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Relaxation of photo-excitations in films of oligo- and poly- (*para*-phenylene vinylene) derivatives

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Abstract

The photo-luminescence from solid films of poly(*para*-phenylene vinylene) polymers and an oligomeric model system, consisting of seven repeat units, are investigated at low temperature (8 K) using time-resolved spectroscopic techniques. Results are compared to those for the materials in solution. In the case of the oligomer, the shape of the visible absorption band observed for the film is quite different from the band shape for the polymer in frozen solution and is characteristic of H-type aggregates. Theoretical models are presented describing the dependence of the band shape of absorption and emission spectra on intermolecular excited state interactions, electron-vibration coupling and disorder represented by distributions of the molecular excitation and intermolecular interaction energies. Using these models, it is concluded that intermolecular interactions in the film of the oligomer are strong ($\geq 1400 \text{ cm}^{-1}$), and the disorder low, implying delocalization of the excitation over several molecules. In accordance with these models the fluorescence lifetime for the film ($\sim 2 \text{ ns}$) is considerably longer than for isolated molecules in solution (0.45 ns). The emission spectra of the film, taken early after excitation, are consistent with delocalization of the excitation over several molecules. A time-dependent red shift of the fluorescence band is observed and interpreted in terms of migration of localized excitations between disorder induced trap sites, which exist in the low energy tail of the density of excited states. For the polymers, differences between the shape of the absorption bands of solid film and frozen solution are smaller than for the oligomer indicating that interchain interactions that are, on average, weaker than for the oligomer. For the polymer films, a time-dependent red shift of the emission is observed and fluorescence depolarization measurements provide direct evidence for migration of the photo-excitations between trap sites. For one polymer, a time dependent change in the band shape of the fluorescence after pulsed excitation is observed with the band shape of the long-lived emission being compatible with that expected for an excitation delocalized over at least two, nearly parallel aligned, chains. For a second polymer, the emission band shape and its time evolution indicate that the major part of the fluorescence originates from disorder induced luminescent sites. These results indicate that the spectroscopic properties of films of π -conjugated polymer critically depend on parameters such as density of defects and excited state interchain interaction energy. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

π -Conjugated polymers are a relatively new class of materials with semiconducting properties and interesting possible applications. They can, for instance, be used as active layer in photonic devices such as polymer light-emitting diodes and solar cells. These prospects have spurred further investigations into the nature of the (photo-)excitations in these materials.

Site selective fluorescence measurements, in which only chromophores in resonance with a narrow laser line are optically excited, have revealed relatively strong inhomogeneous broadening of the absorption bands of films of π -conjugated polymers [1–3]. These studies led to a model in which the conjugation along the polymer backbone is interrupted by conformational and chemical defects. The statistical distribution of the conjugation length of the chain segments results in a broadening of the density of states and within this distribution the excitations can relax by energy transfer to chain segments with longer conjugation length and, hence, lower excitation energy.

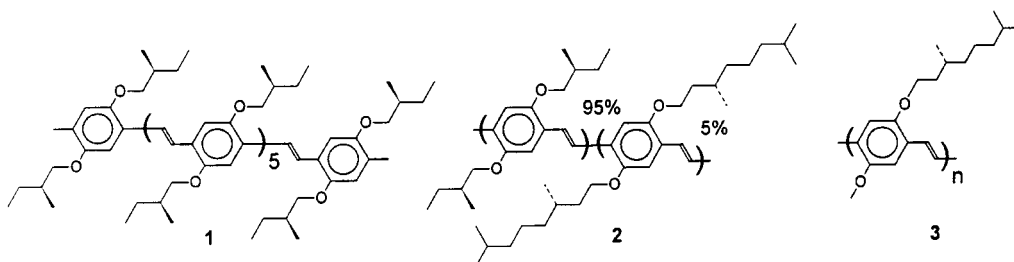
Time-resolved fluorescence measurements have shown a quasi-instantaneous appearance of the vibronic fine structure in the fluorescence, indicating that vibrational relaxation takes place within 300 femtoseconds [4–7]. On a longer time scale, a red shift of the fluorescence spectrum was observed which was interpreted in terms of relaxation of the excitations within the inhomogeneously broadened density of states by energy transfer between chain segments.

Problematic from the applications point of view is the reduction of the luminescence quantum yield

which has been observed comparing fluorescence for polymers in dilute solution and in solid film or aggregated form [8,9]. This reduction has been ascribed to the interchain interactions leading to the formation of excimers (with a low probability for radiative decay) or more generally phrased to inter-chain species in which the excitation is delocalized over neighboring chains [10,11]. Further experimental evidence for the existence for these long-lived species has come from time-resolved luminescence investigations, in which long-lived emission with a red-shifted spectrum has been observed [8].

The question of the extent of delocalization of the excitation and whether they should be regarded as inter- or intra-chain species is still lively debated. Here, we argue that delocalization of the excitation over more than one chain will result in a change in the band shape of the absorption and emission spectra. Therefore, band shape analysis provides an experimental tool to study the issue of delocalization. For aggregates of dye molecules, it has been shown both experimentally and theoretically that intermolecular interaction in the aggregate can lead to rather drastic changes in the band shape of absorption and emission spectra [12].

Here, we present time-resolved fluorescence studies on a dialkoxy substituted *para*-phenylene vinylene oligomer containing 7 repeat units (**1**) [13] and two soluble side-chain substituted poly(*para*-phenylene vinylene) (PPV) type polymers **2** and **3** (Scheme 1). For the oligomer changes in the band shape upon aggregation are indeed indicative of strong intermolecular interactions. For the polymers, effects of interchain coupling are less ap-



Scheme 1.

parent, but may be obscured by the effects of the disorder in the polymer film. For polymer **3**, however, the band shape of the long-lived emission is indicative of interchain delocalization.

2. Experimental

Films of **2** and **3** were drop cast on monocrystalline sapphire plates from a solution of ~5 mg polymer/ml solvent mixture of chloroform and *ortho*-dichlorobenzene (4–1 in volume). After drop casting, the films were annealed for 3 min on a hot plate at 70°C. Microcrystalline films of **1** were made by melting the powder between two sapphire plates at 295°C followed by slow cooling, all performed under a flow of nitrogen. The synthesis of **1** [13], **2** (poly{[2,5-bis[(*S*)-2-methylbutoxy]-1,4-phenylene]vinylene}-co-{[2,5-bis[(3*R*,3*S*)-(3,7-dimethyloctyl)oxy]-1,4-phenylene]vinylene} 5% copolymer) [14] has been described, and **3** was synthesized following the same procedures [14].

Fluorescence lifetime measurements were performed at 8 K in a He flow cryostat. A ~5 picosecond exciting light pulse was obtained from a synchronously pumped cavity dumped dye laser which was operated at a repetition rate of 0.48 MHz. The tunable dye laser (580–620 nm) was pumped with the frequency-doubled output of an actively stabilized mode-locked Nd:YAG laser. The fluorescence light, collected in a backward-scattering geometry, was dispersed by a 0.34 m double monochromator allowing for a spectral resolution of 1 nm. Time-resolved emission spectra were recorded with the time-correlated single photon counting technique in reversed mode using a microchannel plate photomultiplier (Hamamatsu R3809u-51) and a time-to-amplitude converter. The width of the instrument response function amounts to ~60 ps FWHM. Using a single channel analyzer, (EG&G) fluorescence spectra can be recorded within a variable, narrow time window after the excitation pulse. When recording time-resolved emission spectra, the maximal count rate of photons was kept low (~10³ s⁻¹) to prevent distortion of the spectra due to pulse pile-up effects. For the lifetime measurements in solution,

the 600 nm output of the dye laser was frequency doubled with a BBO crystal. By recording the emission of a tungsten filament lamp (Osram) with known emission spectrum [15], a correction for the wavelength dependence of the sensitivity of the detection systems was made.

Linear polarization measurements were made using a piezo-elastic modulator in combination with a differential photon counter [16]. Picosecond time resolution could be achieved by selecting photo pulses in a particular time window with the help of the time-to-amplitude converter in combination with the single channel analyzer. The selected pulses were then sent to a differential photon counter to analyze the polarization of the photons arriving in this window. In the polarization measurements, linearly polarized excitation light is used to create excitations whose transition dipole moment is predominantly oriented along the electric field of the polarized excitation beam. Emission from the photoselected ensemble of chromophores will, in general, be linearly polarized. The degree of linear polarization, p_{lum} , can be defined as

$$p_{\text{lum}} = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}, \quad (1)$$

where I_{\parallel} (I_{\perp}) is the emission intensity with polarization parallel (perpendicular) to the polarization of the excitation beam. When the transition dipole moment of the emissive transition from excited state back to the ground state is exactly parallel to that in the absorptive transition through which the photoexcitation was created, a value for p_{lum} of +1/2 results [17]. If the transition moment in emission would be exactly perpendicular to that in absorption the $p_{\text{lum}} = -1/3$, is expected theoretically. If complete randomization of the direction of the transition moment in the excited state occurs by e.g. rapid migration of the excitation to molecules with a different orientation, then $p_{\text{lum}} = 0$, is expected. These polarization measurements are in general quite sensitive to small amounts of highly polarized scattered excitation light entering the detector. In our case, the use of monochromatic excitation light, a double monochromator and a cut-off filter in the emission

detection channel virtually eliminates the possibility of stray light detection.

3. Results

3.1. Oligomer 1

In Fig. 1, we compare the absorption and photoluminescence spectra for **1** in frozen solution and in solid film. By rapid cooling, a solution of **1** in 2-methyltetrahydrofuran (2-MeTHF), one obtains a glassy solution in which there is little aggregation of the molecules. Under these conditions, the absorption and luminescence spectra are characterized by a vibronic progression built on a 1400 cm^{-1} mode or combination of modes with frequency close to 1400 cm^{-1} (Fig. 1(A)). Such a progression results from simultaneous vibrational and electronic transitions. According to the Franck–Condon principle the appearance of such a progression implies a distortion of the photoexcited molecule along the normal coordinate asso-

ciated with the active mode (vibronic coupling). In conjugated polymers, this mode or modes are associated with a distortion in the excited state corresponding to a reversal of the bond length alternation resulting in a more quinoid-like structure rather than the aromatic structure of the ground state.

For the microcrystalline film (Fig. 1(B)) the absorption spectrum is quite different from that of the isolated molecules. One observes a blue shift of the maximum of absorption and a red shift of the onset of the absorption. The changes in the absorption spectrum are accompanied by changes in the photoluminescence spectrum. The fluorescence from the film, which in contrast to the absorption shows some vibronic fine structure with a 1400 cm^{-1} progression, has shifted to longer wavelength in comparison with the fluorescence from the frozen solution. Interestingly, the shape of the emission band also has changed upon aggregation. For the film, the second vibronic band (0–1) is now the most intense, while for the frozen solution the first (0–0) vibronic band has the highest intensity. The absorption spectrum of the microcrystalline film of **1** at low temperature is comparable to that of nano-aggregates of **1**, which form in a non-solvent [13,18]. Similar spectra have been observed for nano-aggregates of shorter *p*-phenylene vinylene oligomers [19,20].

The changes in the spectrum upon aggregation are attributed to the intermolecular interaction leading to existence of delocalized excitonic states. From the drastic change in the shape of the absorption band and its considerable increase in width, we conclude that the intermolecular interaction in the excited state must be considerable and, hence, that the intermediate to strong coupling case applies to our system [21]. The blue shift of the maximum of the absorption and the red shift and low intensity of the onset of absorption resembles the behavior of H aggregates. This behavior is also observed for crystals and microcrystalline films of sexithiophene [22–28].

