Structure Prediction of Self-Assembled Dye Aggregates from Cryogenic Transmission Electron Microscopy, Molecular Mechanics, and Theory of Optical Spectra

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ABSTRACT: Cryogenic transmission electron microscopy (cryo-TEM) studies suggest that TTBC molecules self-assemble in aqueous solution to form single-walled tubes with a diameter of about 35 Å. In order to reveal the arrangement and mutual orientations of the individual molecules in the tube, we combine information from crystal structure data of this dye with a calculation of linear absorbance and linear dichroism spectra and molecular dynamics simulations. We start with wrapping crystal planes in different directions to obtain tubes of suitable diameter. This set of tube models is evaluated by comparing the resulting optical spectra with experimental data. The tubes that can explain the spectra are investigated further by molecular dynamics simulations, including explicit solvent molecules. From the trajectories of the most stable tube models, the short-range ordering of the dye molecules is extracted and the optimization of the structure is iteratively completed. The final structural model is a tube of rings with 6-fold rotational symmetry, where neighboring rings are rotated by 30° and the transition dipole moments of the chromophores form an angle of 74° with respect to the symmetry axis of the tube. This model is in agreement with cryo-TEM images and can explain the optical spectra, consisting of a sharp red-shifted J-band that is polarized parallel to the symmetry axis of the tube and a broad blue-shifted H-band polarized perpendicular to this axis. The general structure of the homogeneous spectrum of this hybrid HJ-aggregate is described by an analytical model that explains the difference in redistribution of oscillator strength inside the vibrational manifolds of the J- and H-bands and the relative intensities and excitation energies of those bands. In addition to the particular system investigated here, the present methodology can be expected to aid the structure prediction for a wide range of self-assembled dye aggregates.

1. INTRODUCTION

The self-organization of supramolecular structures driven by weak intermolecular interactions is one of the most fascinating thermodynamic phenomena in biology, chemistry, and physics. Because the interactions are weak, many different structures can be formed with the same type of building blocks. In biology, 20 different amino acids serve as building blocks for many unique three-dimensional structures. Each of these structures has been optimized by evolution in order to perform a specific function, e.g., to catalyze a chemical reaction or to create an efficient solar energy converting photosystem. An artificial chemical system with the same goal is an organic solar cell. In some bulk-heterojunction solar cells an interpenetrating network of a polymer phase and a fullerene phase is formed spontaneously. Again, weak interactions between the side groups of the polymer and the fullerene determine the morphology of the solar cell that is key to its function. Another example is self-assembled dye aggregates, called chlorosomes, that function as light-harvesting complexes in green sulfur bacteria. The present work deals with J-aggregates of self-assembled cyanine dyes. While the optical properties of cyanine dyes are mainly determined by the polymethine chromophore, their solution behavior and aggregate morphology can decisively be influenced by the substituents. Cyanines with long alkyl substituents (amphiphilic cyanines) form bilayers in aqueous solution with the side chains facing inward and the polar/charged part of the molecule facing outward, thus stabilizing the aggregate by increasing the entropy of the surrounding water molecules. Besides this so-called hydrophobic interaction, dispersive and electrostatic couplings are important for the formation of the

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aggregate. Dispersive interactions arise from correlated fluctuations of electrons in different molecules. They are significant for cyanine dyes due to the large polarizability of their delocalized \( \pi \)-electron systems. Since the dye molecules are charged, electrostatic interactions between dye molecules among each other and also between dye molecules and solvated counterions are important as well.

The interplay of all of the above interactions determines the three-dimensional structure of the aggregate. Their relative weight can be changed by varying the character of the substituents, the solvent properties, or even the preparation conditions.\(^5\) It is a challenging thermodynamical problem to predict the structure of a J-aggregate. Most likely, the free energy surface is highly frustrated, that is, it consists of many local minima, and slight changes in the above-discussed interactions can shift the global minimum and thereby the equilibrium structure of the aggregate. In recent years v. Berlepsch and co-workers\(^5\) were able to elucidate the morphologies of aggregates formed by many different cyanine dyes by using cryogenic transmission electron microscopy (cryo-TEM). Cryo-TEM provides highly resolved direct images of supramolecular structures in their native environment that are free of the drying artifacts due to the specific sample preparation technique.\(^6\)–\(^11\)

Detected architectures of dye aggregates range from thread-like fibers across ribbons to fascinating single- and double-walled tubes. However, due to the smallness of dye molecules the resolution of cryo-TEM is generally not sufficient to directly resolve their mutual orientation within the aggregates. Probably the simplest way to distinguish different structures is to measure their optical spectra. The Coulomb interaction between the delocalized \( \pi \)-electrons in one cyanine monomer and those in another monomer gives rise to excitonic interaction between the local optical excitations. For a pair of monomers subject to excitonic interaction, if one monomer is excited and another one in the ground state, the first one gets de-excited and simultaneously the second one gets excited. If the excitonic coupling is strong compared to static and dynamic disorder, the excited states of the aggregate are delocalized, the excitation energies of the delocalized states of the aggregate are shifted, and the oscillator strength is redistributed with respect to those of the isolated monomers.\(^12,13\)

The redistribution of oscillator strength depends on the mutual geometry of optical transition dipole moments of the monomers. In the classical aggregates of Jelley and Scheibe\(^14,15\) the transition dipoles are oriented in line, and the oscillator strength in this case is shifted to the lowest exciton state. The corresponding spectral band is very narrow and red shifted with respect to that of the isolated monomers. Because all of the oscillator strength is redistributed to this narrow band it is also said to possess “giant oscillator strength”. In honor of Jelley and Scheibe the red-shifted band is called a J-band and self-aggregated cyanine dyes possessing a dominant J-band are called J- or Scheibe aggregates.

If the mutual geometry of neighboring dye molecules is such that the line connecting molecular centers is perpendicular to the transition dipole moments of both dyes, the oscillator strength is shifted to the exciton state with the highest energy, which is blue shifted with respect to the excitation energy of the isolated monomer. Due to this hypsochromic shift this band is called a H-band, in contrast to the red-shifted J-band discussed before. In any case, there is a critical dependence of the optical spectra of the aggregate on the mutual orientation of the transition dipole moments of the monomers that allows one to use the optical spectra for structure prediction.

A subtlety in the interpretation of spectra of dye aggregates concerns the coupling of excitons to intramolecular vibrations of the chromophores. The vibrational progression that is observed in optical spectra of monomers in solution is distinctly changed by the excitonic coupling in the aggregate. Whereas J-bands do show weaker vibrational side lines, in the case of H-bands these side lines get stronger than those of the isolated chromophores. This remarkable redistribution of oscillator strength was explained by Spano\(^16\) with a model that included one effective vibrational mode per chromophore in the exciton Hamiltonian, which was numerically diagonalized. An alternative description of this effect was given by Briggs and co-workers using a Greens-function approach.\(^17\) Here, we will use the same approach as Spano and in addition investigate a simplified model (assuming the same local electronic transition energies of the chromophores) that can explain the observed redistribution of oscillator strength semianalytically.

Of course, the optical excitation energy of the monomers is not only shifted by excitonic coupling but also by dispersive and electrostatic couplings between monomers in the aggregate. However, the effect of those couplings can be taken into account by shifting the energies of the localized (one-exciton) states of the aggregate. In the simplest approximation these localized energies are assumed to be equal to some reference value \( E_{0}^{(t)\text{tube}} \) that describes at which energy a monomer in the aggregate would absorb if it was not coupled excitonically to the other monomers. In this case \( E_{0}^{(t)\text{tube}} \) can be obtained by comparison of calculated and measured spectra, since variation of \( E_{0}^{(t)\text{tube}} \) just shifts the calculated spectrum along the energy (wavelength) axis.

Pioneering work in the relation of optical spectra to the structure of chromophore aggregates was provided by Kuhn\(^18,19\) and later continued by Knoester and co-workers.\(^20–22\) In the models for simple sheet-like aggregates the dye molecule is represented by a brick containing the transition dipole that is described by two atomic partial charges at a certain distance. The discovery of tubular dye aggregates has led to increasingly complex theoretical models. Knoester et al. created\(^20,22,23\) tubular aggregates by wrapping a brick-layer lattice in certain directions, where the optimal direction was determined by comparing the resulting absorbance and linear dichroism spectra with experimental data, and the radius was estimated by cryo-TEM. Of course, the final geometry depends also on the organization of the layer used to create the tube, and it has to be checked whether the proposed organization is also consistent with the minimum free energy of the molecular aggregate.

Again, pioneering work was provided by Knoester and co-workers, who studied the spontaneous self-aggregation of an alkyl-substituted pseudoisocyanine (amphi-PIC) in aqueous solution by molecular dynamics simulations.\(^24\) Cylindrical and ribbon-like conformations were suggested as possible candidates for the equilibrium structure, but due to the finite simulation times (200–700 ns) it could not be decided which of the two structures is more likely. In contrast, cryo-TEM images suggest that the investigated amphi-PIC dye forms double-walled tubes and multimellar spherical aggregates, at least at high dye concentrations. It seems that there is a need for either longer simulation times or some type of preselection of possible structures that are closer to the equilibrium structure. Knoester and co-workers suggested to take for this purpose the phenomenological dipole models that describe the optical
spectra. In the case of the amphiphilic cyanine dye C8S3, which forms double-walled tubular aggregates, Megow et al. successfully modified the phenomenological dipole model of Knoester et al. by incorporating information from high-resolution cryo-TEM data and running MD simulations, arriving at a model of a stable structure that still describes the optical spectra. A crucial step in the description of optical spectra was to take into account the dispersive shift in site energies that was found to be different for molecules in the outer and the inner cylinder of the aggregate.

