</th>
<th>(f_{osc})</th>
<th>Transition dipole moment (Debye)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C8S3-F</td>
<td>24,980.4</td>
<td>2.31</td>
<td>14.0</td>
</tr>
<tr>
<td>C8S3-Cl</td>
<td>24,245.2</td>
<td>2.53</td>
<td>14.9</td>
</tr>
<tr>
<td>C8S3-Br</td>
<td>23,937.7</td>
<td>2.57</td>
<td>15.1</td>
</tr>
</tbody>
</table>

Table 2.2 | Comparison of the molecular transition energies, oscillator strengths, and transition dipole moments of the S\(_0\) → S\(_1\) transition in the gas phase for the compounds: C8S3-F, C8S3-Cl, and C8S3-Br.

2.6.2. Extended Herringbone (EHB) model

The experimental spectrum of C8S3-Cl aggregates was successfully simulated using an Extended Herringbone structure. For each tube, the lattice contained two molecules per unit cell tilted out of plane. The lattices were rolled onto the inner and outer cylinders forming a double-walled aggregate. In line with this, we also constructed a molecular model to simulate the spectrum of C8S3-Br aggregates using the EHB model.

The transition dipole moment of the C8S3 molecule lies along the polymethine bridge connecting the two indolenine groups. The size and the shape of the dye molecule allow it to be considered as a brick with length \(a\) and thickness \(d\), where the transition dipole vector \(\mu\) of magnitude \(\mu\) is aligned with the long side of the brick as shown in Figure 2.3a.
First, the bricks are packed in the rectangular planar $x$, $y$-lattice with the long side $a$ oriented along the $y$-axis, and their thickness $d$ along the $x$-axis. Then the molecules are rotated clockwise over an angle $\delta$ around their axis and subsequently alternately tilted out of lattice plane over an angle $\pm \beta$ in the plane of the molecule, i.e., the plane defined by the molecule’s axis and the angle $\delta$ (Figure 2.3a). This will lead to a lattice with two molecules per unit cell, where the 1st and 2nd molecules (distinguished by the label $j=1,2$) of the unit cells will be tilted above and below the plane of the lattice, respectively. These rotations are described by the rotation matrix $A_j$ given by:

$$
A_j = \begin{pmatrix}
\cos \delta & \cos \beta & -\sin \delta \cos \beta \\
-\sin \delta & \cos \beta & \sin \delta \cos \beta \\
\sin \delta & (-) \sin \beta & \cos \delta \sin \beta
\end{pmatrix}.
$$

Equation (2.1)

Matrix multiplication of the molecular transition vector $\mathbf{\mu} = \mu \mathbf{\hat{e}_y}$ by $A_j$ will directly give the transition dipole vector with its components $\mu_x,j$, $\mu_y,j$, $\mu_z,j$.

The cylindrical structure is attained by rolling the above planar lattice along the chiral vector $\mathbf{C}$, such that its end point matches with its start point. The vector $\mathbf{C}$ is characterized by its length, which equals the circumference of the cylinder, $|\mathbf{C}| = 2\pi R$, and the rolling angle $\theta$, which it makes with the $x$-axis. The cylindrical aggregate can be regarded as a stack of $N_1$ rings separated by a distance $h$. Each ring has the center of $N_2$ equidistant unit cells and is rotated relative to the adjacent ring over the helical angle $\gamma$. Stacking of the rings occurs in the direction of the cylinder’s axis which is now set along the $z'$-axis with $x'y'$-plane perpendicular to it. We will define the positions and orientations of the transition dipole vectors in this stack-of-ring representation, denoting each unit cell by $n = (n_1, n_2)$. Here, $n_1$ labels the ring ($n_1 = 1, 2, ..., N_1$) and $n_2$ labels the unit cell on the ring ($n_2 = 1, 2, ..., N_2$). The molecular position vector $\mathbf{r}_{n,j}$ and transition dipole moments $\mathbf{\mu}_{n,j}$ within Cartesian coordinates (represented by the unit vectors $\mathbf{\hat{e}_x}$, $\mathbf{\hat{e}_y}$, $\mathbf{\hat{e}_z}$), have the following form:

$$
\mathbf{r}_{n,j} = R \cos(n_1 \gamma + n_2 \phi_2 + \delta_{j,2} \Delta \phi) \mathbf{\hat{e}_x} + R \sin(n_1 \gamma + n_2 \phi_2 + \delta_{j,2} \Delta \phi) \mathbf{\hat{e}_y} + (n_1 h + \delta_{j,2} \Delta z) \mathbf{\hat{e}_z}.
$$