In Fig. 2, we show the evolution of the photoluminescence spectrum with time after pulsed excitation at 589 nm. For comparison, the time-integrated emission spectrum is shown in the top. It is well-known that fluorescence spectra can be

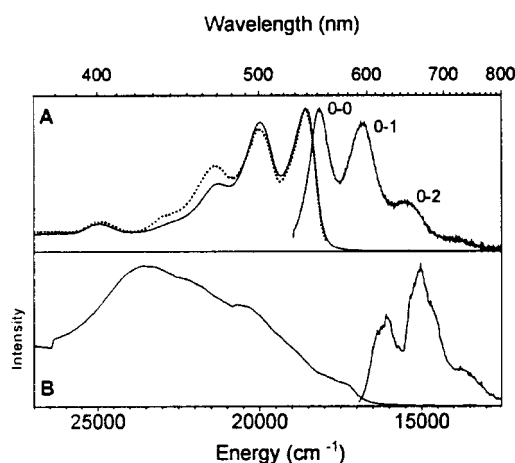


Fig. 1. (A) Absorption (—), fluorescence (solid line, wavelength of excitation 510 nm) and fluorescence excitation spectrum (dotted line, wavelength of detection 580 nm) of **1** in a glassy 2-methyltetrahydrofuran matrix at 95 K. Spectral bandwidth used is 2 nm. The fluorescence spectrum has been corrected for the wavelength dependence of the sensitivity of the detection system. (B) Absorption and photoluminescence (excitation wavelength 585 nm) of a microcrystalline film of **1** at 9 K.

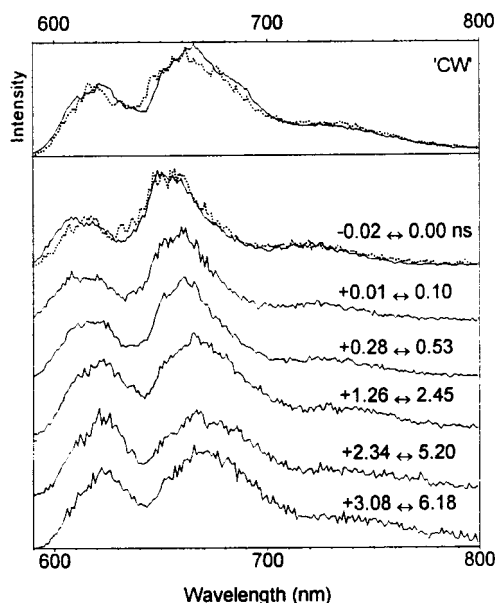


Fig. 2. Time-resolved emission spectra of a microcrystalline film of **1** at low temperature (8 K). Excitation wavelength 585 nm, 4 nJ cm^{-2} pump fluence. Top spectrum shows the time-integrated emission spectrum with front face (thick line) and back face (thin line) excitation (same for the first time-resolved spectrum). Time windows for data acquisition after the excitation pulse are indicated. All spectra are normalized to unit maximal intensity and have been corrected for the wavelength dependent sensitivity of the detection system. Spectral resolution 1 nm.

distorted by self absorption, especially at the blue edge of the emission band, which usually overlaps with the absorption band. In our case, however, the optical density in the long wavelength part of the absorption spectrum is low and therefore, one expects self absorption effects to be small. Under these circumstances it is possible to assess the effect of self absorption by comparing the emission spectra obtained with the excitation beam coming from the front and the back of the sample. In the case of excitation from the back, the emission travels a longer distance through the film and the relative intensity of the emission in the wavelength regions for which self-absorption is important, should be reduced. In Fig. 2, emission spectra with front face and back face excitation are compared and we see virtually no difference indicating that self-absorption effects are small.

With time after excitation, the fluorescence band shows a small red shift. We ascribe this red shift to migration of the excitations to traps. The existence of such trap sites can be shown by scanning the excitation wavelength through the red edge of the absorption band. Results for this experiment are shown in Fig. 3. By exciting the sample in the long wavelength absorption tail it is possible to excite the trap sites selectively. The maxima of the emission bands shift together with the excitation wavelength. At excitation wavelengths of 620 nm and 625 nm, the emission spectrum shows negligible evolution with time indicating that energy transfer to sites with even lower energy does not occur. Incidentally, this also indicates that the contribution from scattered laser light (elastic or inelastic) to the observed signal is negligible.

In Fig. 4, the decay traces of the photoluminescence with excitation at 585 and 610 nm are compared. As can be seen, the two decay traces converge towards a single exponential decay with decay time of 2.1 ns. The same features are observed when a ten times higher excitation density is used and therefore, we conclude that

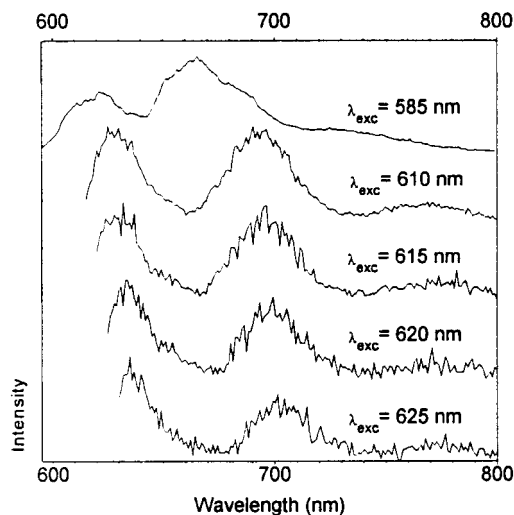


Fig. 3. Dependence of the time-integrated photoluminescence of microcrystalline films of **1** at 8 K on the excitation wavelength. Spectra have been normalized to unit maximal intensity and are corrected for the wavelength dependent sensitivity of the detection.

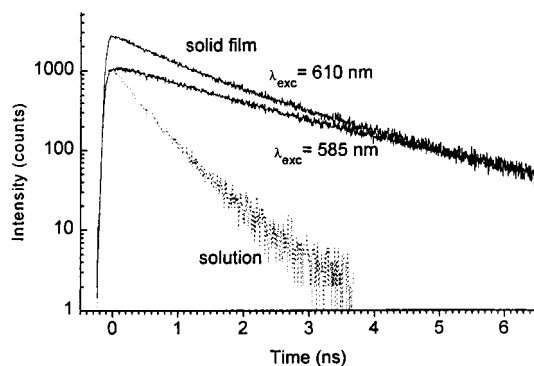


Fig. 4. Decay of the emission intensity of a microcrystalline film of **1** at low temperature (8 K) monitored at 625 nm (spectral bandwidth 1 nm). Excitation at 585 nm (0.1 nJ cm^{-2} pump fluence) and 610 nm (0.2 nJ cm^{-2}). Dashed line emission in tetrahydrofuran at room temperature, excitation wavelength 300 nm, emission detection at 585 nm.

exciton–exciton annihilation does not influence the decay process significantly. The convergence of the two decay traces shows that the excited state populations created by selective excitation at different wavelengths relax towards a common population involving the lowest reachable trap sites. Fig. 4 also shows the decay of the emission intensity in liquid solution at room temperature for which a decay time $\tau_{lum} = 0.45 \text{ ns}$ is determined.

3.2. Polymers 2 and 3

In Fig. 5, the absorption and time-integrated emission spectra for the two polymers at low temperature are compared with oligomer **1**. For films of polymer **2**, a broad featureless absorption band is observed. In contrast, the emission of **2** shows resolved vibronic fine structure together with a considerable Stokes shift. For films of **3**, some vibronic fine structure in absorption may be discerned. For a frozen solution of **3**, the fine structure is clearly observable and the absorption spectrum of the solution is red shifted compared to solid film. Unfortunately **2** does not dissolve in 2-MeTHF and no spectra of the frozen solution could be taken.

The time-resolved emission of a thin film of **2** with excitation at 588 nm is shown in Fig. 6. For this polymer, we observe a gradual red shift of the

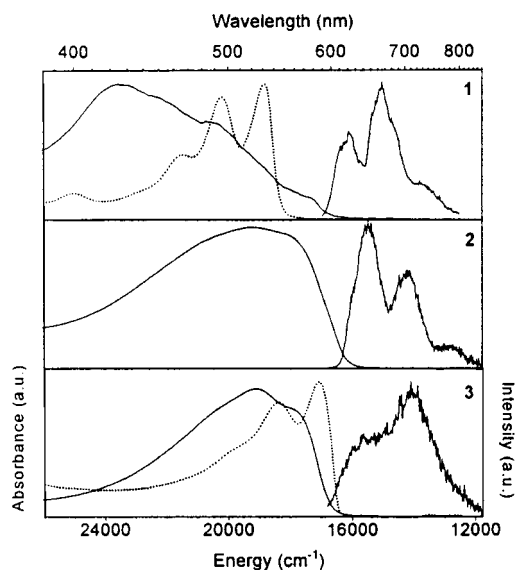


Fig. 5. Absorption and time-integrated photoluminescence of films of **1**, **2** and **3** at 8 K. Excitation wavelength 585 nm. Dotted lines pertain to absorption of frozen 2-MeTHF solution at 90 K.

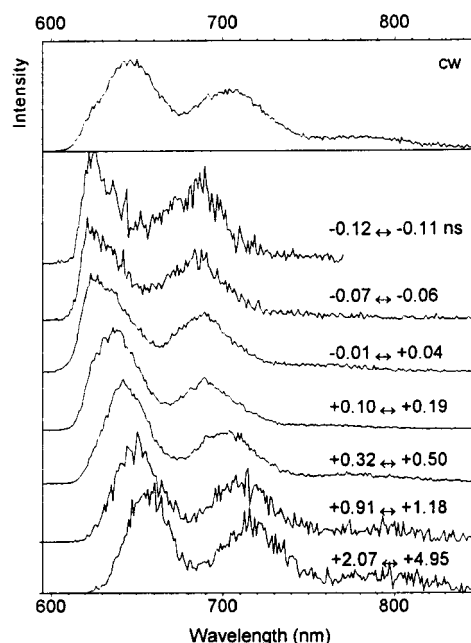


Fig. 6. Low temperature (8 K) time-resolved emission spectra of **2**. Excitation wavelength 588 nm and excitation fluence 2 nJ cm^{-2} . See also legend Fig. 2.

emission bands with time. The emission spectra show the usual vibronic fine structure. The band shape of the emission remains (in contrast to polymer **3**) quite constant with time after excitation. The 0–0 band has the highest emission intensity. When the excitation wavelength is set at 622 nm, similar effects are observed (Fig. 7).

In Fig. 8, the time dependence of the fluorescence intensity of polymer **2** recorded at two different emission wavelengths (620 and 650 nm) is shown. The lifetime of the emission at 650 nm is substantially longer than at 620 nm, consistent with the red shift of the emission spectrum with time as shown in Figs. 6 and 7. For the intensity at 650 nm, a rise time longer than the instrument response function can be observed indicating that the excitations responsible for this emission are created indirectly. We attribute the red shift of the emission band and associated phenomena to energy transfer to chain segments with lower excitation energy.