In the present work, we have taken the structure of cyanine–dye molecular crystals as a basis for generating starting structures for MD simulations. The rationale behind this approach is the expectation that the three-dimensional arrangement of dye
molecules in the respective single crystals reflects their intermolecular interactions. The question to be addressed is whether and if so to what degree these interactions are varied if soft colloidal structures, tubes, or sheets are formed in solution. Nevertheless, we believe that the packing in a dye aggregate is closer to the packing in a molecular crystal than to a random geometry.

As an example, we study the cyanine derivative \(5,5',6,6'\)-tetrachloro-1,1'-3,3' -tetrastilbenyl-benzimidacarbocyanine (TTBC) (Figure 1). Single-walled tubes have been observed in ref 30 in aqueous solutions for this dye after aggregation with \(\text{Cl}^-\) or \(\Gamma^-\) counterions under different solvent conditions. A cryo-TEM image of fibrous aggregates of TTBC-Cl is reproduced here (Figure 2) together with an averaged density profile across a single aggregate, which proves its tubular architecture. TTBC-Cl forms aggregates with an absorption spectrum (type I) that contains a strong broad H-band and a weaker and more narrow J-band, independent of the preparation conditions. In the recent literature this type of aggregate is referred to as hybrid HJ-aggregate.\(^\text{31,32}\) In the case of TTBC-I, tubular aggregates with the same diameter as for TTBC-Cl are seen in cryo-TEM, but the measured absorption spectrum depends strongly on the solvent conditions. Besides the type I spectrum observed at high pH values, an absorption spectrum with a single J-band (in the following referred to as type II) was reported at low pH values.\(^\text{30,33}\)

Interestingly, for TTBC there exist also two distinct single-crystal structures\(^\text{34,35}\) that were obtained for two different solvents. In the case of a 2:1 methanol:TTBC-I solvate, TTBC organizes in separated layers where the molecules in each layer form a herringbone-like arrangement. The structure can be described as a crystal lattice with two molecules per unit cell. Referring to its solvent, it was termed DYEM. In the alternative DYEA structure (an 1:1 acetonitrile:TTBC-I solvate) just a single molecule per unit cell is formed and the molecules inside the crystal sheets are arranged in a brick-layered fashion. Compared to DYEM the distance between layers of TTBC molecules in DYEA crystals are much smaller. Details about these crystal structures are given in the Supporting Information (SI).

A simple explanation of the two types of optical spectra found for the J-aggregates of TTBC discussed above has been suggested in the experimental work.\(^\text{30}\) The explanation has been that the two peaks found in the type I spectrum just represent a Davydow split spectrum, as expected for crystals with two molecules per unit cell. Referring to its solvent, it was termed DYEM. In the present case of TTBC-I, tubular aggregates with the same diameter as for TTBC-Cl are seen in cryo-TEM, but the measured absorption spectrum depends strongly on the solvent conditions. Besides the type I spectrum observed at high pH values, an absorption spectrum with a single J-band (in the following referred to as type II) was reported at low pH values.\(^\text{30,33}\)

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2. THEORY

2.1. Exciton Hamiltonian. We treat the intramolecular vibrational degrees of freedom of the monomers quantum mechanically by introducing one effective vibrational mode per monomer with frequency \(\omega_{mn}\) and Huang–Rhys factor \(S\). The coupling of electronic excitations to these modes is treated within the present one-particle approximation,\(^\text{16}\) that is, vibrational excitations are taken into account only in the electronic excited state of the chromophores. The rationale behind this approximation is that the energy of the quanta of this intramolecular mode is large compared to the thermal energy and, therefore, an electronic transition induced by an external field will always start from the vibrational ground state of the electronic ground state. However, the Coulomb coupling between the vibronic transitions of different monomers mixes the excited intramolecular states of the electronic ground state of the monomers into the excited eigenstates of the aggregate. This mixing is neglected in the present one-particle approximation. All intermolecular degrees of freedom are treated classically by molecular dynamics simulations. Neglecting electron exchange between the monomers results in the following Frenkel–exciton Hamiltonian

\[
H_{\text{exc}}(t) = \sum_{\mu \nu} E_{\mu\nu}(t) \left| \phi_{\mu\nu}^\text{exc} \rightangle \langle \phi_{\mu\nu}^\text{exc} \right| + \sum_{\mu \neq \nu} \sum_{\mu\nu m} T_{\mu\nu m}(t) \left| \phi_{\mu\nu} \rightangle \langle \phi_{\mu\nu} \right| = H_{\text{exc}}^\text{(1)}(t) + H_{\text{exc}}^\text{(2)}(t)
\]

The \(E_{\mu\nu}(t) = E_{\mu\nu}(t) + \mu \hbar \omega_{\mu\nu}\) are the local excitation energies of the monomers between the electronic and intramolecular vibrational ground state and the electronic excited state with \(\mu\) intramolecular vibrational quanta. The off-diagonal element \(T_{\mu\nu m}(t)\) describes the coupling of the transition between the electronic and the intramolecular ground state and the electronic and the \(\mu\)th intramolecular excited vibrational state of monomer \(m\) with the transition between the electronic excited state with \(\nu\) vibrational excitations of monomer \(n\) and its electronic and vibrational ground state. In the Condon approximation\(^\text{13}\) this coupling, termed excitonic coupling, can be factorized into an electronic part \(T_{\mu\nu m}(t)\) and a product of Franck–Condon factors of the monomers \(f_{\mu\nu}\), that is

\[
T_{\mu\nu m}(t) = T_{\mu\nu}(t) f_{\mu\nu}
\]

where the Franck–Condon factor \(f_{\mu\nu}\) is given as \(^\text{13,37}\)
\[ f_s = \exp(-S/2) \frac{\sqrt{S^2}}{\sqrt{k!}} \]  

For the present system we estimated \( S = 0.83 \) and \( \hbar \omega_{ vib} = 800 \text{ cm}^{-1} \) for the effective intermolecular vibrational mode from optical spectra of isolated monomers, as described in detail later.

The electronic factor \( J_{m,n} \) describes the excitonic coupling between intramolecular 0–0 transitions. Please note that the explicit time dependence of the above Hamiltonian results from the classical treatment of the intermolecular vibrational degrees of freedom. The interaction of the aggregate with a monochromatic external field \( E(t) = E_0 e^{\cos o t} \) is described in rotating wave approximation by the Hamiltonian

\[ H_{\text{exc-rad}} = - \sum_{m\mu} e \mu_{\text{m}} f_\mu \frac{E_0}{2} \exp(-i o t) | \phi_{m\mu} \rangle \langle \phi_0 | + \text{h.c.} \]  

where \( \mu_{\text{m}} \) is the local electronic transition dipole moment of monomer \( m \). \( f_\mu \) is the Franck–Condon factor introduced in eq 3, and h.c. denotes the Hermitian conjugate of the first expression on the righthand side.

### 2.2. Theory of Optical Spectra.

The optical spectra are obtained after diagonalization of \( H_{\text{exc}}(t) \) (eq 1), resulting in exciton states

\[ | \phi_m(t) \rangle = \sum_n c_{nm}(t) | \phi_n \rangle \]  

with excitation energies \( \hbar \omega_{ \text{exc} } (t) \). The influence of intermolecular degrees of freedom determines the time-dependence of the above eigenstates and energies. In the calculation of the absorbance \( \alpha(\omega) \) this time dependence is taken into account in the static limit, where it leads to inhomogeneous broadening

\[ \alpha(\omega) \propto \omega (\sum_{m} |d_m(t)|^2 \delta(\omega - \omega_{\text{m}}))_I \]  

with the transition dipole moment

\[ d_m(t) = \sum_{\mu} \sum_{\mu} c_{\mu m}^{(M)}(t) d_{\mu m} f_\mu \]  

The average over inhomogeneous conformations is denoted as

\[ \langle \cdots \rangle_I = \frac{1}{\int_0^T dt} \int_0^T dt \cdots \]  

\[ \times \delta(\omega - \omega_{\text{m}}(t)) \]  

and is performed taking into account the time-dependent trajectories resulting from the classical propagation of intermolecular degrees of freedom. In the case of linear dichroism, the difference in absorbance of light polarized parallel and perpendicular to the symmetry axis of the tube is measured reading

\[ LD(\omega) \propto \omega (\sum_{M} |d_M(t)|^2 (3 \cos \theta_0^2(t) - 1)) \times \delta(\omega - \omega_M(t))_I \]  

where \( \theta_0(t) \) is the angle between the exciton transition dipole moment \( d_0(t) \) and the symmetry axis of the tube.

