CHAPTER 6

Picosecond pump/probe and time correlated single photon counting experiments on TPY aggregates: excitons and polarons

6.1 Introduction

6.2 Polaron concept

6.3 Results

6.3.1 Spectra of monomers and aggregates

6.3.2 Pump/probe experiments

6.3.3 Homogeneous lineshape

6.3.4 Monomer properties

6.3.5 TCSPC results

6.4 Discussion and summary

References
6. TPY-aggregates: Excitons and Polaron

6.1 Introduction

It was recognized early that adequate descriptions of optical excitations in solids must incorporate the influence of the coupling of the optical excitations to phonons [1,2]. Without exciton-phonon coupling the zero order state is an exciton, with exciton-phonon coupling this changes. As was shown in Chapter 2, in particular limits the mixed excitation is best described as a polaron. A polaron is an electronic excitation which drags a lattice deformation along with it. Polaron states are used to explain the spectroscopy of polymers and semiconductors [3–5]. In a number of molecular systems, the energy gain which is the result of the mixing of exciton and phonon states can be so large that self–trapping can take place. Self–trapping of excitations has been observed in pyrene and perylene [6]. The self–trapping in crystals of the last two compounds is the result of excited state dimerization (excimer formation) in the lattice. A related form of self–trapping has been found in Wolfram's red salt, a quasi one–dimensional platinum salt [7]. The pure electronic self–trapping effect has been observed in some alkali halides [8].

The J-aggregates of PIC that were discussed in the preceding chapters are an example of strong coupling of the excited states of the monomers. The exciton that is formed is coupled only weakly to the lattice. The TPY aggregates, which are subject of this chapter, show strong coupling of the monomer excited states, but the excited states also show strong coupling to the lattice. The coupling to the lattice has a profound effect on the spectroscopy. The optical absorption spectrum of TPY aggregates is shifted strongly relative to the monomer spectrum. However, no large motional narrowing effect is observed, and no resonant aggregate emission is found.

The study of molecular aggregates that exhibit strong exciton–phonon coupling is relevant to the study of photobiological systems. The coupling of chromophores in antenna complexes and reaction centers is strong, and "aggregate" states are formed. However, the absorption bands are very broad, and only a small amount of emission is observed. The reason for this fact is that low frequency modes of the protein networks surrounding the antenna complexes couple to the extended exciton states [9,10]. The strong chromophore coupling in photosynthetic systems only leads rapid transfer of energy to acceptor molecules, and does not not lead to an increase of the radiative rates. The energy transfer is necessary to inhibit radiative relaxation of the initially excited molecule.

The aggregate studied in this chapter is TPY (the structure is shown in Fig. (1.1)) in polycarbonate. A strongly enhanced optical frequency doubling efficiency was reported by Wang [11]. The high doubling efficiency shows that the molecules are ordered in the aggregates. At first we thought that in TPY aggregates a more extensive delocalization than in PIC aggregates might occur. This turned out not to be true but a number of other phenomena was encountered.

The first report on TPY aggregates dates back to work of Dulmage et al. [12]; they studied the light–induced conduction properties of
aggregated samples. In the course of that work the structure of a model
system was resolved by X-ray diffraction [13,14], showing that TPY
aggregates consist of layers of molecules. More recently Marchetti et al.
[15] made a study of the DC Stark effect and tried to interpret their
data in terms of aggregate layers which interact strongly. The crystal
and aggregate spectra have been interpreted by Young et al.[16]

The present chapter consists of a summary of the concepts of
exciton–phonon coupling presented in Chapter 2, followed by the results
of time resolved experiments, and the discussion of the dynamics of TPY
aggregates. I will show that the optical excitation which is formed
initially is a polaron. This polaron is a delocalized aggregate state,
extending over many molecular units. From pump/probe spectroscopy it can
be concluded that the polaron excitation relaxes rapidly to a localized
state of lower energy. The transfer can be understood from a model
involving self-trapping of the extended state. The interpretation is
complicated by the occurrence of Förster energy transfer between
different aggregates.

6.2 Polaron concept

The energy of an aggregate exciton contains a static and a dynamic
contribution. The static contribution is caused by the local energy
differences, \( \Delta_n \), which are the result of the different orientations of
the molecules around the exciton. The dynamic part of the coupling either
leads to scattering of the exciton, which is accompanied by either a
change of state, or leads to an energy change of the excitation.

The basic Hamiltonian for a molecular exciton interacting with phonons
is (see Sect. (2.3)):

\[
H_{\text{agg}} = \sum_n \left( H_n + \Delta_n + \sum_{m} J_{nm} \right) + H_{\text{exc-phon}} + H_{\text{loc}} + H_{\text{phon}}. \tag{6.1}
\]

The first summation over the sites \( n \) represents the exciton term
including inhomogeneity. The exciton–phonon coupling is split in a
transfer term which describes the influence of the phonon interaction on
the delocalization over the sites, and a local term which describes the
changes at site \( n \). Finally a phonon term is present to include the phonon
energies. A delocalized state exists when the transfer term \( J_{nm} \) leads to
an intermolecular coupling, \( B \), which is larger than the spread of the
site inhomogeneities \( \sigma \) (this spread is defined as the 1/e half width of
the distribution of site energies \( \Delta_n \)). Two limiting cases of the
exciton–phonon coupling are dominant intersite transfer, and a dominant
local deformation. In the former case the resultant state can be
described as an exciton scattered by phonons. When the latter (local)
exciton–phonon term is dominant a potential deformation occurs along the
phonon coordinate, resulting in a polaron state.