Additional proof for migration of the excitations in the film comes from polarization measurements. Fig. 8 shows the degree of linear polarization in the luminescence, p_{lum} , upon excitation with vertically polarized light. Data for two

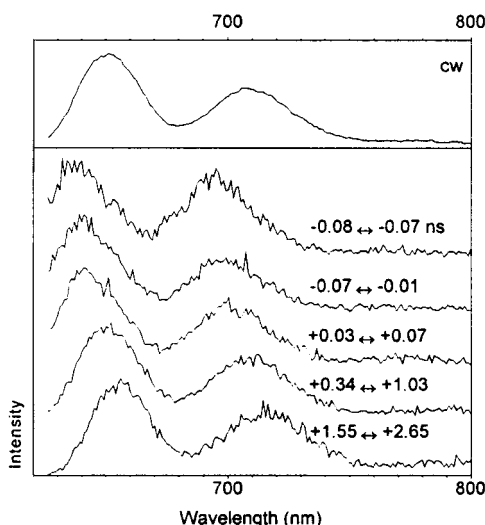


Fig. 7. Low temperature (8 K) time-resolved emission spectra of **2**. Excitation wavelength 622 nm and excitation fluence 4 nJ cm^{-2} . See also legend Fig. 2.

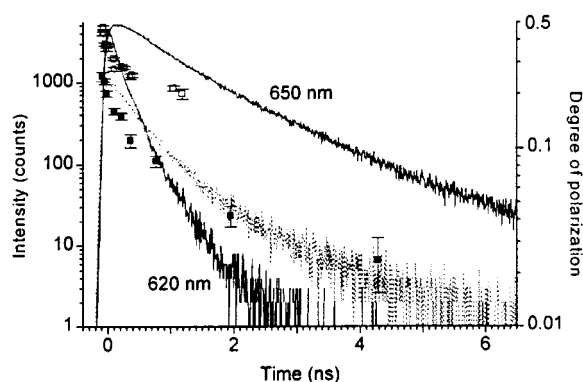


Fig. 8. Decay of the fluorescence intensity of a thin film of **2** at 8 K monitored at emission wavelengths of 620 and 650 nm. Decay of the degree of polarization, p_{lum} , monitored at 610 (\square) and 650 nm (\blacksquare). Excitation wavelength 588 nm. Excitation fluence 2 nJ cm^{-2} . The dashed line shows the decay of the emission intensity at 585 nm upon excitation at 300 nm for **2** in dichloromethane solution at room temperature.

different emission wavelengths are shown. Soon after excitation, p_{lum} is close to the theoretical limit of $+1/2$ showing that the transition dipole moment in emission is still parallel to the polarization direction of the excitation light. With time p_{lum} decreases, showing that the excitation moves to chain segments for which the transition dipole moment has a different direction. Assuming that the direction of the transition dipole moment is parallel to the direction of the polymer chain, the decrease of p_{lum} can be interpreted in terms of energy transfer to chain segments with a different orientation. The polarization decays to values close to zero indicating that the distance over which the energy is transferred is long compared to the domain size, i.e. the length over which the orientation of the polymers is still correlated.

For comparison, also the decay of the fluorescence intensity of **2** in dichloromethane solution at room temperature is shown in Fig. 8. As can be seen, the decay shows a tail with a long lifetime. We tentatively interpret this tail as luminescence from aggregated polymer chains formed, because of the low solubility of the material. In the first 2 nanoseconds the decay is approximately exponential with a lifetime $\tau_{\text{lum}} = 0.43 \text{ ns}$, a value comparable to that of the oligomer. For the film, because of the relaxation of the excitations on trap

sites, it is difficult to define a luminescence lifetime. To give an indication of the typical decay times we mention that for the emission from polymer film monitored at 650 nm, the fluorescence decays with $\tau_{\text{lum}} \approx 1.1$ ns in the time window 2–6 ns.

Time-resolved fluorescence spectra for **3** are shown in Fig. 9. As can be seen, for this polymer also a gradual red shift of the emission spectrum with time after excitation is observed. In the spectra taken early after excitation, the vibronic fine structure can be observed and the spectrum is comparable to that observed for polymer **2**. However, at later times the band shape changes, the 0–1 vibronic transition becomes relatively more intense than the 0–0. The change in the band shape of the emission spectrum observed with long delay times cannot be due to self absorption, since the optical density for wavelengths >620 nm is negligible. From the time-resolved experiments it is apparent that the difference in band shape of the emission spectra of **2** and **3**, recorded under con-

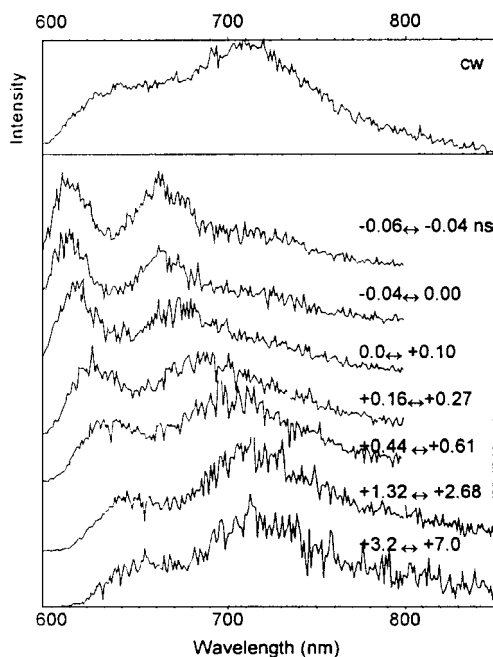


Fig. 9. Low temperature (8 K) time-resolved emission spectra of **3**. Excitation wavelength 588 nm and excitation fluence 10 nJ cm⁻². Emission spectrum corrected for wavelength dependent sensitivity of the detection. Spectral resolution 1 nm.

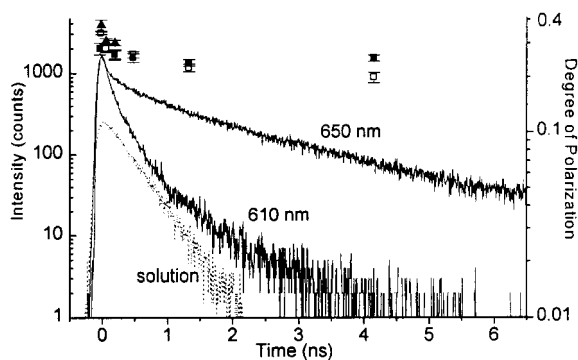


Fig. 10. Decay of the fluorescence intensity of **3** at 8 K at emission wavelength 610 and 650 nm. Decay of the degree of polarization, p_{lum} , monitored at 620 (▲), 650 (■) and 700 nm (□). Excitation wavelength 588 nm and excitation fluence 10 nJ cm⁻². The dashed line shows the decay of the emission intensity at 585 nm upon excitation at 300 nm for **3** in dichloromethane solution at room temperature.

tinuous wave excitation (Fig. 9), results to a large extent from the contribution of the long-lived emission components with the red-shifted emission spectra. Therefore, self absorption alone cannot account for the difference in band shape of the time-integrated emission spectra of **2** and **3**.

Also for this polymer, the decay of the fluorescence intensity is non-exponential. Linear polarization measurements (Fig. 10) show that the excitations migrate to chain segments with different orientation. The degree of polarization at $t = 0$ is lower than for **2** (0.38 vs. 0.47), which we attribute to very rapid energy transfer steps. The limiting value is higher than observed for **2**, indicating that the ratio of the exciton diffusion length and the domain size for this sample is smaller. Also shown is the decay of the luminescence in solution at room temperature, which decays exponentially with $\tau_{\text{lum}} = 0.38$ ns. For the film at low temperature, the fluorescence with 650 nm wavelength decays quasi-exponentially with $\tau_{\text{lum}} \approx 1.5$ ns in the time window from 2–6 ns.

4. Theory

In this section, we investigate the effect of interchain interaction on the spectroscopic proper-

ties of disordered molecular solids. First, we will investigate the effect of disorder on the extent of delocalization of the photoexcitation over an aggregate of chromophoric molecules arranged in a two-dimensional lattice. Disorder is taken into account choosing the zero-order excitation energies of the individual molecules comprising the aggregate from a Gaussian distribution. Also, the effect of variation of the magnitude of the intermolecular interaction is evaluated. In these simulations, both the molecules and the lattice are assumed to be rigid. In the second part we will investigate the influence of vibrations on the molecules on the band shape of the optical spectra of the aggregate. Under influence of the vibronic coupling, the relative intensities of the vibronic bands in absorption and emission depend on the degree of delocalization of the excitation.

4.1. Numerical simulations of two-dimensional arrays of rigid chromophores

Numerical calculations have been performed to investigate the relation between disorder and the extent of delocalization of the optical excitations. These model studies pertain to arrays of regularly stacked chromophores and the so called tight-binding Hamiltonian (2) was employed. This type of Hamiltonian has been studied extensively in relation with the Anderson localization [29]:

$$H = \sum_i c_i \varepsilon_i c_i + \frac{1}{2} \sum_{i,j} c_i V_{ij} c_j, \quad (2)$$

where c_i is the coefficient of excited state c at chromophore i . ε_i is the zero-order excitation energy of chromophore i (i.e. the excitation energy of the isolated chromophore) and V_{ij} the excited state interaction energy of molecule i with its neighboring chromophores j . In our calculations, only nearest-neighbor interactions are considered with interaction energy V_{12} . Standard software routines were used [30].

We have chosen to model the molecular solids with a two dimensional rectangular array of chromophores, aligned parallel. The dipole moment for the transition from ground to first excited singlet state is taken to be perpendicular to the two-

dimensional plane of stacked chromophores. V_{12} is taken to be positive and the coupling between molecules in the vertical and horizontal directions of the rectangular lattice is taken to be of equal strength. Of course, this type of arrangement does not fully represent a three-dimensional structure of real molecular aggregates. We assume, however, that in a three-dimensional structure consisting of two-dimensional layers placed on top of each other, the interactions between molecules in different layers are much smaller than the interactions between the chromophores in one layer [31].

To model disorder, the excitation energies of the individual molecules (ε_i) were chosen randomly from a Gaussian distribution with $\sigma = D$ (diagonal disorder). For reasons of simplicity, the average excitation energy $\langle \varepsilon \rangle$ was set to zero. We first discuss the case in which V_{12} is constant, the effect of variations in nearest-neighbor interaction (off-diagonal disorder) will be discussed later. By diagonalization of the Hamiltonian matrix, the excitation energies of the aggregate are obtained. From the eigenvectors, the total transition dipole moment can be calculated by summing the product of the dipole moment of an individual molecule (taken as 1) with the coefficient of the excited state at each site. The square of the transition dipole moment (μ) then gives the relative probability for absorption of light and also for radiative decay.

Fig. 11 shows the simulations of the absorption spectrum of a two-dimensional aggregate comprising 25×25 molecules. The calculations have been done for various degrees of disorder, i.e. for various ratios of D/V_{12} ranging from 5 to 0.375. The absorption coefficient for the transition from the ground state to the first excited state, which is the product of the density of states and the average dipole strength in a particular energy interval is plotted as a function of the excitation energy (in units of D). Each curve shown in Fig. 11 represents an average over the results of twenty diagonalizations.