In the following, we consider a simplified Hamiltonian for which it is possible to disentangle the diagonalization of \( H_{\text{exc}}(t) \) (eq 1) into a diagonalization of the bare exciton Hamiltonian and a subsequent diagonalization of the exciton–vibrational Hamiltonian, separately for every eigenstate of the bare exciton Hamiltonian. In this way a simple explanation of the different redistribution of oscillator strength by the exciton–vibrational coupling for J- and H-bands will be obtained.

#### 2.2.1. Redistribution of Oscillator Strength by Exciton–Vibrational Coupling.

We consider a simplified Hamiltonian without static disorder, that is, the Hamiltonian in eq 1 is assumed to be time independent. In addition, we assume that all local electronic transition energies of the chromophores are equal, i.e., we have \( E_{\text{exc}}(t) = E_0^{\text{tub}} + \mu \hbar \omega_{\text{ vib}} \) where \( E_0^{\text{tub}} \) is the transition energy between the vibrational ground states of the electronic excited and ground state. The coefficients \( c_{nm}(t) \) of the eigenstates \( | \phi_n \rangle \) (eq 5) then fulfill the following equation

\[ E_{\text{exc}}(t) = (E_0 + \mu \hbar \omega_{\text{ vib}}) c_{nm}^{(M)} + \sum_{mn} (1 - \delta_{mn}) J_{m,n} f_{\mu} c_{nm}^{(M)} \]  

where \( E_0 \) is the eigenenergy of \( | \phi_{\text{m}} \rangle \). In addition, we investigate the bare exciton Hamiltonian \( H_{\text{exc}} \) that does not include the intramolecular vibrational mode of the chromophores

\[ \hat{H}_{\text{exc}} = \sum_{m} E_0 |m\rangle \langle m| + \sum_{m n} (1 - \delta_{mn}) J_{m,n} |m\rangle \langle n| \]  

where \( E_0 \) is the local vertical transition energy of the chromophore in the tube taken at the equilibrium position of nuclei in the electronic ground state

\[ E_0 = E_0^{\text{tub}} + \hbar \omega_{\text{ vib}} \]  

with the Huang–Rhys factor \( S \) introduced in eq 3. The eigenstates \( |k\rangle \) of \( \hat{H}_{\text{exc}} \) read

\[ |k\rangle = \sum_{m} c_{k m}^{(k)} |m\rangle \]  

The coefficients \( c_{k m}^{(k)} \) are obtained from the solution of the eigenvalue problem

\[ \sum_{n} (1 - \delta_{mn}) J_{m,n} c_{k m}^{(k)} = (\hat{E}_k - E_0) c_{k m}^{(k)} \]  

with the eigenenergy \( \hat{E}_k \) of \( \hat{H}_{\text{exc}} \). We rewrite the second expression in eq 9 as

\[ \sum_{n} (1 - \delta_{mn}) J_{m,n} f_{\mu} c_{nm}^{(M)} = \sum_{n m' n'} (1 - \delta_{m'n'}) J_{m,n} \delta_{n',n} \delta_{\mu,\mu'} c_{m'n'}^{(M)} \]  

\[ = \sum_{n m' n'} (1 - \delta_{m'n'}) J_{m,n} \sum_{k,l} c_{k m}^{(k)} c_{k m'}^{(l)} f_{\mu} c_{k m'}^{(M)} \]  

\[ = \sum_{k} \sum_{n m'} (\hat{E}_k - E_0) c_{k m'}^{(k)} f_{\mu} c_{k m'}^{(M)} \]  

where we used the orthogonality of wave functions, that is, \( \sum_{m} c_{k m}^{(k)} c_{k m}^{(l)} = \delta_{k,l} \) and \( \sum_{m} c_{k m}^{(k)} c_{m m}^{(M)} = \delta_{k,0} \) as well as eq 13. We proceed by introducing coefficients

\[ c_{k m}^{(M)} = \sum_{n} c_{k m}^{(k)} c_{m n}^{(M)} \]  

Hence, it holds that

\[ c_{m n}^{(M)} = \sum_{k} c_{k m}^{(k)} c_{k n}^{(M)} \]  

Using the above expressions, eq 9 can be rewritten as
The optical transition dipole moment \( \mathbf{d}_\mu \) then follows from the eigenvalue coefficients \( \langle M_k | \mathbf{d}_\mu \rangle \) (eq 9) using eq 16 as

\[
\mathbf{d}_\mu = \sum_k \sum_{\nu} \langle M_k | \mathbf{d}_\mu \rangle \mathbf{d}_k = \sum_k \sum_{\nu} \langle M_k | \mathbf{d}_\mu \rangle \mathbf{d}_k \mu
\]

(19)

where \( \mathbf{d}_k = \sum_{\nu} \langle \nu | \mathbf{d}_k \rangle \) is the transition dipole moment of the bare exciton state \( | \nu \rangle \) (eq 12), \( \langle \nu | \mathbf{d}_k \rangle \) is the Franck-Condon factor defined in eq 3, and \( \langle M_k | \mathbf{d}_\mu \rangle \) is obtained from the solution of the eigenvalue problem in eq 18.

The above result is remarkably simple and tells us how the intramolecular exciton-vibrational coupling redistributes the oscillator strength of an exciton transition. Since eq 18 is diagonal with respect to \( k \), no mixing of different exciton states \( k \) and \( l \) occurs due to the intramolecular exciton-vibrational coupling. In other words the quantum number \( v \) and \( \nu \) couple differently vibronic transition dipole moments \( \langle \nu | \mathbf{d}_k \rangle \) which have a nonvanishing bare exciton transition dipole moment \( \langle \nu | \mathbf{d}_k \rangle \), that is, there is no mixing with dark exciton states \( \nu \).

The latter effect can be qualitatively understood by a perturbative treatment of the off-diagonal couplings in eq 18 that couple different vibrational states \( \nu \) and \( \mu \). For this purpose we can identify the eigenstate \( | M_k \rangle \) in the vibronic manifold of the \( k \)th exciton state with a state \( | \nu \rangle \) that for absent off-diagonal coupling equals \( | \nu \rangle \langle \nu | \mathbf{d}_k \rangle \). Taking into account the off-diagonal coupling \( \langle \nu | \mathbf{d}_k \rangle \) we have to first order, the coefficient \( \langle \nu | \mathbf{d}_k \rangle \) is obtained as

\[
\langle \nu | \mathbf{d}_k \rangle \approx \delta_{\nu \mu} + \frac{\langle \nu \rangle \langle \nu | \mathbf{d}_k \rangle}{(\nu - \mu) \hbar \omega_{\nu \mu} + (\langle \nu \rangle \langle \nu | \mathbf{d}_k \rangle)^2 - \langle \nu | \mathbf{d}_k \rangle^2} \quad (1 - \delta_{\nu \mu})
\]

(22)

The resulting optical transition dipole moment \( \mathbf{d}_M = \mathbf{d}_{\mu} \) then reads using eq 20

\[
\mathbf{d}_M \approx \mathbf{d}_\nu (f_\nu + \sum_{\mu} C_{\mu \nu} f_\mu)
\]

(23)

where the coefficient \( C_{\mu \nu} \) mixing different transitions \( \mu \neq \nu \) is given as

\[
C_{\mu \nu} = \frac{(\langle \nu \rangle \langle \nu | \mathbf{d}_k \rangle - \langle \nu | \mathbf{d}_k \rangle^2)}{(\nu - \mu) \hbar \omega_{\nu \mu} + (\langle \nu \rangle \langle \nu | \mathbf{d}_k \rangle)^2 - \langle \nu | \mathbf{d}_k \rangle^2} \quad (1 - \delta_{\nu \mu})
\]

(24)

The Franck-Condon factor \( f_\nu \) for the present Huang-Rhys factor \( S < 1 \), decreases with increasing \( k \). In general, the low-energy exciton states \( (\langle \nu \rangle \langle \nu | \mathbf{d}_k \rangle < 0) \) have \( C_{\mu \nu} \) for \( \mu > \nu \). In particular, it holds that \( C_{\mu \nu} > 0 \) for all \( \mu = 1 \ldots N_{\nu} \) in eq 23, where \( N_{\nu} \) denotes the number of vibrational levels included per chromophore. Hence, there is constructive superposition of vibronic transition dipole moments \( \mathbf{d}_k f_\nu \) and \( \mathbf{d}_M C_{\mu \nu} f_\mu \) in the optical transition to the vibrational ground state \( \nu = 0 \) of the low-energy exciton states (with nonvanishing bare exciton transition dipole moment \( \mathbf{d}_0 \)). In the case of high-energy exciton states we have \( (\langle \nu \rangle \langle \nu | \mathbf{d}_k \rangle > 0 \) and obtain constructive superposition, that is, \( C_{\mu \nu} > 0 \), if it holds that \( (\nu - \mu) \hbar \omega_{\nu \mu} \) for \( (\langle \nu \rangle \langle \nu | \mathbf{d}_k \rangle)^2 - \langle \nu | \mathbf{d}_k \rangle^2 \). The magnitude of \( C_{\mu \nu} \) goes rapidly to zero for large \( \mu \) or \( \nu \), because the respective Franck-Condon factors are small. Hence, in general, the mixing of vibronic transitions goes to zero in this case. Therefore, the redistribution toward higher vibronic transitions, as may occur in the case of high-energy exciton states, will never be as strong as the redistribution toward low-energy vibronic transitions in the case of low-energy exciton states. This effect in essence explains the difference in the vibrational progression of J- and H-bands.