Equation (2.2)

$$
\mathbf{\mu}_{n,j} = \left[ \mu_z,j \cos(n_1 \gamma + n_2 \phi_2 + \delta_{j,2} \Delta \phi) \
- (\mu_x,j \cos \theta + \mu_y,j \sin \theta) \sin(n_1 \gamma + n_2 \phi_2 + \delta_{j,2} \Delta \phi) \right] \mathbf{\hat{e}_x} \\
+ \left[ \mu_z,j \sin(n_1 \gamma + n_2 \phi_2 + \delta_{j,2} \Delta \phi) \
+ (\mu_x,j \cos \theta + \mu_y,j \sin \theta) \cos(n_1 \gamma + n_2 \phi_2 + \delta_{j,2} \Delta \phi) \right] \mathbf{\hat{e}_y} \\
+ \left[ - \mu_x,j \sin \theta + \mu_y,j \cos \theta \right] \mathbf{\hat{e}_z},
$$

Equation (2.3)

where $\phi = 2\pi / N_2$, and $\delta_{j,2}$ is the Kronecker delta. The relative position of the first
molecule of a unit cell relative to the second one is described by $\Delta \phi$ and $\Delta z$, given by:

$$\Delta \phi = \frac{\Delta y \sin \theta + \Delta x \cos \theta}{R}, \quad \Delta z = \Delta y \cos \theta - \Delta x \sin \theta,$$

with $\Delta x$ and $\Delta y$ being the distances between the rows of the molecules in the $x$ and $y$ directions, respectively, in the planar lattice after rotations (Figure 2.6).

![Figure 2.6](image)

**Figure 2.6 | Schematic representation of the EHB lattice.** The distances between the rows of the molecules along $x$ and $y$ directions are denoted as $\Delta x$ and $\Delta y$, respectively.

### 2.6.3. Model Hamiltonian

We model the electronically excited states of the double-walled tubular aggregates by a Frenkel exciton Hamiltonian. Previous studies\(^8\) suggest that the excitation transfer interaction between the inner and the outer walls may be ignored. Hence, we may consider the Hamiltonian of a single cylinder (either the inner or outer wall), which for $\hbar = 1$ reads:

$$H = \sum_{n,j} \omega_{n,j} b_{n,j}^\dagger b_{n,j} + \sum_{n,j \neq m,j'} J_{n,j,m,j'} b_{n,j}^\dagger b_{m,j'},$$

where $b_{n,j}^\dagger$ and $b_{n,j}$ are the Pauli creation and annihilation operators of an electronic excitation on the $j^{th}$ ($j=1,2$) two-level molecule in the unit cell $n$ and $\omega_{n,j}$ is its transition energy from the ground to the excited state. We restrict ourselves here to a homogeneous aggregate, where all transition frequencies are equal, i.e. $\omega_{n,j} = \omega_0$. The second term $J_{n,j,m,j'}$ describes the excitation transfer interaction between the molecule $j$ of the unit cell $n$ and the molecule $j'$ of the unit cell $m$. The transfer interactions are calculated using the extended dipole model,\(^{113}\) where the transition dipole moment of a molecule is considered as a dipole moment of length $l$ between two point charges $+Q$ and $-Q$ such that the magnitude and orientation of the original dipole moment is reproduced. In this approximation, the transfer interaction $J_{n,j,m,j'}$ is then explicitly
given by the distance between the four charges:

\[ J_{n,j,m,j'} = A \frac{\mu^2}{l^2} \left[ \frac{1}{r_{n,j,m,j'}^{++}} - \frac{1}{r_{n,j,m,j'}^{+-}} - \frac{1}{r_{n,j,m,j'}^{-+}} + \frac{1}{r_{n,j,m,j'}^{--}} \right], \tag{2.6} \]

where \( \mu = Ql \) and

\[ r_{n,j,m,j'}^{++} = |r_{n,j,m,j'} + l(e_{n,j} - e_{m,j'})|, \]

\[ r_{n,j,m,j'}^{+-} = |r_{n,j,m,j'} - l(e_{n,j} + e_{m,j'})|, \tag{2.7} \]

\[ r_{n,j,m,j'}^{-+} = |r_{n,j,m,j'} + l(e_{n,j} + e_{m,j'})|, \]

\[ r_{n,j,m,j'}^{--} = |r_{n,j,m,j'} - l(e_{n,j} - e_{m,j'})|, \]

with \( r_{n,j,m,j'} = r_{n,j} - r_{m,j'} \). The constant \( A = 5.04 \text{ cm}^{-1} \text{ nm}^3 \text{ Debye}^{-2} \) comes from a conversion of units allowing one to express transition dipole moments, distances and energies in Debye, nm, and cm\(^{-1}\), respectively.\(^{21}\) The vector \( r_{n,j} \) is given by eq. 2.2. The vector \( e_{n,j} \) is the unit vector related to the transition dipole moment, \( \mu_{n,j} = \mu e_{n,j} \), which is given by 2.3.