When V_{12} is small compared to D , the shape of the absorption spectrum follows the Gaussian distribution of the zero-order excitation energies, ε_i . All the states are essentially localized on a single

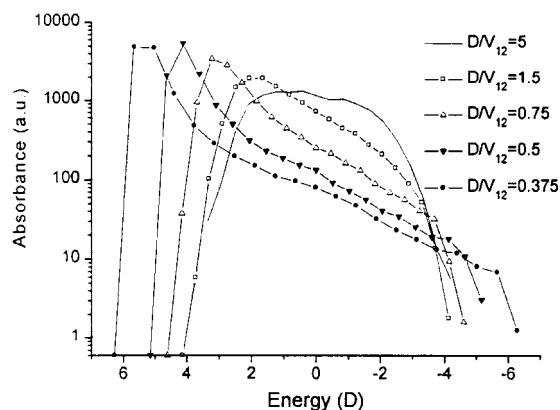


Fig. 11. Simulated absorption spectra of a two-dimensional aggregate comprising 25×25 molecules for varying ratios of the nearest neighbour interaction energy (V_{12}) and the standard deviation D of the gaussian distribution of zero-order excitation energies of the constituent molecules (see text for further details).

chromophore and the transition dipole moment for each transition is close to 1, i.e. the same value as for the isolated molecule. When V_{12} becomes comparable in magnitude to D , the absorption maximum shifts towards higher photon energies and the onset of absorption towards lower. (For $V_{12} < 0$, the maximum shifts towards lower frequency.) For the case $D/V_{12} = 1/2$, the extent of delocalization of the excitations is illustrated in Fig. 12. The coefficients describing the contribution of each molecular site to a particular excited state were evaluated and for each state the square of the coefficient with the highest absolute value is plotted against the excitation energy (in units of V_{12}). In the middle of the band the maximum coefficients are quite small, typically $c_{\max}^2 = 0.02$. This implies delocalization of the excitation over at least 50 molecules. Analyzing the eigenvectors we find that some excited states are in fact delocalized over practically the whole aggregate.

For an infinite two-dimensional aggregate with no disorder, the band of excitation energies would extend from $-2V_{12}$ to $+2V_{12}$. Looking at Fig. 12, it can be seen that due to the disorder also a small number of states with an energy outside the range from $-2V_{12}$ to $+2V_{12}$ exist. These states share the property of being strongly localized and the states at the low energy side can act as traps for the

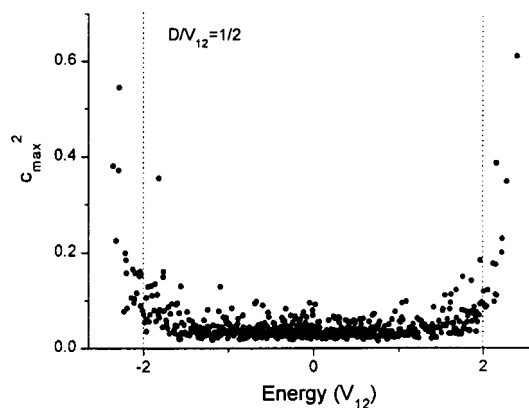


Fig. 12. Extent of delocalization of the excited states of a 25×25 two-dimensional disordered molecular aggregate. Of the coefficients c_i , describing the contribution of molecule i to the excited state, the square of the coefficient with the highest absolute value is plotted versus the excited state energy (in units of V_{12}).

photoexcitations. To analyze the properties of these trap states further we calculated the transition dipole moments (μ) for the excited states in one hundred 25×25 clusters with $D/V_{12} = 1/2$ and the results are illustrated in Fig. 13. Most of the oscillator strength is accumulated in the transitions from the ground state to the highest exciton levels and the average value of μ^2 reduces gradually for the lower excited levels. For the states at the low-energy side of the band, the probability for radiative decay (which is proportional to μ^2) is strongly reduced compared to the isolated molecule. Within a particular energy interval, there is however a spread in transition probability and some states can be considered as ‘dark’ while others in the interval will have an appreciable transition probability and can act as luminescent center. Interestingly, at the very low-energy side of the spectrum, it can be seen that for the localized states with $E < -2V_{12}$ ($= -4D$), there are relatively few states with $\mu^2 < 0.01$. In fact, the average value of μ^2 for the lowest twelve states amounts to 0.08, while the average over the lowest one hundred states amounts to 0.04. From the model calculation, it thus follows that the lowest localized states can be regarded as arising from luminescent trap sites which are expected to luminesce quite efficiently in comparison with the lower delocalized

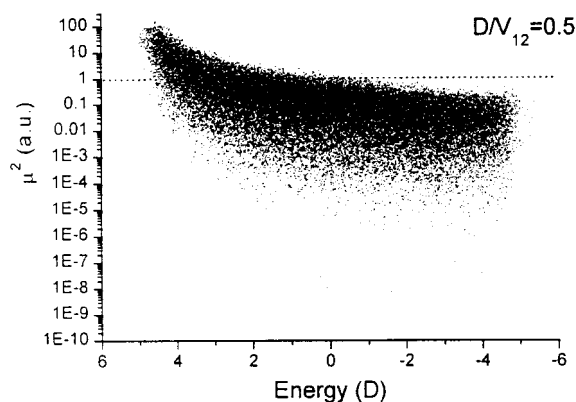


Fig. 13. Square of the transition dipole moment plotted as function of the energy of the excited state (in units of D), for the S_0 – S_1 transition of a 25×25 , two-dimensional disordered molecular aggregate. The figure pertains to $D/V_{12} = 0.5$.

states. For comparison we have also plotted the oscillator strength for the transition between the ground state and the excited state as a function of the excited state energy for the case of $D/V_{12} = 3$ (Fig. 14). In this case, the excited states are more localized than in the case of $D/V_{12} = 1/2$. Also, here the average value of μ^2 decreases with decrease in excitation energy but the dependence is less strong. Focusing our attention on the low-energy side of the spectrum, it can be seen that although the average value of μ^2 is lower than 1 (i.e. the probability for radiative decay is reduced comparison with the isolated molecule) even the low energy side of the spectrum states exist with $\mu^2 > 2$. The latter states can be regarded as luminescent centers. In this case, it can be expected that among the processes determining the luminescent lifetime of the aggregate the transport of the excitations from dark to luminescent sites also has to be included. For one-dimensional systems strongly localized excited states have also been found to exist near the edges of the band of exciton coupled states [32]. We find, however, that for one-dimensional systems the change from delocalized to localized states occurs more gradually than for the two-dimensional case.

To investigate the effect of off-diagonal disorder, we have performed additional calculations for the case $D/V_{12} = 1/2$ in which the actual interaction between each pair of neighboring molecules i ,

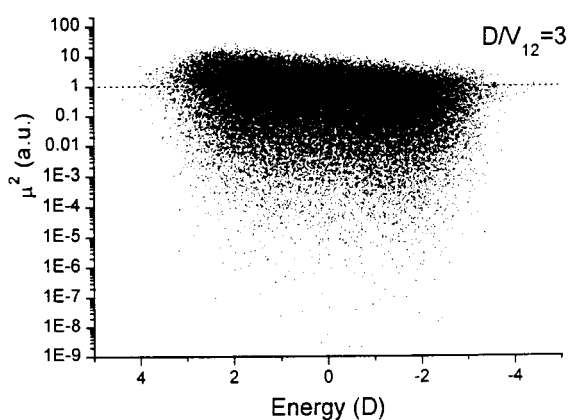


Fig. 14. See legend for Fig. 13. This figure pertains to $D/V_{12} = 3$.

j was chosen from a distribution according to $V_{ij} = 2D(1 - dr_{ij})$, where r is a random number taken from a uniform distribution between 0 and 1 and d an adjustable parameter ranging from 0 (no off-diagonal disorder) to 1. The simulated absorption spectra are shown in Fig. 15. As can be seen, the off-diagonal disorder reduces the width of the absorption band. It also induces stronger localization of the excited states.

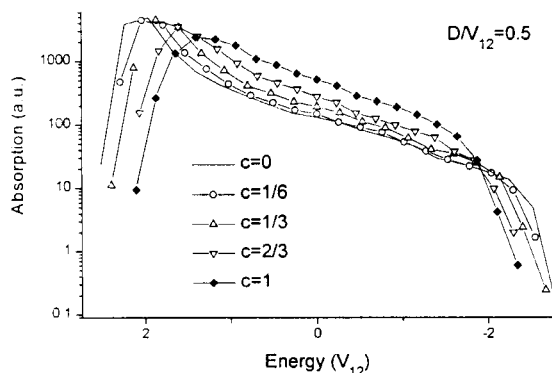


Fig. 15. Simulated absorption spectra of a two-dimensional aggregate comprising 25×25 molecules including the effect of diagonal and off-diagonal disorder. The interaction energy (V_{ij}) between each pair of neighboring molecules i, j is taken as $V_{ij} = D(1 - dr_{ij})$, where r is a random number taken from a uniform distribution between 0 and 1, d an adjustable parameter and D , the standard deviation of the gaussian distribution of zero-order excitation energies. (See text for details).

In the model calculations described above, only the influence of static disorder was taken into account. The influence of molecular vibrations on the electronic excited states has been neglected. The vibronic fine structure in the emission and fluorescence spectra of **1** under matrix isolated conditions, shows however that the vibrational degrees of freedom of the molecule couple to the electronic degrees of freedom (vibronic coupling). In the following section, we will analyze the influence of exciton–phonon coupling on the spectroscopic properties. The focus will be on the effect of vibrational motion on the emission properties of the materials.

4.2. Vibronic coupling: the weak coupling case

In describing the coupling between nuclear and electronic motion in aggregates of molecules, two limiting situations can be discerned [21,33–35]: weak and strong coupling. In the first case, the interchain interaction is much smaller than the vibrational energy quantum, implying that an excited molecule vibrates for several periods before the excitation jumps to a neighboring molecule. This has two important consequences. First, since the excitation moves slowly through the aggregate, the molecule on which the excitation is momentarily localized, has the time to relax its geometry and adopt the excited state equilibrium geometry. Second, the fact that the interchain interaction is much smaller than the vibrational energy quantum also means that only excited states with the same vibrational quantum number mix to form a collective excited vibronic state. Hence, the absorption spectrum shows vibronic fine structure which is reminiscent of the fine structure of the isolated molecule. Due to the excitonic interactions, the maxima of the vibronic bands will be slightly shifted with respect to the isolated molecules but their relative intensity remains the same.

The central approximation in our treatment of the vibronic coupling in aggregates will be the assumption that only one totally symmetric molecular vibration is coupled to the electronic degrees of freedom. Although the shape of the absorption and emission spectra of the matrix isolated oligomer can be modeled with a single active vibration,

fluorescence studies on PPV employing line narrowing techniques have revealed that at least two medium-frequency vibrations (1300 and 1600 cm^{-1}) couple with the excited state [36].