Concerning the shift in energies due to the off-diagonal coupling in eq 18 we note that the first nonvanishing contribution is obtained in second order in this coupling and the resulting energy \( E_\nu \) reads

\[
E_\nu \approx E_\nu (1 - f_\nu^2) + \tilde{E}_\nu f_\nu^2 + \nu \hbar \omega_{\nu \mu} + \sum_{\mu \neq \nu} \delta E_{\nu \mu}^0
\]

(25)

with

\[
\delta E_{\nu \mu}^0 = \frac{((\langle \nu \rangle \langle \nu | \mathbf{d}_k \rangle - \langle \nu | \mathbf{d}_k \rangle^2)^2}{(\nu - \mu) \hbar \omega_{\nu \mu} + (\langle \nu \rangle \langle \nu | \mathbf{d}_k \rangle)^2 - \langle \nu | \mathbf{d}_k \rangle^2}
\]

(26)

For large \( \nu \), the respective Franck-Condon factors \( f_\mu \) are practically zero and \( E_\nu \approx E_0 + \nu \hbar \omega_{\nu \mu} \), that is, there is no
influence of the excitonic interactions and the aggregate absorbs light as the monomers. For small $\nu$, however, there is a $\nu$-dependent change of the vibronic transition energies, which become nonequidistant and experience a further shift $\delta E_{\nu}(\mu)$ by coupling with other vibronic transitions $\mu$.

Along the same line of discussion used above, we see that for low-energy exciton states $(E_k - E_0 < 0)$ and Huang–Rhy factors $S < 1$ it holds that $\delta E_{\nu}(\mu) < 0$ for $\nu < \mu$, that is, there is always a red shift due to the coupling with higher energy vibronic transitions. In the case of high-energy exciton states $(E_k - E_0 > 0)$ it depends on the relative magnitude of $\hbar \omega_{\text{vb}}$ and $E_k - E_0$ whether the shift goes to the red or to the blue.

In the following it will be discussed how the aggregate Hamiltonian in eq 1 is parametrized by combining quantum chemical, electrostatic, and molecular mechanics calculations.

2.2.2. Parametrization of the Hamiltonian. The diagonal elements of the exciton Hamiltonian (eq 1) describe the energies at which the chromophores would absorb light if they were not coupled excitedly. These diagonal elements $E_{\text{iso}}(\nu) = E^{(0)} + \Delta E_{\text{iso}}(\nu)$ contain the vertical excitation energy $E^{(0)}$ of a TTBC molecule taken at the equilibrium position of nuclei in the electronic ground state and a shift $\Delta E_{\text{iso}}(\nu) \approx \Delta E_{\text{iso}}^{(d)}(\nu) + \Delta E_{\text{iso}}^{(disp)}(\nu)$ that is described by taking into account intermolecular electrostatic coupling and intermolecular London dispersive interactions, respectively.

The electrostatic transition energy shift of chromophore $m$ is obtained as

$$\Delta E_{\text{iso}}^{(d)}(\nu) = \sum_{k \neq m} \left( J_{mk}(eg, ge)(t) - J_{mk}(gg, gg)(t) \right)$$

where $J_{mk}(eg, ge)$ denotes the Coulomb coupling between the charge densities of the electronic excited state of chromophore $m$ and that of the electronic ground state of the chromophore $k$, which may represent another chromophore or a solvent molecule including the counterions, and $J_{mk}(gg, gg)$ is the same type of Coulomb coupling but between the ground state charge densities of chromophore $m$ and its environment. The charge density couplings are evaluated by performing quantum chemical calculations on the isolated chromophore and fitting the electrostatic potentials by that of atomic partial charges, which are then used to calculate the couplings

$$J_{mk}(ag, ga)(t) = \sum_{l} \frac{q_{l}^{(ag)}(a, a)q_{l}^{(ga)}(g, g)}{|R_{l}(t) - R_{k}(t)|}$$

Here $q_{l}^{(ag)}(a, a)$ is the partial charge placed at atom $l$ of chromophore $m$ for the ground ($a = g$) and excited state ($a = e$) and $q_{l}^{(ga)}(g, g)$ is the partial charge at atom $l$ of the environmental molecule $k$ in its electronic ground state. We used (time-dependent) density functional theory and the B3LYP exchange correlation functional for the calculation of the electrostatic potential of the ground (excited) state of the isolated chromophores. The numerical values of the atomic partial charges that fit the respective potentials are given in the SI.

In next higher order in the molecule–environment interaction there are inductive and dispersive transition energy shifts. Inductive shifts arise due to the polarization of the wave function of a molecule by the charge density of its environment and vice versa. We follow our previous work on J-aggregates and neglect the inductive shifts, noting, however, that for some systems these shifts were reported to be significant.

In order to allow for a microscopic description of static disorder we will include besides the $\Delta E_{\text{iso}}^{(d)}(\nu)$ in eq 27 a description of the dispersive transition energy shifts, introduced in our previous work as

$$\Delta E_{\text{disp}}^{(m)}(\nu) = -Q \sum_{k} V_{\text{mk}}^{2}(t)$$

where $V_{\text{mk}}(t)$ is the coupling of two effective extended dipoles carrying unit charges and being located at molecules $m$ and $k$. The distance between the two charges on a given chromophore should reflect the extent of the $\pi$-electron system of the chromophore. For the present TTBC molecule we take a distance of 14.0 Å between these unit charges. The factor $Q$ in the above equation is a constant that was derived using second-order perturbation theory in the intermolecular interaction and contains information about energies and oscillator strengths of higher excited states. This factor can be obtained from experiments on transition energy shifts of the isolated chromophores in different solvents. Describing the latter by a homogeneous dielectric of refractive index $n_2$ and the solute as a sphere of radius $R$ results in a dispersive shift of

$$\Delta E_{\text{disp}}^{(m)}(\nu) = -F \frac{n_2^2 - 1}{2n_2^2 + 1}$$

with the prefactor $F = ((\Delta d)_{\text{exc}} - (\Delta d)_{\text{iso}})/R^2$ that contains the difference in the variance of the permanent dipole moment between the excited and the ground state of the solute. From the absorption peaks of TTBC in methanol and water we obtain $F \approx 0.78$ and extrapolate a vacuum transition energy of the chromophore $E_{\text{vac}} = 2.545$ eV (487 nm). By taking many different tube geometries and averaging the dispersive shift (eq 29) of a molecule with its neighbors one should obtain a similar result as from the continuum approximation in eq 30. Hence, $Q$ follows as

$$Q = \frac{F}{(V_{\text{mk}}^{2})_{\text{orient}}} \frac{n_2^2 - 1}{2n_2^2 + 1}$$

where $< \cdots >_{\text{orient}}$ denotes an average over many tube geometries and over time and $F$ is taken from the experimental shift measured in different solvents. With this $Q$ the dispersive shifts in eq 29 can be calculated for every monomer $m$ if the refractive index $n_1$ is known. For a monolayer of a related compound $n_1 = 1.64$ was measured in ref 45. As discussed before, the main effect of the diagonal elements of the exciton Hamiltonian is to shift the center of the spectrum along the energy (wavelength) axis. In the present work, we find that for $n_1 \approx 1.5$ we can explain the shift of the absorbance spectrum of our final suggestion for the TTBC tube with respect to that of the isolated monomer in methanol ($n_1 = 1.33$). The deviations between the above $n_1 = 1.5$ and $n_1 = 1.64$ measured in ref 45 could be due to the difference in morphology (tube versus plane monolayer), but it could also reflect the neglect of inductive transition energy shifts, discussed above. Using $n_1 \approx 1.5$ we obtain $Q \approx 2.28$ eV Å$^2$ from eq 31, which is used to obtain dispersive shifts from eq 29 along the MD trajectories, that will be used for a microscopic description of static disorder.