### 2.6.4. Linear absorption spectrum

For describing the linear optical response, we may consider only the one-exciton states, where the molecules share one excitation. The exciton eigenstates of the molecular aggregate can be obtained by numerical diagonalization of the Hamiltonian from eq. 2.5. The eigenstates then may be written:

\[ |q\rangle = \sum_{n,j} q_q(n, j) |n, j\rangle, \tag{2.8} \]

where \( q_q(n, j) \) denotes the coefficient of the \( q \)th eigenstate on a molecule \( j \) of the unit cell \( n \). The corresponding eigenvalue of the state is the energy \( E_q \).

The general form of the linear absorption spectrum for an isotropic solution, obtained from the Fermi golden rule,\(^{36}\) is given by:

\[ A(\omega) = \sum_q O_q \delta(\omega - E_q), \tag{2.9} \]

with the oscillator strength of the state \( O_q \) given by:

\[ O_q = \sum_{n,j,m,j'} q_q(n,j)q_q(m,j')^* \langle \mu_{n,j} \cdot e \rangle (\mu_{m,j'} \cdot e). \tag{2.10} \]

The brackets \( \langle \ldots \rangle \) represent the isotropic average over the orientations of the cylinder relative to the electric polarization vector \( e \) of the incident linearly polarized electromagnetic wave. The obtained stick spectrum of eq. 2.9 was convoluted with Lorentzian
2.6. Appendix: Theoretical calculations and modeling

line shapes of different linewidths, i.e., different transitions \( q \) were given a different width, in order to fit the experimental line shape.

2.6.5. Linear dichroism spectrum

The linear dichroism (LD) spectrum of a cylindrical aggregate oriented along the \( z'-\)axis can be calculated as the difference in the absorption of light linearly polarized parallel and perpendicular to the cylinder axis, respectively:

\[
LD(\omega) = A_\parallel(\omega) - A_\perp(\omega).
\]  

(2.11)

Assuming perfect alignment of the cylinders along the \( z'-\)axis, the expression for the LD spectrum is given by

\[
LD(\omega) = \sum_q LD_q \delta(\omega - E_q),
\]  

(2.12)

with the corresponding LD oscillator strength\(^{36}\)

\[
LD_q = \sum_{n,j,m,j'} \varphi_q(n,j)\varphi_q(m,j')^* [\langle (\mu_{n,j} \cdot \hat{e}_{z'}) (\mu_{m,j'} \cdot \hat{e}_{z'}) - \langle (\mu_{n,j} \cdot \hat{e}_\perp) (\mu_{m,j'} \cdot \hat{e}_\perp) \rangle],
\]  

(2.13)

where \( \hat{e}_{z'} \) is the polarization vector along the \( z'-\)axis (parallel to the axis of the tube), and \( \langle \ldots \rangle \) in the last term denotes the average of the polarization vector \( \hat{e}_\perp \) over all orientations within the \( x'y'\)-plane of the cylinder. The obtained normalized LD spectrum presented in Figure 2.4b was scaled with a factor 0.58 to account for disorder in the angles of alignment in the experiment.

2.6.6. Parametrization and fitting procedure

The EHB model has a number of parameters that are known from experiment or previous studies and, therefore, were kept fixed, while the others were fitted to experiment. A detailed account of the fitting procedure is given below.

We begin with the structural parameters that determine the geometry of the tubular aggregates. Unit cell parameters corresponding to the length and thickness of the C8S3 molecules, that are fixed to the values \( a = 2.0 \) nm and \( d = 0.4 \) nm, are taken from Refs. \(^{113}\) and \(^{21}\). The geometrical parameters \( \Delta x \) and \( \Delta y \) determine the distances between the adjacent rows in the \( x \) and \( y \)-directions in the lattice, respectively (Figure 2.6). \( \Delta x \) is mainly determined by the \( \pi - \pi \) interactions of the phenyl groups of the C8S3-molecules. This value was estimated in Ref. \(^{114}\) to be 0.55 nm. \( \Delta y \) is assumed to ensure closed packing requirements and depends on the angle \( \beta \), hence \( \Delta y = d / \sin \beta \).\(^8\) The radii of the cylinders were resolved experimentally from line scans of cryo-TEM images (Figure 3c of Ref. \(^{103}\)), where we took dip-to-dip distances of the walls to reflect the center positions of the molecules. This gave us an inner wall radius of \( R_{IW} = 6.25 \pm 0.5 \) nm and
an outer wall radius of $R_{\text{OW}} = 8.15 \pm 0.5$ nm. During the fitting procedure, we keep these values fixed within the experimental error, allowing, however, for small deviations arising from the discrete character of $R$ imposed by the underlying lattice.