For the individual molecules we apply the Condon approximation and write the total Hamiltonian as a sum of a electronic and nuclear parts

$$H = H_{\text{el}} + H_{\text{nuc}}, \quad (3)$$

where the nuclear Hamiltonian H_{nuc} in the ground state is given by

$$H_{\text{nuc}}^0 = P^2 + Q^2. \quad (4)$$

The term P^2 describes the kinetic and Q^2 the potential energy (in units of $h\nu_{\text{vib}}/2$). Here, we take into account only one totally symmetric vibration with normal coordinate Q . In the first excited singlet state, the equilibrium geometry of the nuclei may be different from that in the ground state and, hence, in a first approximation the nuclear Hamiltonian for the excited state may be given by

$$H_{\text{nuc}}^1 = P^2 + Q^2 + 2\sqrt{2}\gamma Q, \quad (5)$$

where the term linear in Q results from vibronic coupling to another excited state of the same symmetry. The term linear in Q causes a displacement of the minimum of the potential energy curve in the excited state with respect to the minimum in the ground state. The corresponding relaxation energy in the excited state equals $2\gamma^2$ (in units of $h\nu_{\text{vib}}/2$). According to the Franck–Condon principle, this then leads to the appearance of a vibronic progression based on the normal coordinate Q in the absorption and emission spectra. The intensities of the vibronic bands labeled with n relative to the first vibronic band is given by

$$\frac{I(0-n)}{I(0-0)} = \frac{\gamma^{2n}}{n!}. \quad (6)$$

In Eq. (3), the term linear in Q arises from Herzberg–Teller coupling of the lowest excited state with a higher excited state of the same symmetry. Assuming that excited state under study (labeled 1) mixes with only one higher excited state (2) under the influence of a perturbation $H^{(1)}$, the admixture of the higher electronic state may be estimated using perturbation theory. In the first-

order, the admixture of a state 2 to 1 is given by the coefficient $c_{12}^{(1)}$. This admixture corresponds (in second-order) to a correction of the energy of the state 1 by $W_1^{(2)}$

$$c_{12}^{(1)} = \frac{\langle \Psi_1 | H^{(1)} | \Psi_2 \rangle}{E_1^{(0)} - E_2^{(0)}}, \quad (7)$$

$$W_1^{(2)} = \frac{\langle \Psi_1 | H^{(1)} | \Psi_2 \rangle \langle \Psi_2 | H^{(1)} | \Psi_1 \rangle}{E_1^{(0)} - E_2^{(0)}}. \quad (8)$$

For known $W_1^{(2)}$ (e.g. from analysis of the vibronic intensities) and energy separation between the states, the coefficient $c_{12}^{(1)}$ can be estimated:

$$|c_{12}^{(1)}|^2 \cong \frac{W_1^{(2)}}{E_1^{(0)} - E_2^{(0)}}. \quad (9)$$

Trivially, when $W_1^{(2)}$ is small compared to the separation in energy of the mixing states, the coefficient describing the admixture of the higher excited state remains small.

For the molecules under study, no excited states with large absorption cross-section are found close to the lowest excited singlet state. According to Eq. (9), the admixture of higher excited states S_n with large transition dipole moment for the S_n – S_0 transition under the influence of the molecular vibration, is small. Therefore, we neglect the admixture of the S_n states to S_1 and assume that the transition dipole moment, μ , is independent of Q .

In the weak coupling case, the lower vibronic excited state p of the aggregate (ϕ_p^0) can be written as a linear combination of states in which one molecule of the aggregate (say n) is excited. This excited molecule n is in its first electronically excited state (1) and the superscript $\tilde{0}$ signifies that it is in its lowest vibrational states of the *excited state* equilibrium geometry. All the other $N - 1$ molecules are in their electronic and vibrational ground state (0^0).

$$\phi_p^0 = \sum_{n=1}^N c_n^p |0_1^0 \dots 1_n^{\tilde{0}} \dots 0_N^0\rangle. \quad (10)$$

The coefficients c_n can be obtained from matrix diagonalization (Section 4.1). As discussed, given these coefficients, the transition dipole moment for the transition to the ground state, ψ^0 ,

$$\psi^0 = |0_0^0 \dots 0_N^0\rangle, \quad (11)$$

can be computed in a straightforward manner. In the case of $V_{12} > 0$ and vanishing disorder, this 0–0 transition in emission will be forbidden due to out of phase coupling of the transition dipole moments.

To calculate the intensity of the 0–1 vibronic transition in emission we evaluate the transition from the excited state (ϕ_p^0) to the ground state with molecule n vibrationally excited ψ^{1_n}

$$\psi^{1_n} = |0_0^0 \dots 0_n^1 \dots 0_N^0\rangle. \quad (12)$$

The dipole moment for this transition is simply $c_n^p \mu^{\tilde{0}1}$ with $\mu^{\tilde{0}1}$, the transition dipole moment for the 0–1 vibronic transition in emission of the individual molecule (taken equal for all molecules). To obtain the total intensity of the 0–1 vibronic transition in the emission from the aggregate, the squares of the transition dipole moments for the transitions to all possible singly vibrationally excited forms of the ground state (ψ^{1_n} with $n = 1-N$) have to be added. Since the sum of $(c_n^p)^2$ over n yields 1 (normalization), it follows that in the weak coupling case the probability for the 0–1 transition in the aggregate fluorescence is the same as for an isolated molecule. This also holds for the higher vibronic transitions in emission. As only the 0–0 transition is forbidden for the aggregate and the transition probability for the higher vibronic transitions, the same as for the isolated molecules, the increase of the radiative lifetime due to interchain interactions is limited and depends on the value of γ :

$$\frac{\tau_{\text{rad}}^{\text{monomer}}}{\tau_{\text{rad}}^{\text{aggregate}}} = \frac{1 + e^{\gamma^2}}{e^{\gamma^2}}, \quad (13)$$

which amounts to 1.6 for $\gamma^2 = 1$. As discussed in Section 4.1, in the presence of diagonal disorder the 0–0 transition becomes partially allowed and the difference in radiative lifetime of aggregate and free molecule will be even smaller.

For a disordered aggregate we can now make qualitative predictions for the band shape of the emission spectrum. If we consider the case of $\gamma = 1$, it follows from Eq. (5) that the intensity of the 0–0 and 0–1 vibronic bands in emission of the

isolated molecule are equal. We look back at the Figs. 12 and 13 and focus the attention on the states with $\mu^2 \approx 1$. For these states, the likelihood for radiative decay via the 0–0 transition is the same as for the isolated molecule. The same holds for radiative decay via the 0–1 transition and therefore, for the states with $\mu^2 \approx 1$ the 0–0 and 1–0 transition will have the same intensity in the emission spectrum. For states with $\mu^2 > 1$ the 0–0 transition will be more intense than the 0–1, while for states with $\mu^2 < 1$ the 0–1 transition will dominate.

4.3. Vibronic coupling: the intermediate coupling case

4.3.1. Strong coupling limit

In the case of strong coupling ($V_{12} \gg \hbar\nu_{\text{vib}}$) and low disorder the electronic excitation jumps from one molecule to the next in a time far shorter than the vibrational period. This implies that the molecule on which the excitation is momentarily localized does not have the time to relax its geometry and adapt the excited state equilibrium geometry. The lower excited states of the aggregate involve mainly linear combinations of the states:

$$|n^0\rangle = |0_1^0 \dots 1_n^0 \dots 0_N^0\rangle. \quad (14)$$

Hence, in limit of very strong coupling, the molecules in the excited aggregate will have the same nuclear geometry as in the ground state. This then implies that the Franck–Condon factors for the higher vibronic transitions in emission vanish in the limit of strong coupling and therefore, the transitions are forbidden. When $V_{12} > 0$ and disorder is low, the 0–0 transition is practically forbidden due to out of phase coupling of the transition dipole moments of the individual molecules. So the probability for emission vanishes in the limit of strong coupling.

When the coupling is of intermediate strength ($V_{12} \cong \gamma^2 \hbar\nu_{\text{vib}}$) the motion of the electronic excita-

tion is sufficiently slow to allow for at least some geometrical relaxation of the excited molecule. As a result, the higher vibronic transitions are allowed. For this case, it is very difficult to develop an analytic theory and one usually resorts to numerical calculations. For example, very recently the absorption spectrum of two-dimensional aggregates of *para*-distyrylbenzene was simulated [37]. In this study, the fluorescence properties were not modeled and effects of disorder were not taken into account. Later, we will investigate the intermediate coupling case for the simplest possible system, a dimer of two parallel molecules (see for earlier work on this problem [38]). Here, we also allow for a difference in the zero-order excitation energy of the molecules. After analysis of the dimer case we will generalize the results in a qualitative manner in order to understand the properties of aggregates with more than two molecules.

4.3.2. Intermediate coupling in a dimer

In the limit of strong coupling, the dimer may be treated as a ‘super’ molecule with the dimer in the excited state vibrating as a whole (i.e. strongly coupled active vibrations of the two individual molecules). In this case, one may apply the Born–Oppenheimer approximation to the aggregate and express its excited states as a product of an electronic and nuclear part:

$$\Phi(q, Q) = \Psi_{\text{el}}(q, Q) \chi_{\text{nuc}}(Q), \quad (15)$$

where the delocalized electronic wave function, Ψ_{el} , depends only parametrically on the nuclear coordinates Q . In general, the electronic energy depends on Q and provides a *potential energy surface* on which the vibrational motion of the nuclei can take place. The surface can be calculated by diagonalization of the Hamiltonian expressed in the basis functions describing excitations localized on the individual molecules a and b in the dimer:

$$\begin{bmatrix} E_1 + \frac{4}{2} + Q_b^2 + Q_a^2 + 2\sqrt{2}\gamma Q_a & V_{12}/2 \\ V_{12}/2 & E_1 - \frac{4}{2} + Q_a^2 + Q_b^2 + 2\sqrt{2}\gamma Q_b \end{bmatrix}. \quad (16)$$

Here, Q_a and Q_b are the normal coordinates on molecule a and b. V_{12} describes the electronic interaction between the molecules. By introducing a parameter Δ we can allow a small difference in the (zero-order) excited state energy of molecule a and b due to e.g. a slightly different conformation. The eigenvalue problem can be simplified by introducing symmetry adapted electronic states and normal coordinates:

$$|l\rangle = \frac{1}{\sqrt{2}}(|01\rangle + |10\rangle), \quad (17)$$

$$|u\rangle = \frac{1}{\sqrt{2}}(|01\rangle - |10\rangle), \quad (18)$$

$$Q_s = 1/\sqrt{2}(Q_a + Q_b), \quad (19)$$

$$Q_{as} = 1/\sqrt{2}(Q_a - Q_b), \quad (20)$$

where $|01\rangle$ describes the state with molecule a in the excited state and b in the ground state. This yields:

$$\begin{bmatrix} V_{12}/2 + Q_s^2 + Q_{as}^2 + \gamma' Q_s & \gamma' Q_{as} + \Delta/2 \\ \gamma' Q_{as} + \Delta/2 & -V_{12}/2 + Q_s^2 + Q_{as}^2 + \gamma' Q_s \end{bmatrix}. \quad (21)$$

To simplify the expression, the excited state energy E_1 has been subtracted from the diagonal and $\gamma' = 2\gamma$ (reduction by a factor of $\sqrt{2}$). The energy of two electronic states is given by

$$E_{\pm}(Q_s, Q_{as}) = Q_s^2 + Q_{as}^2 + \gamma' Q_s \pm \sqrt{(\gamma' Q_{as} + \Delta/2)^2 + (V_{12}/2)^2}. \quad (22)$$

These energies occur as potential energy terms in the nuclear Hamiltonian, H_{nuc} . In this expression no cross terms between Q_{as} and Q_s occur and this means that the vibrational wave function in the excited state (1) can be written as a product of a function for the symmetric ($\chi_{as}^{\text{in}}(Q_s)$) and asymmetric coordinate ($\chi_s^{\text{in}}(Q_{as})$). Oscillatory motion along Q_s is harmonic, but this is not true for motion along Q_{as} , where the square root term acts as

a perturbation giving rise to a double minimum in the potential energy curve. Hence, the vibrational frequency is different from that in the ground state and the eigenfunctions are a linear combination of the well-known harmonic oscillator eigenfunctions. They can be computed numerically.