The excitonic coupling between the transition densities of the monomers is obtained from the Poisson-TrEsp method, which allows us to take into account polarization effects of the
environment. The environment in the present case comprises the transitions between the ground state and higher (than first) excited states of the other monomers and the excitations of solvent molecules. The excitonic coupling $J_{mn}$ between monomers $m$ and $n$ is obtained in the following way. First, the transition density of the isolated TTBC monomer is calculated with time-dependent density functional theory using the B3LYP exchange-correlation functional. The electrostatic potential of this transition density in vacuum is fitted by atomic transition charges $q_i(g, e)$. The latter are placed into molecule-shaped cavities of monomers $m$ and $n$ that are surrounded by a dielectric continuum of optical dielectric constant $\epsilon^c$. A Poisson equation is solved in order to obtain the electrostatic potential $\phi_m^c(\mathbf{r})$ of the transition charges of monomer $m$

$$\nabla \cdot (\epsilon(\mathbf{r}) \nabla \phi_m^c(\mathbf{r})) = -4\pi \sum_i q_i^{(m)}(g, e) \delta(\mathbf{r} - \mathbf{R}_i^{(m)})$$

(32)

where $\epsilon(\mathbf{r})$ equals 1 if $\mathbf{r}$ points into the cavities of monomers $m$ or $n$ and $\epsilon(\mathbf{r}) = n_r^e$ otherwise. Please note that in the original Poisson-TrEsp method all chromophore cavities (and not just those of chromophores $m$ and $n$) have $\epsilon = 1$ and the protein solvent environment has $\epsilon = 2$. In the present case there is no protein environment forming binding pockets for the chromophore, but the chromophores self-aggregate. Since the excitonic coupling between the low-energy excitations is taken into account explicitly in the Hamiltonian a certain amount of polarization is included in this way. However, additional polarization is contributed by higher excited states of the chromophores. It is this residual polarization that contributes to the screening in the present Poisson-TrEsp calculations. We take $n_r = 1.5$ as has been estimated from the dispersive shift in monomer transition energies discussed above. The excitonic coupling $J_{mn}$ then follows as

$$J_{mn} = \sum_j \phi_m^c(\mathbf{R}_j) q_j^{(m)}(g, e)$$

(33)

In order to simplify the above procedure, the above coupling is compared with the coupling in vacuum

$$J_{mn}^\text{vac} = \sum_{l,j} \frac{q_j^{(m)}(g, e) q_j^{(m)}(e, g)}{|\mathbf{R}_j^{(m)} - \mathbf{R}_i^{(m)}|}$$

(34)

and a screening/local field correction factor $f_{mn} = J_{mn}/J_{mn}^\text{vac}$ is determined. As will be shown below $f_{mn}$ varies between 0.50 and 0.60 and depends on the mutual geometries of monomers in the tube aggregate. The variation in $f_{mn}$ by the nuclear dynamics is found to be small in the MD simulations (see below). Therefore, time-independent factors $f_{mn}$ can be assumed. In rough estimations of optical spectra, we take an average screening/local field correction factor $f \approx 0.55$, determined as described in detail later.

Since different quantum chemical methods give a similar shape of the transition density but magnitudes that may differ by a factor of up to 1.5, it is necessary to rescale the quantum chemical transition density by a constant factor that is used to reveal the experimental transition dipole moment. As shown by Knox and Spring25 the dipole strength $\tilde{d}$ (in units of $D^2$) of a chromophore in a certain spectral region $\Delta \nu$ is given as $9.186 \times 10^{-18} n_r A(\Delta \nu)$, where $n_r$ is the refractive index of the medium and $A(\Delta \nu) = \int \Delta \nu d\nu c(\nu)/\nu$, with the absorption coefficient $c(\nu)$. We measured the absorption coefficient of TTBC in DMSO, which has a refractive index $n_r = 1.48$ that is practically identical to the one estimated for the tube and obtained a dipole strength of 14.4 D. Taking into account an average screening/local field correction factor of $f \approx 0.55$ results in an effective transition dipole moment of $d_{\text{eff}} = \sqrt{f}d = 10.7$ D, which is close to the $d_{\text{eff}} = 11.4$ D that has been used before for this type of chromophore.20 Please note that the present estimate of $d_{\text{eff}}$ is an upper bound, since the $d$ in Poisson-TrEsp refers to the vacuum rather than the medium transition dipole moment of the chromophore. Smaller $d_{\text{eff}}$ however did not lead to any reasonable agreement between calculated and measured spectra. The Franck–Condon factor $S$ of the effective vibrational mode has been estimated from optical spectra of TTBC monomers in methanol. The monomer absorption is given as

$$a_{\text{mon}}(\omega) = \frac{\omega}{\sigma_0} \sum_{\mu} f_{\mu} \delta(\omega - E_\mu/\hbar - \mu \omega_{\text{broad}})$$

(35)

with the Franck–Condon factor $f_{\mu}$ that is related to the Huang–Rhys factor $S$ in eq 3. For comparison with experimental data we have dressed the $\delta$-functions in eq 35 with Gaussians of width $\sigma_\mu = (\mu + 1) \sigma_0$ in order to take into account inhomogeneous broadening. The larger broadening of the higher vibrational states corrects for the limitations of the effective mode model. The absorption spectrum calculated for $S = 0.83$, $\omega_{\text{broad}} = 800$ cm$^{-1}$ and a 0–0 transition energy $E_{\text{00}} = 2.407$ eV corresponding to a wavelength of 515 nm, is compared in Figure 3 to the experimental data, revealing good agreement. In addition, we also show a homogeneous spectrum, calculated by dressing the sticks in eq 35 by Lorentzians of width 30 cm$^{-1}$, in order to visualize the vibrational progression that will be important later when we will discuss how it is changed by the excitonic coupling in the aggregate.

**2.3. Simulation of Cryo-TEM Micrographs.** For a direct consistency check of our final structural model, we also simulated the TEM images. To this end, we estimated the actual degree of noise in the raw data and determined the contrast transfer function (ctf) of the used microscope. The latter data allow one to calculate projection images of the theoretical molecular model structures with a resolution and degree of noise as found for the raw data. As raw cryo-TEM image data are of poor contrast we used the single-particle analysis approach to construct a noise-reduced sum image of some tube segments. To get an impression of the reached consistency this sum image and the simulated
images, the class sum image of tubes or only their density profiles are compared. Technical details of the image processing and simulation procedures are given in the SI.

3. RESULTS AND DISCUSSION

3.1. Generation of Tubular Structures. Cryo-TEM images show thin elongated thread-like structures which are interpreted as a projection of single-walled dye tubes. This interpretation becomes clear at high magnification, where a pattern of fine lines with a spacing of about 19 Å is visible for isolated individual fibers. A line scan perpendicular to the long axis of a single fiber reveals a cylindrical structure, where the parallel lines with high contrast correspond to the walls of a tubular aggregate. The outer diameter of the tubes amounts to about 35 Å. The wall thickness of about 15 Å points to a unimolecular wall structure. The TEM data provide one constraint for our structure model; the compatibility with the crystal lattice of DYEA or DYEM provides another one. These constraints will be fulfilled simultaneously by using the following lattice-wrapping procedure.

First, a crystal layer is defined. Because of its dense packing the crystal plane (100) is taken for both DYEA and DYEM. Then a wrapping vector \( \mathbf{C} \) is chosen, the length of which becomes the circumference of the tube after wrapping. To be compatible with wrapping vector \( \mathbf{C} \) has to be a lattice vector itself. From the range of likely tube diameters \( d = |\mathbf{C}|/\pi \) a set of possible wrapping vectors \( \mathbf{C} \) follows. Each of them can be described by lattice indices \( (N_1, N_2) \). The choice of wrapping vectors is illustrated in Figure 4. Figure 5 depicts the wrapping procedure for both solvate lattices. The two half circles in the (100) plane define the range of possible tube circumferences, and the different vectors \( \mathbf{C} \) define the wrapping directions considered. The inner circle corresponds to \( d_{\text{min}} = 16 \) Å and the outer one to \( d_{\text{max}} = 26 \) Å. Mathematical details of the wrapping procedure are given in the SI.

For small diameters this procedure may fail to provide a reasonable structure, because it creates steric overlaps between dye molecules in some cases. Some of the overlapping structures can be “repaired” by increasing the tube diameter or increasing the spacing between dye molecules in the direction along the tube axis. This change corresponds to a distortion of the primitive unit cell of the wrapped lattice which increases the unit cell area and decreases the packing density. For the wrapping directions of Figure 4 the resulting lattice parameters (after removing steric overlaps) are given in the SI. Two examples for resulting structures are shown in Figure 5.

3.2. Comparison of Optical Spectra of Structure Candidates. After wrapping a representative subset of tubes for DYEA and DYEM, linear optical spectra were calculated according to eq 6. The following simplifications, which turned out to be uncritical for a qualitative interpretation of the spectra, were applied in order to save computational time. (i) Static disorder was described by applying a Gaussian distribution function for the local transition energies of the monomers. A width of 118 meV (fwhm) was estimated for this distribution function based on a comparison of the calculated and measured low-energy absorbance peak. Static disorder in excitonic couplings is neglected. (ii) The mean local electronic transition energy \( E_{\text{tot}} \) of all monomers was set equal to \( E_{\text{tot}} = E_{\text{f(tube)}} = 2.224 \text{eV} \), corresponding to a wavelength of 557 nm, based on a comparison of calculated and experimental spectra. (iii) An average screening local field correction factor \( f = 0.55 \) was used for the calculation of excitonic couplings with the TrEsp method resulting in an effective transition dipole moment of 10.7 D, as discussed before.