The rest of the structural parameters, i.e. the rolling angle $\theta$, as well as the rotational angles $\delta$ and $\beta$, are not known \textit{a priori} and are treated as fitting parameters. In view of the similarity of C8S3-Br to C8S3-Cl, the initial values for these three angles were chosen equal to those found for the C8S3-Cl aggregates.\(^8\)

Along with the structural parameters, there are energetic ones, that include the molecular transition frequencies, $\omega_0$, the extended dipole charge, $Q$, and the dipole length, $l$. We use these parameters identical to those in Ref. 21. The molecular transition energy $\omega_0 = 18,868 \text{ cm}^{-1}$ corresponds to a single-molecule transition wavelength at 530 nm. The extended dipole charge $Q = 0.34$ e (with $e$ the electron charge) is separated by a length $l = 0.7$ nm\(^{113}\) where the value of $l$ corresponds to the distance between the nitrogen atoms of the indolenine groups. This gives a single molecule transition dipole $\theta = 11.4$ Debye.

We took the same lattice and rolling angle while adjusting the radii. This gave rise to a congestion of the transitions, however, small adjustments of the structural parameters were still needed to optimize the energy peak positions and relative oscillator strengths. We applied the same procedure for both inner and outer walls simultaneously in order to find an optimal agreement between computed and experimental spectra. The optimal set of parameters obtained for the C8S3-Br aggregate are summarized in Table 2.1 along with the original parameters of C8S3-Cl for comparison. The values for the fitted lattice parameters confirm that the molecular packing of the C8S3-Br molecules is very similar to the one of C8S3-Cl.

### 2.6.7. Couplings in C8S3-Cl and C8S3-Br aggregates

The largest excitation transfer interaction between a molecule in the outer wall and a molecule in the inner wall for C8S3-Br aggregates amounts to 72 cm$^{-1}$, which is to be compared to 1500 cm$^{-1}$ for the largest interaction inside a wall (Table 2.3). For C8S3-Cl the same numbers are 28 cm$^{-1}$ and 1500 cm$^{-1}$, respectively.\(^{115}\) While for C8S3-Br the interwall coupling is about 2-3 times larger as for C8S3-Cl owing to the decreased interwall separation, it is still significantly smaller than the intrawall coupling. Moreover, the interwall couplings are smaller than the homogeneous linewidth of the exciton states, estimated as 200 cm$^{-1}$. These values imply that the interwall couplings are too small to give rise to collective excitonic states shared by both walls,\(^{116}\) thus justifying our approach to model the system’s absorption spectrum as the sum of the spectra of uncoupled inner and outer cylindrical walls. This conclusion is also supported by time-resolved fluorescence measurements (see SI of Ref. 103).
Table 2.3 | The strongest positive and negative excitation transfer interactions in C8S3-Cl and C8S3-Br aggregates.

<table>
<thead>
<tr>
<th></th>
<th>C8S3-Cl</th>
<th>C8S3-Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner wall strongest coupling (cm(^{-1}))</td>
<td>1497.7</td>
<td>1462.5</td>
</tr>
<tr>
<td></td>
<td>−1072.2</td>
<td>−1043.9</td>
</tr>
<tr>
<td>Outer wall strongest coupling (cm(^{-1}))</td>
<td>1509.9</td>
<td>1489.0</td>
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<tr>
<td></td>
<td>−1044.0</td>
<td>−993.2</td>
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<tr>
<td>Interwall coupling (cm(^{-1}))</td>
<td>28.2</td>
<td>71.8</td>
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<tr>
<td></td>
<td>−15.8</td>
<td>−39.8</td>
</tr>
<tr>
<td>Radius inner wall (nm)</td>
<td>3.55</td>
<td>6.50</td>
</tr>
<tr>
<td>Radius outer wall (nm)</td>
<td>6.47</td>
<td>8.61</td>
</tr>
<tr>
<td>Interwall distance (nm)</td>
<td>2.92</td>
<td>2.11</td>
</tr>
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</table>