Vibrational motion along Q_{as} results in a mixing of the exciton states $|l\rangle$ and $|u\rangle$:

$$\Psi_{\pm}(Q_{as}) = c_{\pm}^l(Q_{as})|l\rangle + c_{\pm}^u(Q_{as})|u\rangle. \quad (23)$$

In Fig. 16, the shape of the potential energy curve and the vibrational wave functions for lower exciton level are illustrated. The left curve pertains $V_{12} = 2h\nu_{\text{vib}}$, $\gamma = 1$ and $\Delta = 0$. In the right Δ is set to $1/2h\nu_{\text{vib}}$. The vibrational wave functions were calculated by diagonalization of the matrix representation of the Hamiltonian

$$H_{\text{nuc}} = P^2 + Q^2 - \sqrt{(\gamma' Q_{as} + \Delta/2)^2 + (V_{12}/2)^2}, \quad (24)$$

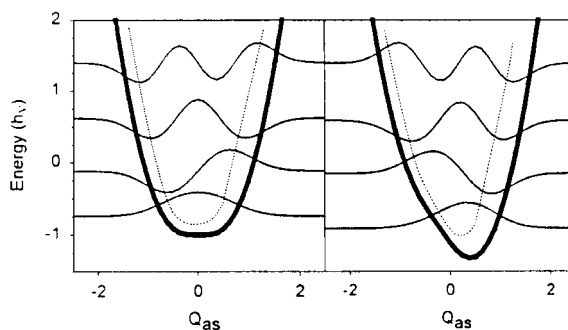


Fig. 16. Potential energy curve for vibrational motion along Q_{as} in the lowest exciton state of the dimer. Left: $V_{12} = 2h\nu_{\text{vib}}$, $\Delta = 0$, $\gamma = 1$. The dotted line shows the parabolic potential energy curve for the ground state. Eigenmodes are also shown. Right: $\Delta = 1/2h\nu_{\text{vib}}$.

with the lowest seven harmonic oscillator eigenfunctions as basis. In the literature, the validity of the Born–Oppenheimer approximation for the dimer as a whole has been discussed [39] and it is well-known that in the case of weak interaction the approximation holds for the individual molecules rather than for the dimer as a whole. For the dimer model described above, we have numerically calculated corrections to the Born–Oppenheimer state functions. For $V_{12} = 2\hbar\nu_{\text{vib}}$, $\gamma = 1$ and $\Delta = 0$, we find the coefficient describing the contribution of the state function $\Psi_{-}(Q_{\text{as}})\chi_{-}^0(Q_{\text{as}})\chi(Q_{\text{as}})$ to the lowest excited state is >0.97 . We conclude that the Born–Oppenheimer approximation can be applied.

Given the vibrational wave functions in the excited state, it is possible to calculate the dipole moment, μ , for the transition between the lowest electronically excited state and the electronic ground state with n vibrational quanta in the symmetric mode and m in the asymmetric mode:

$$\begin{aligned}\mu_{-}^{0-n_s m_{\text{as}}} &= \int dQ_s \chi^n(Q_s) \chi^0(Q_s) \\ &\quad \times \int dQ_{\text{as}} \chi_0^m(Q_{\text{as}}) (c_{-}^l(Q_{\text{as}}) \langle 0|\mu|l \rangle \\ &\quad + c_{-}^u(Q_{\text{as}}) \langle 0|\mu|u \rangle) \chi_{-}^0(Q_{\text{as}}) \\ &= \mu_l \int dQ_{\text{as}} \chi_0^m(Q_{\text{as}}) c_{-}^l(Q_{\text{as}}) \chi_{-}^0(Q_{\text{as}}) \\ &\quad \times \int dQ_s \chi^n(Q_s) \chi^0(Q_s) + \mu_u \\ &\quad \times \int dQ_{\text{as}} \chi_0^m(Q_{\text{as}}) c_{-}^u(Q_{\text{as}}) \chi_{-}^0(Q_{\text{as}}) \\ &\quad \times \int dQ_s \chi^n(Q_s) \chi^0(Q_s) \\ &= \mu_l d(n, m)_{-}^l + \mu_u d(n, m)_{-}^u.\end{aligned}\quad (25)$$

In the case where the transition dipole moments of the two molecules are parallel, the electronic transition from the ground state to $|l\rangle$ level is forbidden and $\mu_l = 0$. In the case where $\Delta = 0$, the expression $c_{-}^u(Q_{\text{as}})$ is an antisymmetric function of Q_{as} . Hence, transitions from the lowest excited state to vibrationally excited levels of the ground state with an even number of quanta in the asymmetric mode are forbidden.

Transitions to states with an odd number of quanta in the Q_{as} mode are allowed and the transition to the state with one quantum will generally be the most intense. Hence, there is a false origin in the fluorescence spectrum and the symmetric vibration along Q_s gives rise to a vibronic progression built upon this false origin. The relative intensities of the vibronic bands in this progression are described by an apparent Huang–Rhys factor $\gamma^2/2$, where γ^2 is the Huang–Rhys factor for the monomeric molecule. Thus, the band shape of the emission spectrum of the dimer is quite different from that of the monomer. Numerical calculations for the case $\gamma = 1$, $V_{12} = 2\hbar\nu_{\text{vib}}$ show that the rate constant for radiative lifetime (τ_{rad}) from the lowest excited state in dimer is longer than for the monomer: $\tau_{\text{rad}}^{\text{dimer}}/\tau_{\text{rad}}^{\text{monomer}} \approx 5$. This value is higher than the one obtained for the weak coupling case from Eq. (12). The calculated probabilities for absorptive and emissive transitions are listed in Table 1 summarized in Fig. 17 in the form of simulated spectra.

For the case $\gamma = 1$, $V_{12} = 2\hbar\nu_{\text{vib}}$, $\Delta = 1/2\hbar\nu_{\text{vib}}$, we calculate a higher probability for radiative decay: $\tau_{\text{rad}}^{\text{dimer}}/\tau_{\text{rad}}^{\text{monomer}} \approx 3$. Looking at Fig. 16, the difference in zero-order electronic energy leads, in the lowest vibronic level, to a (partial) localization of the excitation in the lowest vibronic state on the molecule with the lowest energy. For the higher vibronic levels, this is less evident. As a result of the localization, the 0–0 transition is now allowed (Fig. 17). It has been recognized that electron–vibrational coupling and disorder act synergistically to induce localization of charge carriers or excitations [40]. Fig. 16 provides a numerical illustration of this phenomenon.

4.3.3. Intermediate coupling in one- and two-dimensional aggregates

In this section, we attempt to analyze the band shape of the fluorescence for infinitely long one- and two-dimensional aggregates with the constituent molecules aligned parallel and the intermolecular interaction limited to only nearest-neighbor molecules with $V_{12} > 0$. Effects of static disorder will be neglected as this would complicate the analysis too much. As mentioned above, the intensity of the higher vibronic transition vanishes in

Table 1

Calculated transition dipole strengths for vibronic transitions in absorption and emission of a dimer of parallel oriented molecules involving its lowest electronically excited singlet state ($S_{1,-}$)^a

Vibronic transition	$(\mu_-)^2$		$(\mu_-)^2$	
	$V_{12} = 2\hbar v_{\text{vib}}, \gamma = 1, \Delta = 0$		$V_{12} = 2\hbar v_{\text{vib}}, \gamma = 1, \Delta = (1/2)\hbar v_{\text{vib}}$	
	$S_0 \rightarrow S_{1,-}$	$S_{1,-} \rightarrow S_0$	$S_0 \rightarrow S_{1,-}$	$S_{1,-} \rightarrow S_0$
0–0 _{as} 0 _s	0	0	0.07	0.07
0–1 _{as} 0 _s	0.07	0.11	0.02	0.12
0–2 _{as} 0 _s	0	0	0.02	0.01
0–1 _{as} 1 _s	0.04	0.06	0.03	0.06
0–3 _{as} 0 _s	0.01	0.0004	0.0003	0.001

^a The dipole strengths, μ^2 , are relative to the *total* dipole strength of the $S_0 \rightarrow S_1$ transition of the isolated molecule. The difference in zero-order excitation energy between the two molecule is denoted by Δ .

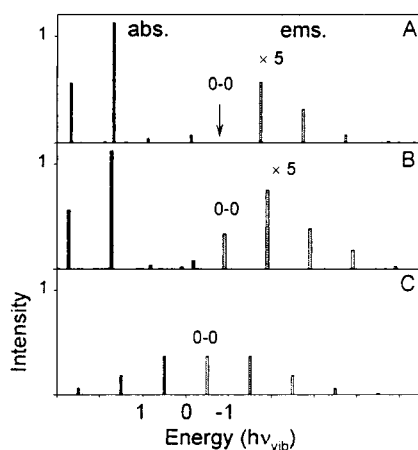


Fig. 17. Simulated absorption and emission spectra for the dimer with (A) $V_{12} = 2\hbar v_{\text{vib}}, \Delta = 0, \gamma = 1$, (B) the dimer with $V_{12} = 2\hbar v_{\text{vib}}, \Delta = 1/2\hbar v_{\text{vib}}, \gamma = 1$ and (C) the monomer $\gamma = 1$. In (A) and (B), the intensity of the emission bands has been multiplied by 5. The energies are relative to the pure electronic excitation energy of the monomer.

the strong coupling case. In the weak coupling case, however, their intensity is the same as for the isolated molecule. This suggests that the dipole strength of the 0– n vibronic transition ($n > 1$) in emission depends on the value of γ/V_{12} and changes continuously from zero to the value for the isolated chromophore as γ/V_{12} increases.

First, we consider a one-dimensional linear aggregate with N chromophores, all aligned parallelly. To compute the intensities of the 0–1 and 0–2 vibronic bands in emission in the intermediate coupling case one may try to use perturbation

theory. In analogy to the case of the dimer described above, we apply the Born–Oppenheimer to the aggregate as a whole and write the eigenstates as a product of a delocalized electronic wave function and a vibration function (E – V coupling scheme) [41]. The intensity of the 0–1 transition may be calculated using first-order perturbation theory [41]. To compute the 0–2 intensity, second-order perturbation theory has to be used.

The zero-order electronic exciton states can be labeled with a vector k describing the exciton momentum. When only nearest neighbor interactions are taken into account, with the interaction energy $V_{12} > 0$, the exciton state with $k = 0$ has the highest energy and corresponds to in-phase coupling of the transition dipole moments of the individual molecules. In a lattice with only one chromophore per unit cell, the only allowed transition is between $k = 0$ exciton state and the ground state (conservation of momentum). Transitions between ground and all other exciton states are forbidden. When only nearest neighbor interactions are taken into account the $k = \pi$ exciton state is the lowest in energy, when also next nearest neighbor interactions are included this is not necessarily true. Here, we assume that the $k = \pi$ state is the lowest in energy. The energy of the electronic levels is given by

$$E_k = E_1 + V_{12} \cos(k). \quad (26)$$

Using Born–Oppenheimer approximation for the aggregate as a whole, the zero-order states can be written as a product of an electronic and

a vibrational wave function. For the vibration function we use delocalized vibrational normal coordinates. These may be defined by

$$\tilde{q}_k = \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{ikn} q_n, \quad (27)$$

where q_n is the vibrational coordinate of the n th molecule in the aggregate. The perturbation term in the Hamiltonian can, taking into account conservation of momentum, be rewritten as [42]:

$$\begin{aligned} H' &= \tilde{\gamma} \sum_{n=1}^N |n\rangle q_n \langle n| \\ &= \frac{\tilde{\gamma}}{\sqrt{N}} \sum_{k'=0}^{\pi} \sum_{k=0}^{\pi} |k+k'\rangle \tilde{q}_{k'} \langle k| \end{aligned} \quad (28)$$

with $\tilde{\gamma} = 2\sqrt{2}\gamma$. The zero-order state excited state φ^0 with $k=m$ electronic momentum and one vibrational quantum in the $\tilde{q}_{k=p}$ mode can now be written symbolically as:

$$\varphi^0 = |k=m; 1_p\rangle. \quad (29)$$

In the strong coupling case emission from the lowest excited $k=\pi$ state is forbidden. In the intermediate coupling case, however, the electronic wave functions are mixed by the perturbation (28) and probability for 0–1 vibronic transition in emission is induced by admixture of the $|k=0; 1_{k=\pi}\rangle$ state to the $|k=\pi; 0\rangle$ state. The coefficient c describing this admixture reads

$$\begin{aligned} c_{\pi,0}^{(1)} &= \frac{\langle k=\pi; 0 | H' | k=0; 1_{k=\pi} \rangle}{2V_{12} + 2} \\ &= \frac{\tilde{\gamma}(0|q|1)}{\sqrt{N}(2V_{12} + 2)}, \end{aligned} \quad (30)$$

where $(0|q|1)$ denotes the matrix element of the operator q between the eigenfunctions of the harmonic oscillator with zero and one vibrational quanta ($1/\sqrt{2}$). Since the energies are in units of $1/2\hbar\omega$, V_{12} can be regarded as a dimensionless number. The dipole strength of the transition between the ground state and $k=0$ level equals N times the dipole strength of the isolated chromophore (μ^2). The transition probability for the