These approximations allow us to obtain the optical spectra from a static structure instead of a whole set of structures generated by MD simulations. As will be shown later the inhomogeneous spectra obtained by evaluating the variations of site energies from the MD trajectories are very similar to the spectra obtained with the present simple method. Here, the average over static disorder in local optical transition energies is performed by generating random combinations of transition energies and averaging the resulting optical spectra. We find that sufficient convergence of the spectra is obtained if 10000 configurations of disorder are taken into account in the Monte Carlo simulation procedures are given in the SI.
Figure 6. Absorbance (left) and linear dichroism (right) spectra of DYEA tubes that were generated by wrapping the (100) plane of the DYEA crystal in directions as described by the wrapping vector $\mathbf{C} = N_1 \mathbf{c} + N_2 \mathbf{b}$ denoted by $(N_1, N_2)$ in comparison to experimental data (bottom). Vertical dashed lines are placed at the experimental maxima for easy comparison with the calculations.

Figure 7. Absorbance (left) and linear dichroism (right) spectra of DYEM tubes that were generated by wrapping the (100) plane of the DYEM crystal in directions as described by the wrapping vector $\mathbf{C} = N_1 \mathbf{c} + N_2 \mathbf{b}$ denoted by $(N_1, N_2)$ in comparison to experimental data (bottom). Vertical dashed lines are placed at the experimental maxima for easy comparison with the calculations.
Carlo average. We varied the length of the tube and found that taking into account around 100 chromophores leads to convergence of the absorption spectra.

The calculated linear optical spectra resulting from the different wrapping directions are compared to experimental data in Figures 6 and 7 for DYEA and DYEM tubes, respectively. We see that for structures generated from DYEA only the wrappings in (6,0) and (5,−5) directions qualitatively match the experimentally determined linear dichroism and absorbance spectra. The intensity ratio between the main peaks is somewhat closer to the experimental value for the (6,0) tube. For DYEM the wrapping direction (6,0) fits best, although the red-shifted peak carries somewhat too little intensity. We take into account the (6,0)-DYEA and (6,0)-DYEM structures for further optimization.

3.3. Stability of the Candidates and Analysis of Fragments from MD Simulations. To test the stability of the (6,0)-DYEA and (6,0)-DYEM candidate structures, MD simulations were carried out using the NAMD program package, the AMBER force field, and the GAFF parameter set. The particle mesh Ewald method was utilized in order to establish periodic boundary conditions.

Two snapshots for (6,0)-DYEA taken at 60 ps and 2.7 ns are shown in Figure 8a and 8b, respectively. After 60 ps the structure is partially ripped apart by the solvent. The instability can be attributed to intermolecular distances being too large in the initial structure. The large intermolecular distances stem from removing steric clashes as described before. At 2.7 ns a well-ordered tube is recovered in the central region of the simulation box.

In the case of the alternative (6,0)-DYEM starting geometry we find that the structure breaks apart in the course of the MD simulations. At 0.5 ns the molecules partially realign and form a structure which is similar to the (6,0)-DYEA tube discussed above (Figure 8c). Hence, we conclude that the (6,0)-DYEM structure is further away from the stable tube structure than the one of (6,0)-DYEA. In a next step, the partially ordered central segment of the MD-simulated DYEA tube at 2.7 ns (Figure 8b) was used to determine new structure parameters. A least-squares fit between the disordered tube and an ideal helical tube revealed the primitive lattice vectors of the latter, given in the SI, which deviate from the lattice vectors of the original crystal plane of DYEA. Next, these new lattice vectors were used to create a new (6,0) tube. This geometry was found to be stable within a new MD run which took 100 ns. A representative snapshot of this structure is shown in Figure 9.

The structure obtained after 100 ns MD simulation was used again to determine primitive lattice vectors used to create an ideal tube, which represents our suggestion for the structure of the

**Figure 8.** Snapshots of structures during MD simulation with initial structures obtained from wrapped crystal planes: (a) (6,0)-DYEA after 60 ps, (b) (6,0)-DYEA after 2.7 ns, and (c) (6,0)-DYEM after 0.5 ns.

**Figure 9.** (a) MD snapshot of the final tube structure viewed along the symmetry axis of the tube (top) and perpendicular to this direction (bottom). (b) Space-filling model of the final ideal tube structure with lattice parameters $c = 13.582\,\text{Å}$, $b = 8.832\,\text{Å}$, $\alpha = 140.344^\circ$, and $\theta = 74.000^\circ$ extracted from the final MD structure by a least-squares fit.
between these vectors, and the angle $\alpha$ is the angle between the transition dipole moment of the dye molecule and the symmetry axis of the tube. A space-filling model of this tube is shown in Figure 9b. The optical spectra resulting for this structure are compared in Figure 10 with the experimental data (black solid line). For comparison, we also show the homogeneous spectra resulting from the bare exciton Hamiltonian, that is, without including the effective vibrational mode (green and red dashed lines).

In the homogeneous spectrum we find a single low-energy peak at around 590 nm (the J-band), the transition dipole moment of which is polarized along the symmetry axis of the tube, and a number of peaks between 450 and 550 nm (the H-band) with transition dipole moments that are polarized perpendicular to this axis. In the bare exciton spectra it is seen that part of the broadening of the H-band is due to the presence of multiple exciton transitions with nonzero transition dipole moments. In the case of the J-band practically all of the oscillator strength is contained in a single transition. Switching on the coupling of excitons to the effective intramolecular vibrational mode changes the H-band qualitatively but leaves the J-band unchanged, except for a 10 nm red shift and a slight reduction in intensity. Interestingly, practically no vibrational progression is visible for the J-band. This remarkable behavior is explained by our analytical treatment and the perturbation theory. As shown by the analytical treatment of the homogeneous spectrum, the coupling to the effective vibrational mode does not lead to a mixing between different eigenstates of the bare exciton Hamiltonian. The perturbation theory explains how for every eigenstate of the bare exciton Hamiltonian the vibrational progression, which one would naively expect, is changed by the off-diagonal elements of the exciton–vibrational coupling. Whereas in the case of the J-band the majority of the oscillator strength is redistributed to the lowest energy transition, that is, to the $\nu = 0$ state of the lowest exciton state, in the case of the transitions in the H-band, there is redistribution of oscillator strengths toward transitions with larger $\nu$. For the present system we have $\nu < 1$, and therefore, all of the mixing coefficients $c_{\mu \nu}^{(0)}$ (eq 24) for $\nu = 0$ in the case of the J-band are positive. In addition, we have $E_{\alpha} - E_{\beta} < \hbar \omega_{\alpha \beta}$ for all H-band exciton states $\alpha$ with strong transition dipole moments, and therefore, it holds that $c_{\mu \nu}^{(0)} > 0$ for $\mu < \nu$. Hence, there is redistribution of oscillator strength toward the states with larger $\nu$. This effect is illustrated in Figure 12, where for the bare exciton transition with the largest oscillator strength of the H-band and that of the J-band the redistribution of oscillator strength by the exciton–vibrational coupling to the effective mode is analyzed in detail. As seen in Figure 12 the exciton–vibrational coupling (the first part in eq 18) leads to a vibrational progression in the exciton spectrum (Figure 12b), which is, however, qualitatively changed by the off-diagonal elements (the second part in eq 18) of the exciton–vibrational coupling (Figure 12c and 12d). Whereas for the exciton transitions in the J-band practically all oscillator strength is redistributed to the $\nu = 0$ transition, for the transitions in the H-band it is redistributed toward several vibronic transitions with larger $\nu$, as expected. The perturbative analysis already explains the effect qualitatively as Figure 12c (perturbation theory) in comparison to Figure 12b (no redistribution of oscillator strength between different vibronic transitions of the same excitonic transition) and Figure 12d (exact numerical diagonalization) demonstrates.

We note that the present finding of a different redistribution of oscillator strength for H- and J-bands is in line with earlier numerical results by Spano. We are, however, not aware of such a simple analytical explanation of the effect, as presented in this work. Experimentally this effect is known since the work of Jelley and Scheibe on the classical J-aggregates. We also have to note that Spano went beyond the single-particle approx-

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**Figure 10.** Linear absorbance (solid lines) and linear dichroism (dashed lines) spectra calculated for the final structural model for the TTBC:Cl tube (green lines) compared to experimental data (black lines).

**Figure 11.** Homogeneous absorption spectra obtained by diagonalizing the bare exciton Hamiltonian (dashed lines) and the full Hamiltonian that includes the coupling to one effective intramolecular vibrational mode per chromophore (solid green and red lines). For illustrative purposes, stick spectra were broadened by Lorentzians of width 10 meV (fwhm). Red lines indicate a polarization parallel to the symmetry axis of the tube, and green lines mark those transitions which are polarized perpendicular to this axis. For comparison, we also show the experimental absorption spectrum (black solid line).
and counting the eigenstate of the ring by \( k \), we get for \( k > 0 \) (see eq 12 in ref 23)

\[
\phi_k(n_1, n_2) = \phi_{k,k_2}(n_1, n_2) = \frac{1}{\sqrt{N_2}} \exp(ik\phi_2 n_2) \phi_{n_1}(n_1, k_2)
\]  

(37)

Hence, the eigenstate \( |k\rangle = |k_1, k_2\rangle \) of the tube in eq 36 can be written as

\[
|k_1, k_2\rangle = \sum_{n_1} \phi_{k_1}(n_1, k_2) n_1 k_2
\]  

(38)

where

\[
ln_1 k_2 = \frac{1}{\sqrt{N_2}} \sum_{n_2} \exp(ik_2 \phi_2 n_2) ln_1 n_2
\]  

(39)

denotes the contribution of the excited state that is localized at the \( k_1 \)th eigenstate of the \( n_1 \)th ring to the overall exciton state \( |k_1, k_2\rangle \). In particular, it holds that the transition dipole moment

\[
\mu_{0,k_1,k_2} = \sum_{n_1} \phi_{k_1}(n_1, k_2) \mu_{n_1,n_2}
\]  

(40)

is only nonzero for those \( k_2 \) values for which the transition-dipole moment \( \mu_{0,n_k} \) of the isolated rings is nonzero. Transforming the bare-exciton Hamiltonian from the localized basis \( ln_1 n_2 \) to that of delocalized states of the rings \( ln_1 k_2 \) gives rise to off-diagonal elements, that is, coupling \( J(n_1, k_2) \) between the eigenstates of different rings in the same \( k_2 \) state, that are \( n_1 \) rings apart. This coupling reads

\[
J(n_1, k_2) = \sum_{n_2} J(n_1, n_2) \exp(-ik_2 \phi_2 n_2)
\]  

(41)

Here \( J(n_1, n_2) \) is the excitonic coupling between a pair of chromophores in the two rings, where the position inside the rings differs by \( n_2 \). The prime in the sum indicates that for \( n_1 = 0 \) we do not sum over \( n_1 = 0 \). For \( n_1 = 0 \) both chromophores are in the same ring and the excitation energy of the \( k_2 \) state of the isolated ring follows as

\[
E_{k_2} = E_0 + \sum_{n_2} J(n_2, 0) \exp(-ik_2 \phi_2 n_2)
\]  

(42)

where \( E_0 \) denotes the local vertical exciton energy of the chromophore in the tube (eq 11). The transition dipole moments \( \mu_{0,n_k} \) of the delocalized states in the rings are obtained as

\[
\mu_{0,n_k} = \frac{1}{\sqrt{N_2}} \sum_{n_1} \exp(ik_2 \phi_2 n_2) \mu_{0,n_1,n_2}
\]  

(43)

Thereby it is seen that only \( k_2 = 0 \) and \( k_2 = \pm 1 \) lead to a nonzero transition dipole moment \( \mu_{0,n_k} \) of the ring. If the transition dipole moment of the chromophores in the ring \( \mu_{0,n_1,n_2} \) have an angle \( \theta \) with respect to the symmetry axis of the tube, the parallel component \( \mu_{0,n_1,n_2} \parallel = \mu_{0,n_1,n_2} \cos \theta \) adds up constructively only for \( k_2 = 0 \) in eq 43, whereas the perpendicular components \( \mu_{0,n_1,n_2} \perp = \mu_{0,n_1,n_2} \sin \theta \) of the single chromophores give a nonzero transition dipole moment of the ring only for \( k_2 = \pm 1 \) because of the rotational symmetry of arrangement of transition dipole moments. The linear absorption spectrum is obtained from the transition dipole moments of exciton states \( \mu_{0,k_1,k_2} \) in eq 40.
Taking into account the rotational symmetry in the location of chromophore transition dipole moments $\mu_{n,n'}$, and that of the eigenstates in the rings, where eigenstates with $k_2 = 1$ and those with $k_2 = -1$ are degenerate, and performing an average over random orientations of tubes with respect to the polarization of the external light field gives for the absorption spectrum\(^{23}\)

$$\alpha(\omega) \propto \omega \cos^2 \frac{\theta}{3} \sum_{k_1} M(k_1, 0) \delta(\hbar \omega - E_{k_1,0})$$

$$+ \omega \sin^2 \frac{\theta}{3} \sum_{k_1} M(k_1, 1) \delta(\hbar \omega - E_{k_1,1})$$

(44)

where the oscillator strength reads

$$M(k_1, k_2) = N \mu^2 \left| \sum_{n_1} \Phi_{n_1} \langle n_1 | k_2 \rangle \exp(-i n_1 k_2 \gamma) \right|^2$$

(45)

Here, the angle $\gamma$ describes the relative rotation of neighboring rings around the symmetry axis of the tube. Using the parameters $N_1$, $N_2$, $c$, $b$, and $\alpha$, which define the unit cell and the circumference vector, this can be written as

$$\gamma = 2\pi \max(N_1 c^2 + N_1 b \cos \alpha + N_2 b^2\sin^2(\theta/2))$$

$$N_1^2 b^2 + N_1^2 c^2 + 2N_1 N_2 b \cos \alpha$$

(46)

For the present system we find $\gamma = 30^\circ$. Contrary to the rest of this section, in the above equation $N_1$ and $N_2$ stand for the components of the circumference vector as described in the SI.

In the case of linear dichroism, the tubes are oriented in a flow cell and the absorption is measured with light polarized parallel and perpendicular to the symmetry axis of the tube.\(^{30}\) Linear dichroism is defined as the difference between these two absorbances (parallel minus perpendicular). Taking into account an average over random orientations of the complexes with respect to rotation around the symmetry axis yields the linear dichroism spectrum\(^{23}\)

$$LD(\omega) \propto \omega \cos^2 \frac{\theta}{3} \sum_{k_1} M(k_1, 0) \delta(\hbar \omega - E_{k_1,0})$$

$$- \omega \sin^2 \frac{\theta}{3} \sum_{k_1} M(k_1, 1) \delta(\hbar \omega - E_{k_1,1})$$

(47)

As in the case of isotropic absorption, bands with nonzero oscillator strength are created for the three values of $k_2 = 0, \pm 1$. The internal states of the bands are counted by $k_1$. As discussed above, due to the rotational symmetry of the tube, the $k_2 = 0$ band is polarized parallel to the symmetry axis of the tube and the $k_2 = \pm 1$ bands are polarized perpendicular to this axis. The oscillator strengths $M(k_1, k_2)$ (eq 45) of the different transitions will be calculated below in different approximations.

Before a general conclusion can be drawn about the angle $\theta$ between the chromophore’s transition dipole moments and the symmetry axis of the tube. As seen from the expression for $LD(\omega)$ in eq 47, $\tan^2 \frac{\theta}{2}$ equals the ratio between the negative and the positive part of the LD spectrum. Hence, within the present approximations of neglecting static disorder and homogeneous broadening we can get an estimate for the angle $\theta$ directly from the positive and negative parts of the experimental LD spectrum. Analyzing this spectrum in this way results in $\theta \approx 70^\circ$, which is close to the $\theta = 74^\circ$ obtained indirectly by optimizing the structure and calculating optical spectra with a theory that includes static disorder. Due to the presence of static disorder the rotational symmetry in the rings is broken and a mixing between transitions that are polarized in parallel and perpendicular directions occurs, which changes the relative oscillator strengths in the LD spectrum. Integrating the oscillator strength calculated in the presence of disorder and using the same analysis as applied to the experimental LD spectrum results in an angle $\theta \approx 71^\circ$, which is practically identical to the $\theta \approx 70^\circ$ inferred above.

The oscillator strength $M(k_1, k_2)$ in eq 45 can be obtained analytically using either a nearest neighbor approximation for the inter-ring couplings or periodic boundary conditions for the ends of the tube.\(^{23}\) Inspection of the inter-ring couplings for the present system (Table 1) suggests that in particular for the $k_2 = \pm 1$ bands the coupling between rings falls off too weakly with increasing $n_1$ to justify a nearest neighbor approximation. Indeed, we find large deviations between the spectrum obtained in this approximation and the one resulting from an exact numerical diagonalization, as discussed in the SI. For periodic boundary conditions the eigenenergies of the tube are obtained as\(^{23}\)

$$E_{k_1 k_2} = E_0 + \sum_{n_1 n_2} J(n_1, n_2) \cos(k_1 \Phi_n + k_2 \Phi_n)$$

(48)

The oscillator strengths of the transitions in the $k_2 = 0$ band read\(^{33}\)

$$M(k_1, 0) = (N_1 + N_2) \mu^2 \delta_{k_1,0}$$

(49)

and that of the $k_2 = \pm 1$ bands are\(^{33}\)

$$M(k_1, \pm 1) = \frac{(N_1 + N_2) \mu^2 \sin^2[N_1(k_1 \Phi_1 - \gamma)/2]}{N_1^2 \sin^2[(k_1 \Phi_1 - \gamma)/2]}$$

(50)

Hence, in the case of $k_2 = 0$ all oscillator strength is concentrated in the $k_1 = 0$ transition, which occurs at a transition energy

$$E_0 \equiv E_{0,0} = E_0 + \sum_{n_1 = 1}^N J(n_1; k_2 = 0)$$

(51)

By applying the values for $J(n_1, k_2 = 0)$ in Table 1 it is seen that $E_0 = 2.145$ eV (578 nm) is strongly red shifted with respect to the monomer excitation energy $E_0 = 2.306$ eV (537 nm) since all $J(n_1, k_2 = 0)$ are negative.