0–1 _{$k=\pi$} vibronic transition in emission is then given by the product of c^2 and the dipole strength of the $k=\pi$ level:

$$\mu^2(0-1_{k=\pi}) = \left(\frac{\gamma}{V_{12} + 1} \right)^2 \mu^2. \quad (31)$$

To calculate the intensity of the 0–2 vibronic band in the emission spectrum one has to sum up the intensities of the transitions from the lowest excited state to vibrationally excited forms of the electronic ground state $|0; 1_{k=\pi-m}\rangle$. To do so, one has to calculate the coefficient describing the admixture of the $|k=0; 1_{k=\pi-m} 1_{k=m}\rangle$ states to the lowest excited state. Using second-order perturbation theory one finds

$$\begin{aligned} c_{\pi,\pi-m,0}^{(2)} &= \frac{\langle k=\pi | H' | k=\pi-m; 1_{k=m} \rangle}{(V_{12} - V_{12} \cos(m) + 2)} \\ &\times \frac{\langle k=\pi-m; 1_{k=m} | H' | k=0; 1_{k=m} 1_{k=\pi-m} \rangle}{(2V_{12} + 4)}. \end{aligned} \quad (32)$$

The total intensity of the 0–2 band in emission gives

$$\begin{aligned} \mu^2(0-2) &= \mu^2 \left(\frac{(\tilde{\gamma}^2)(0|q|1)(1|q|0)}{2V_{12} + 4} \right)^2 \\ &\times \frac{1}{N} \sum_{m=\pi/N}^{N-\pi/N} \left(\frac{1}{V_{12} - V_{12} \cos(m) + 2} \right)^2. \end{aligned} \quad (33)$$

In the limit of large aggregates this can be rewritten as

$$\begin{aligned} \mu^2(0-2) &= \mu^2 \left(\frac{(\tilde{\gamma}^2)(0|q|1)(1|q|0)}{2V_{12} + 4} \right)^2 \\ &\times \frac{1}{\pi V_{12}^2} \int_0^\pi \left(\frac{1}{1 - \cos(m) + a} \right)^2 dm \\ &= \mu^2 \left(\frac{\tilde{\gamma}}{2V_{12}} \right)^4 \left(\frac{1}{(2+a)^2} \right) \\ &\times \frac{1}{\pi} \int_0^\pi \left(\frac{1}{1 - \cos(m) + a} \right)^2 dm, \end{aligned} \quad (34)$$

where $a = 2/V_{12}$. The integral can be solved and this gives

$$\mu^2(0-2) = \mu^2 \left(\frac{\tilde{\gamma}}{2V_{12}} \right)^4 \left(\frac{a^2 + 3a + 2}{(1+a)^2 \sqrt{a^3(2+a)^5}} \right). \quad (35)$$

There is no contribution from second-order terms to the 0–1 intensity. The ratio of the intensity of the 0–2 and 0–1 vibronic bands is therefore given by

$$\frac{\mu^2(0-2)}{\mu^2(0-1)} = \frac{\gamma^2}{2} \frac{\sqrt{V_{12}+1}}{V_{12}+2}. \quad (36)$$

This ratio reaches zero as V_{12} increases. Hence, when the system is close to the strong coupling limit, the small probability for the transition from the lowest excited state back to the ground state is almost entirely due to the 0–1 vibronic transition. The perturbational treatment of the vibronic coupling described above holds when γ/V_{12} and $1/V_{12}$ are small. The error involved in the perturbational treatment of the coupling may be estimated by considering the limit of small V_{12} , i.e. the weak coupling case. In this limit, we know that the ratio of the 0–2 and 0–1 vibronic bands in emission

$$\frac{\mu^2(0-2)}{\mu^2(0-1)} = \frac{\gamma^2}{4}. \quad (37)$$

It follows that Eq. (37) is off by only a factor of 2, and this surprising result can most likely be attributed to (partial) cancellation of various errors involved in the approximation.

Aggregates with a two-dimensional structure can be treated in a similar way. We assume that the chromophores are arranged in a rectangular lattice with the transition dipole moment oriented parallel perpendicular to the plane of chromophores. The nearest-neighbor interaction in the two perpendicular directions is taken to be of equal strength. The intensity of the 0–1 vibronic band can be calculated:

$$\begin{aligned} c_{(\pi,\pi),(0,0)}^{(1)} &= \frac{\langle k = (\pi, \pi); 0 | H' | k = 0; 1_{k=(\pi,\pi)} \rangle}{4V_{12} + 2} \\ &= \frac{\tilde{\gamma}(0|q|1)}{\sqrt{N}(4V_{12} + 2)}, \end{aligned} \quad (38)$$

$$\mu^2(0-1) = \left(\frac{\gamma}{2V_{12} + 1} \right)^2 \mu^2. \quad (39)$$

For the intensity of the 0–2 vibronic band we write

$$\begin{aligned} c_{(\pi,\pi),(\pi-m,\pi-p),(0,0)}^{(2)} &= \frac{\langle k = (\pi, \pi) | H' | k = (\pi - m, \pi - p); 1_{k=(m,p)} \rangle}{(2V_{12} - V_{12} \cos(m) - V_{12} \cos(p) + 2)} \\ &\times \frac{\langle k = (\pi - m, \pi - p); 1_{k=(m,p)} | H' | k = 0; 1_{k=(\pi-m,\pi-p)} \rangle}{(4V_{12} + 4)}. \end{aligned} \quad (40)$$

is given by $\gamma^2/2$ (the value for the isolated chromophore, Section 4.2 and Eq. (6)). In the limit of small V_{12} , Eq. (36) reduces to

For the total intensity of the 0–2 band in emission this gives

$$\mu^2(0-2) = \mu^2 \left(\frac{(\tilde{\gamma}^2)(0|q|1)(1|q|0)}{4V_{12} + 4} \right)^2 \frac{1}{N^2} \sum_{m=\pi/N}^{N-\pi/N} \left(\frac{1}{2V_{12} - V_{12} \cos(m) - V_{12} \cos(p) + 1} \right)^2. \quad (41)$$

In the limit of large aggregates this can be re-written as

$$\mu^2(0-2) = \mu^2 \left(\frac{(\tilde{\gamma}^2)(0|q|1)(1|q|0)}{4V_{12} + 4} \right)^2 \frac{1}{\pi^2 V_{12}^2} \int_0^\pi \int_0^\pi \left(\frac{1}{2 - \cos(m) - \cos(p) + a} \right)^2. \quad (42)$$

The integral cannot be solved easily. We write for the ratio of intensities

$$\frac{I(0-2)}{I(0-1)} = \gamma^2 \left(\frac{(2V_{12} + 1)^2}{(V_{12} + 1)^2 V_{12}^2} \right) R(a), \quad (43)$$

$$R(a) = \frac{1}{\pi^2} \int_0^\pi \int_0^\pi \left(\frac{1}{2 - \cos(m) - \cos(p) + a} \right)^2 dm dp. \quad (44)$$

From numerical evaluation of the function $R(a)$ we find that it can be approximated by $0.16/a$ for small a . So when V_{12} is large we obtain the two dimensional system

$$\frac{I(0-2)}{I(0-1)} \cong \frac{\gamma^2}{1.6V_{12}}. \quad (45)$$

This formula may be compared to Eq. (36) pertaining to the one-dimensional case which predicts $I(0-2)/I(0-1) = \gamma^2/(2\sqrt{V_{12}})$ for large V_{12} . It thus follows that in the two-dimensional system the intensities of the higher vibronic transitions is suppressed relative to the one-dimensional case. This result can be interpreted with help of theoretical work by Emin and others who have shown that that self-trapping in one-dimensional systems is qualitatively different from that in systems with higher dimensionality [43]. In systems with higher dimensionality the tendency to form polaronic, self localized species is reduced. The more delocalized the polaronic excitation becomes the lower will be the Franck–Condon factor for the higher vibronic bands in the emission spectrum. In the limit of small V_{12} (43) reduces to $\gamma^2/4$.

4.4. Summary

(1) When molecules in an aggregate are aligned with their transition dipole moments parallel and

the intermolecular interactions $V_{12} > 0$, then the probability for radiative decay of the lower exciton

states is reduced compared to the monomer due to the delocalization of the excitation.

(2) When the degree of disorder is high, localized excited states exist at the low energy side of the band, which act as luminescent sites with a probability for radiative decay comparable to that of the free molecule. For the localized states to exist, interchain interaction should be small or comparable to the width of the distribution of zero-order excitation energies of the chromophores in the aggregate. Variation of the interchain interaction V_{12} can also induce localization.

(3) When the degree of disorder is low, delocalized excited states predominate and fluorescence from these states is induced by vibronic ‘mixing’. In this case the band shape of the emission from the aggregate is different from that of the individual molecule. The intensity of the 0–0 vibronic transition is reduced in intensity. In the case of weak coupling in ordered arrays ($D \ll V_{12} \ll \gamma^2 h\nu_{\text{vib}}$) the vibronic mixing mechanism works very efficiently. The probability for radiative decay via higher order vibronic transitions is the same as for the isolated molecule. For intermediate coupling in ordered arrays ($D \ll V_{12} \cong \gamma^2 h\nu_{\text{vib}}$) vibronic mixing also occurs. The probability for radiative decay via higher order vibronic transitions is now reduced compared to the isolated molecule and the relative intensity of the higher vibronic emission bands of the aggregate has changed when compared to the spectrum of the isolated molecule. The intensity accumulates in the 0–1 vibronic band for high values of V_{12} . In the limit of strong coupling ($D \leq \gamma^2 h\nu_{\text{vib}} \ll V_{12}$) fluorescence from the aggregate is (practically) forbidden.

(4) Intermediate disorder (diagonal and off-diagonal) in the aggregates leads to the existence

of partially localized excited states for which the 0–0 transition in emission is allowed. Its intensity will increase with increasing degree of disorder. This holds for both the weak and strong coupling cases. In the weak coupling case the delocalized states are of course scattered by defects more strongly than in the case of strong coupling.