In the case of the $k_2 = \pm 1$ bands, the oscillator strength is distributed over several transitions and the one with the largest oscillator strength occurs at a transition energy that is close to

| $n_1$ | $k_2$ | $J(n_1; k_2)$ (cm$^{-1}$) |
|-------|-------|-----------------------------|
| 0     | 0     | -986.574                    |
| 1     | 0     | -121.731                    |
| 2     | 0     | -45.337                     |
| 3     | 0     | -22.661                     |
| 4     | 0     | -13.760                     |
| 5     | 0     | -9.200                      |
we use the MD trajectories for a microscopic description of static bands. There are however quantitative deviations between the obtained in the two different calculations. As shown in ref 23, for very long tubes and the periodic boundary conditions considered, this transition is the only one carrying oscillator strength for \( k_2 = \pm 1 \). For the present system (Table 1) we obtain \( E_k = 2.460 \text{ eV} \) (504 nm), which is blue shifted with respect to the monomer transition energy \( E_0 \). As seen in Tables 1 and 2, the inter-ring couplings are responsible for the blue shift. In Figure 13 the absorption spectrum resulting from numerical diagonalization of the bare exciton Hamiltonian by numerical diagonalization (black) or analytical theory (eqs 48, 49, and 50) using periodic boundary conditions (green). Stick spectra (vertical lines) were dressed with Lorentians of fwhm 10 meV. Dashed lines represent transitions that are polarized perpendicular to the symmetry axis of the tube and solid lines those which are polarized parallel to this axis. Vertical dashed—dotted line denotes the vertical monomer transition energy \( E_0 = 2.306 \text{ eV} \) (537 nm) (eq 11).

### Table 2. Real and Imaginary Parts of Excitonic Couplings \( J(n_i; k_2) \) (eq 41) for \( k_2 = 1 \)

| \( n_1 \) | \( k_2 \) | \( \text{Re}(J(n_i; k_2)) \) (cm\(^{-1}\)) | \( \text{Im}(J(n_i; k_2)) \) (cm\(^{-1}\)) | \( \text{Re}[J^*(n_i; k_2)] \) (cm\(^{-1}\)) |
|---|---|---|---|---|
| 0 | 1 | 316.938 | 0.000 | 316.938 |
| 1 | 1 | 353.235 | 115.081 | 469.376 |
| 2 | 1 | 248.596 | 82.548 | 391.113 |
| 3 | 1 | 74.059 | -103.891 | 207.488 |
| 4 | 1 | 1.978 | -74.900 | 127.545 |
| 5 | 1 | -24.283 | -38.874 | 80.791 |

**The quantity** \( \text{Re}[J^*(n_i; k_2)] \) **in the last column is used in eq 52 to estimate the energy of the most intense transition of the H-band.**

![Figure 13. Homogeneous absorption spectrum resulting from the bare exciton Hamiltonian by numerical diagonalization (black) or analytical theory (eqs 48, 49, and 50) using periodic boundary conditions (green). Stick spectra (vertical lines) were dressed with Lorentians of fwhm 10 meV. Dashed lines represent transitions that are polarized perpendicular to the symmetry axis of the tube and solid lines those which are polarized parallel to this axis. Vertical dashed—dotted line denotes the vertical monomer transition energy \( E_0 = 2.306 \text{ eV} \) (537 nm) (eq 11).](image)

### 3.4. Microscopic Description of Static Disorder.

Finally, we use the MD trajectories for a microscopic description of static disorder in transition energies and excitonic couplings. For this purpose 500 snapshots between 22 and 72 ns of the MD trajectories were taken, and for each of the nuclear configurations the fluctuation in transition energies \( \Delta E_{\text{vac}}(t) \) (eq 27) was calculated. In addition, we used this parametrization to explain the redshift between the vacuum transition energy \( E_{\text{vac}}(0) = 2.545 \text{ eV} \) (487 nm) estimated for the monomer in methanol and the \( E_{\text{tube}}(0) = 2.224 \text{eV} \) (557 nm) estimated above from the calculations of the optical spectra of the tube. For this purpose, we take the \( E_{\text{vac}}(0) \) and explicitly calculate the electrostatic (eq 27) and dispersive (eq 29) transition energy shift induced by the interchromophore Coulomb coupling in the tube.

Concerning the excitonic couplings, an analysis of the screening factors \( f_{\text{mn}} \) of selected snapshots revealed that the fluctuations of \( f_{\text{mn}} \) along the MD trajectories are small (Figure 14). The screening factors \( f_{\text{mn}} \), however, depend on the mutual orientation of chromophores, and 6 major groups of screening factors are identified. For these groups we determined averaged screening factors that range between 0.58 for group 1 down to 0.47 for group 2, the overall average being 0.55 used before. In the calculation of static disorder along the MD trajectories we distinguish between the different groups and apply these average screening values to the calculation of inhomogeneously broadened optical spectra.

![Figure 14. Screening factors of excitonic couplings, obtained by the Poisson-TrEsp method, as a function of the vacuum coupling, taking into account nuclear coordinates from 5 different snapshots along the MD trajectories (at 37, 42, 47, 52, and 57 ns). Screening factors are grouped by the vertical lines, and dashed horizontal lines denote the average screening factor for a given group. These average factors are used in the calculation of inhomogeneously broadened optical spectra.](image)
molecules. This shift is within the range of 50–100 meV estimated before for this type of interaction.28

3.5. Comparison of Theoretical Model and Experimental Cryo-TEM Data. For comparison of theoretical model structures with experimental cryo-TEM data, projection images of the model structures were simulated, filtered, and normalized in the same way like the experimental data. At the available resolution the visual comparison demonstrates a high level of consistency (Figure S11 in the SI). However, due to the small size of dye monomers and the high degree of statistical noise details of the molecular packing within the tubes cannot be resolved by cryo-TEM and are also invisible in the mimicked model TEM images. To provide a quantitative assessment we generated cross-sectional density profiles of both the simulated images and the sum image of the TEM data. As shown in Figure 16 the curve progression of the density profile derived from the experimental data (red line) corresponds very well to the mean gray value of the background (121.6 ± 11.0 (Std. Dev.)).

Figure 16. Calculated cryo-TEM 2D-density profiles of the (6,0) DYEA tube model (black lines) for 10 “tomographic projections”. Experimental density profile from the sum image of cryo-TEM of the tube (red line). Horizontal straight line corresponds to the mean gray value of the background (121.6 ± 11.0 (Std. Dev.)).

4. CONCLUSIONS

A systematic procedure for the structure prediction of self-organized single-walled tubes of cyanine dyes has been developed and successfully applied to TTBC. The method combines information from cryo-TEM with that from molecular crystals of TTBC from molecular mechanics and optical spectra of the monomer and the aggregate. The Frenkel exciton Hamiltonian of the aggregate, used to calculate optical spectra, is parametrized by using quantum chemical/electrostatic methods, developed before. The arrangement of molecules in DYEA crystals, containing one molecule per unit cell, is found to be closer to the final structure than that of the alternative DYEM containing two molecules per unit cell. Thus far we have not found any DYEM tube that can explain the optical spectra and is also stable during the MD simulations. In contrast, our iterative refinement of the (6,0) DYEA tube, which effectively adjusted the unit cell, finally resulted in a stable tube. Although this result at first glance is somewhat counterintuitive, it sheds some light on our strategy of choosing the starting structure for the MD simulations. Obviously the interaction in a plane in a 3D crystal does not always contain the major interaction of a solvent-exposed single-walled tube.

The proposed structure of the (6,0) DYEA tube consists of rings of 6 chromophores with rotational symmetry. The transition dipole of each chromophore forms an angle of $\theta = 74^\circ$ with respect to the symmetry axis of the tube. Neighboring rings are rotated by an angle $\gamma = 30^\circ$ with respect to each other. This structure explains all experimental data available so far and allows for a detailed investigation of the effect of interchromophore couplings on the optical properties of the aggregate that after all allowed for the prediction of the structure.

From the monomer spectrum in methanol a mean $0^\circ$ transition energy corresponding to a wavelength of 515 nm, an effective vibrational frequency of 800 cm$^{-1}$, and a Huang–Rhys factor $S = 0.83$ have been estimated. The interchromophore coupling in the tube leads to a striking change in the optical properties. Two main absorption bands, the transition-dipole of each chromophore forms an angle of $\theta = 74^\circ$ with respect to the symmetry axis of the tube.

In order to check how unique the present proposal is, additional optical experiments like pump–probe and 2D electronic spectra would be helpful. It will be interesting to study exciton transfer/relaxation between the H- and the J-bands in this system. We expect that the inclusion of exciton–
relaxation-induced lifetime broadening will further improve the agreement between calculated and measured spectra.

**ASSOCIATED CONTENT**

1. Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b05856.

DYEA and DYE M crystal structures, details of the quantum chemical calculations, coordinates of the geometry-optimized TTBC dye and atomic partial charges of the ground and excited state and optical transition excitonic couplings between chromophores for our final structural model of the tube, as well as exciton eigenenergies and transition dipole strengths obtained for the homogeneous case (no static disorder) in comparison to results obtained using approximate analytical solutions; approximate analytical model that takes into account excitonic couplings between neighboring rings in the tube; details about the wrapping procedure used to create tubes from crystal planes; details about the analysis of the cryo-TEM images (PDF)

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Notes

The authors declare no competing financial interest.

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