For highly disordered aggregates relaxation of the photo-excitations within the manifold excited state has the character of energy transfers between localized excited states and is therefore expected to occur relatively slow on a time scale longer than that of the nuclear vibrations. This will lead to a time-dependent red shift of the emission. As the density of states with high probability for radiative decay decreases with decrease in excited state energy, the band shape of the emission may be time dependent. For the emission from the lower excited states, which are reached after cooling of the excitations when prepared with pulsed excitation, the vibronic coupling mechanism is expected to make a larger contribution to the probability for radiative decay and hence the band shape of the emission will be different from that of the monomer with the 0–1 transition being more intense. For two-dimensional aggregates with low disorder in the intermediate to strong coupling case, relaxation of the excitations within the band of delocalized excited states is expected to be very rapid. This rapid relaxation process is then expected to be followed by a slower process of energy relaxation with the band of low lying localized states. These states are predicted from the tight binding Hamiltonian (1) and are few in number. The very deepest states are localized on a single molecule and have a probability for radiative decay which approaches that of the individual molecule. Hence, the emission from the very deepest trap levels is expected to resemble the monomer emission in band shape than the emission from the delocalized states. Emission from delocalized states is expected to be very weak due to unfavorable Franck–Condon factors. In systems with higher degree of disorder the transport between the localized state will be expected to be slow so that the deepest states may not be reached within the excited state lifetime.

5. Discussion

For the oligomer **1**, a significant difference between the absorption spectra of the microcrystalline film and the frozen solution is observed. This shows that interchain interactions between the molecules in the aggregate influence the photo-physical properties of the excited state. The changes in the band shape of visible absorption band (blue shift of the maximum, red shift of the onset) are consistent with the results from model calculations for rigid aggregates with parallel oriented molecules and $V_{12} > 0$ (Fig. 11). In accordance with this model, the emission from the solid film is red shifted in comparison to that of the isolated molecules and its lifetime is considerably longer.

Since the total width of the visible absorption band of the film is larger than the width of the visible absorption band of the isolated molecule, the intermediate to strong coupling case applies according to the criterion given by Simpson and Peterson [39].

From the spectra obtained for frozen solutions of **1** it is evident that the isolated molecule deforms considerably upon photoexcitation. If we ascribe the vibronic progression observed to a single active mode, we calculate $\gamma^2 = 0.9$ from the absorption and, consistently, $\gamma^2 = 0.9$ from the emission spectrum. The energy released by the geometrical deformation in the excited state, $\gamma^2 h\nu_{\text{vib}}$ with ν_{vib} the frequency of the active vibration is considerable (estimated at 1400 cm^{-1}).

If the electronic coupling between the molecules in the aggregate occurs in two directions with equal strength (a two-dimensional aggregate) one estimates from the energy difference between the maximum and onset of absorption of the solid film of **1** ($23500 - 17000 = 6500 \text{ cm}^{-1}$) $V_{12} = 1.6 \times 10^3 \text{ cm}^{-1}$. In the case that interchain interaction occurs in mainly one direction one finds $V_{12} = 3.2 \times 10^3 \text{ cm}^{-1}$. Since the vibrational fine structure observed in the absorption spectrum of the isolated chromophore is not observed for the film and with the visible absorption band considerably broadened it follows that the weak coupling case does not apply, nor does the strong coupling case where the absorption band should be very narrow. We

conclude that the intermediate coupling case ($V_{12} \cong \gamma^2 \hbar v_{\text{vib}}$) applies to our problem. Our estimate of the magnitude of V_{12} may be compared to recent results obtained by others. Quantum chemical calculations on a cofacial dimer of two the oligo phenylene vinylene molecules with seven repeat units have yielded a splitting of $V_{12} = 1.6 \times 10^3 \text{ cm}^{-1}$ at a separation of 4 Å [44]. Analysis of optical spectra of sexithiophene crystals has yielded a Davydov splitting of $2.6 \times 10^3 \text{ cm}^{-1}$ [22], consistent with an excited state interaction energy between neighboring π -conjugated oligomers on the order of 10^3 cm^{-1} .

The lifetime of the luminescence of **1** in solid film is considerably longer than for solutions of **1** and this agrees with the expectations from the model calculations for aggregates with parallel aligned transition dipoles and $V_{12} > 0$. The band shape of the fluorescence spectrum from the film is consistent with that expected for delocalized excitations. The relative intensity of the 0–0 is reduced and the 0–1 band is the strongest in emission. As explained in Section 4, this altered band shape can be explained by vibronically induced transition probability. We find that in the emission spectra taken from the film in the time window –0.02 to 0.0 ns (Fig. 2), the intensity of the 0–2 vibronic band relative to the 0–1 band is reduced by a factor of 1.5, when compared to the emission from the isolated molecule (Fig. 1). A change in the relative intensity of the higher vibronic emission bands is not consistent with vibronically induced intensity in the weak coupling limit, such a change only occurs for intermediate (or strong) coupling (Section 4). Using $V_{12} = 3.2 \times 10^3 \text{ cm}^{-1}$ Eq. (36) predicts for the case of one-dimensional electronic coupling a reduction of the relative intensity of the 0–2 band by a factor of 2.8. For the case of two-dimensional electronic coupling, a reduction by a factor of 3.6 is calculated from Eq. (45) using $V_{12} = 1.6 \times 10^3 \text{ cm}^{-1}$. The observed reduction of the 0–2 intensity is approximately a factor of 2 smaller than predicted, theoretically. An important factor contributing to the relative intensity of the 0–2 band being higher than predicted may be the following. If the early emission from the film is due to photo-excitations, which are partially localized by disorder (Section 4.1) the 0–2 band

would not be as strongly reduced as predicted for a completely delocalized excitation. The analysis of the dimer emission (Section 4.2) illustrates this. The fact that the 0–0 vibronic band is observed in the early fluorescence spectrum with medium intensity can also be explained by disorder induced localization of the excitation (Fig. 17). Although disorder seems the most likely explanation for the intensity of the 0–0 emission band, we mention that vibronic coupling through low-energy vibrations also may contribute to the intensity in the 0–0 region of the spectrum.

The observed time-dependent red shift of the fluorescence spectrum indicates relaxation of the excitations by migration to trap sites and shows that disorder indeed influences the photophysics of the excitations. The lowest energy trap sites in films of **1**, observed under selective excitation (Fig. 3) are tentatively assigned to localized states in the red edge of the band of exciton states as calculated for the two-dimensional aggregate using the tight-binding Hamiltonian (Eq. (1), Fig. 12). For these states, the 0–0 transition has a higher probability than for the delocalized ones. Observation of time and excitation wavelength dependent changes in the band shape of the emission for microcrystalline films and single crystals of sexithiophene are also consistent with this model [22–24]. In the fluorescence spectra taken early after excitation, the 0–1 vibrational transition is the most intense.

For the polymer film the width of the visible absorption band is considerably smaller than for the oligomer (Fig. 5). Also in this case, the maximum of the absorbance of the film is blue shifted with respect to that of the frozen solutions, but the shift is much smaller than for the oligomer. The smaller width of the spectrum implies that the average value for the interchain interaction must be smaller for the polymers than for the oligomer. A possible explanation is that for the polymers the packing of the chains is far less regular, with interchain distances being larger for the oligomer and with the relative orientation of neighboring chains not being parallel. Because of this, one expects the strength of interchain coupling for various pairs of neighboring chains to be distributed statistically with a mean value lower than for parallel chains in van der Waals contact. Our

model calculations predict that this type of off-diagonal disorder indeed causes a decrease in the width of the absorption band (Fig. 15). Recent theoretical calculations [44–46] have shown that for long oligomers the nearest neighbor interchain interaction energy decreases with the oligomer length. For the polymers studied here, the effective conjugation length is most likely higher than seven units, the length of the oligomer **1**. Therefore, according to the theoretical results cited, apart from the disordered packing also, an intrinsically smaller value of V_{12} may contribute to the smaller width of the absorption spectrum of the polymer films.

From the relatively small difference in band shape between the absorption spectrum of the isolated chains in frozen solution and the films one concludes that the strength of the interchain coupling must be comparable to the vibrational energy quantum for the active vibration, i.e. the intermediate to weak coupling case applies to the polymers. Measurements of the circular polarization in absorption and in luminescence [47] for films of this polymer provide an experimental indication that interchain interactions are of intermediate strength.

The time-dependent red shift of the fluorescence from the films shows that disorder in the polymer films must be considerable. Therefore, the excited states cannot be delocalized over a large number of chains. The depolarization data (Figs. 8 and 10) are consistent with hopping of localized excitations. The lifetime of the emission from the films is considerably longer than for the solution indicating a reduced radiative lifetime due to electronic coupling between the chains. For polymer **3**, the band shape of the long-lived emission is indeed compatible with that expected for a photoexcitation delocalized over parallel oriented chains: just as for the oligomer the 0–1 vibronic band is expected to be the most intense. Early after excitation (Fig. 9) the wandering excitation still encounter sites with high probability for radiative decay (luminescent sites) and with the excitations reaching the low energy side of the band, where the density of luminescent sites is lower, the vibronic coupling mechanism becomes more important in providing the probability for radiative decay. As

discussed, the relative intensity of the 0–1 vibronic transition should be enhanced when this mechanism is active (Fig. 17). For the polymer **2**, however, no significant change in emission band shape could be observed when studying the time evolution of the emission spectra. To account for these features we propose that the density of luminescent sites is higher for polymer **2** than for **3**. This may be caused by a higher diagonal or off-diagonal disorder. In addition, luminescent sites may arise from orientational disorder of the polymer chains.

The present results indicate that the fluorescence quantum yield of films of π -conjugated polymer may be improved by introduction of disorder (diagonal, off-diagonal and orientational). This will however result in a broadening of the emission bands and hence a lower color purity of the emission. Another strategy to improve the emission output is the use of well ordered π -conjugated compounds with strong electron-vibration coupling combined with relatively weak interchain interaction. In this case, the oscillator strength accumulates in the first vibronic band of the emission spectrum and an emission with a high color purity may be obtained.

The combination of both strategies most likely yields adverse effects in terms of spectral purity. In this case, the higher vibronic transition from the low lying excited states would be most intense and yield an additional broadening of the emission spectrum. For polymer solar cells it is often advantageous to have a long radiative lifetime and a high mobility of the excitation. This could be accomplished by choosing a π -conjugated material with low γ for which the polymer chains stack preferentially parallel and for which the diagonal and off-diagonal disorder is as low as possible.

6. Conclusion

The shape of the visible absorption and emission band of π -conjugated materials depends on the degree of interchain delocalization of the excitation. It therefore seems that band shape analysis provides a powerful tool to study photo-physical processes in these materials. For films of

the *para*-phenylene vinylene heptamer, the band shape of the absorption indicates relatively strong interchain interaction in the excited state with an interaction energy for neighboring molecules on the order of a thousand wave numbers. The band shape of the fluorescence spectrum collected early after pulsed excitation is consistent with a delocalized excitation and the time evolution of the fluorescence indicates that relaxation of the excitation by energy transfer to localized states occurs. Theoretical model studies show that at the low energy edge localized states can exist. This adds to the growing body of experimental evidence that in aggregates of oligomeric π -conjugated materials exciton coupling between the molecules is relatively strong.

For the polymers, the band shapes indicate that interchain interactions are (at least on average) weaker than for the oligomer. This then implies that interchain delocalization is more easily perturbed by defects and disorder. Therefore, band shape, quantum yield, and lifetime of the fluorescence may depend critically on polymer and film preparation. For the two polymers investigated here, signatures of interchain delocalization are readily observed for one polymer, while for the other, the luminescence from disorder induced trap sites is dominant.

What is presently not well understood is the relation between excited state interchain interaction energy and the effective conjugation length of the π -conjugated polymer. Theoretical arguments have been given for a decrease of the interchain interaction energy with effective conjugation length [45,46], and these await further experimental verification. The proposed decrease in interaction energy, when found to be real, may then explain the seemingly different photophysical behavior of oligo- and polymeric π -conjugated materials.

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