Self-trapping of a delocalized state can occur in the limit where the
coupling of the units is large enough to overcome the inhomogeneities,
\( B > \sigma \). This condition implies that the state which is formed after optical
excitation is a delocalized exciton or polaron. The extent of the
relaxation of this delocalized state along the deformation coordinate will determine the character of the final state. Only in the limit where the relaxation energy is larger than the bandwidth of the delocalized state self-trapping can occur. A transition of the delocalized aggregate state into the localized self-trapped state is accompanied by the collapse of the extended state into a single molecule state. Static and dynamic spectroscopies reflect the transition between these two regimes.

6.3 Results

6.3.1 Spectra of monomers and aggregates

In Fig. (6.1) the absorption and emission spectra of TPY monomers and aggregates are depicted. In the monomer spectra (left side of Fig. (6.1)) no sharp features are observed in either absorption or emission. The shape of the monomer absorption spectrum deviates slightly from a Gaussian of width of 3000 cm\(^{-1}\). This width is extraordinarily large for a dye molecule in polymer matrix. Therefore a large fraction of the width may be caused by vibronic activity. The monomer fluorescence maximum shows a large shift relative to the absorption maximum, indicating that the excited state relaxes strongly. The pure electronic transition can be estimated to be located at the low energy side of the absorption at about 620 nm (16100 cm\(^{-1}\)).

![Figure 6.1 Absorption (drawn line) and emission (dashed) spectra of TPY monomers (left) and aggregates (right) at 80 K.](image)

The absorption spectrum of the aggregated sample differs markedly from the monomer spectrum. A strongly red-shifted absorption is observed at 685 nm (14600 cm\(^{-1}\)) with a broad tail at 1500 cm\(^{-1}\) higher energy. Assuming that the coupled molecular transition dipoles form a linear chain, the optically allowed state is the \(k=0\) exciton level. The aggregate absorption is red-shifted by more than 1500 cm\(^{-1}\) relative to the monomer. The shift is the sum of a van der Waals shift and a monomer coupling term. When, as for PIC aggregates, the red shift is dominated by the intermolecular coupling, this coupling must be about 700 cm\(^{-1}\), and
the total exciton bandwidth ($4B$) must be 2800 cm$^{-1}$. Although a large red shift is observed, no strong narrowing effect is observed. The width of the exciton absorption is 1700 cm$^{-1}$, similar to isolated dye molecules in polymer matrices. No large amount of oscillator strength is present in the top of the exciton band [12], therefore it can be concluded that significant narrowing of the absorption profile does not occur.

The large red shift of the aggregate emission relative to the absorption implies that the aggregate excited state which is prepared after absorption relaxes strongly. TPY and PIC aggregates show comparable coupling strengths ($B$) and monomer inhomogeneities ($\sigma$). The absence of motional narrowing and resonant emission in TPY is caused by strong coupling of the exciton to the lattice.

6.3.2 Pump/probe experiments

By pump/probe experiments the change of the absorption coefficient of the sample is detected at short time delays after the passage of a pump pulse through the sample. Mapping the absorption change as a function of time and excitation wavelength gives information about the transient absorption spectrum.

The pump and probe pulse can either come from the same laser, or from two different lasers. In the former case the time resolution is better, because it is determined by the intensity autocorrelation. In the latter case the time resolution is determined by the intensity crosscorrelation. In general the time jitter between pulses of two different synchronously pumped dye-lasers completely determines the crosscorrelation. The autocorrelation function of the pulses used was typically 4 ps wide, whereas the crosscorrelation was about 15 ps. The advantage of using two different lasers is the separate tunability of the pump and probe wavelengths. The fastest experimental way to achieve the wavelength scan is to use a continuum probe and optical multichannel detection. Scanning two lasers is more time consuming but leads to the same results.

In Fig. (6.2) a result of a single laser pump/probe experiment is shown. The two transients are responses at different wavelengths. The upper trace was detected at the maximum of the aggregate absorption (680 nm) and can be fitted with a decay component of 45 ps and a component of about 3.5 ns (the total trace is not shown). The lower trace has been measured with pump and probe wavelengths of 670 nm. At this wavelength the bleaching grows with the same time constant of 45 ps to and after that decays with a time constant of about 3.5 ns. The long component is not easily measured because of the impractical long optical path length differences necessary for those experiments.

The measured pump/probe responses did not show any depolarization at the temperatures considered (1.5 to 80 K). Within the experimental error the polarization ratio $\rho(t)$ (see Sect. (3.2)) was constant. Some initial depolarization may occur, but the value of $\rho(t)$ was close to 0.4, which is the theoretical maximum for a random sample.

The two-color pump/probe experiments were done in two ways. First the pump wavelength was varied, and the probe wavelength was held fixed. Independent of the pump wavelength the same transient response was found.
When the reverse experiment is performed, pump wavelength fixed and probe variable, the transient spectrum is recorded. The pump was tuned to the maximum of the absorption around 680 nm, and the probe was scanned from 625 to 705 nm. As can be seen from Fig. (6.2) the 45 ps fast component and the slow component behave differently. The fast component changes from a bleaching into an increased absorption at around 675 nm, while the slow component changes at 665 nm. In Fig. (6.3) the transmission changes are plotted as function of the probe wavelength. It must be noted that the zero crossing points of the two curves are located at positions in the absorption band close to the maximum, and do no coincide with the edge of the absorption band. The increased absorption at wavelengths shorter than 665 nm, shows that at these wavelengths the transition strength between the initially excited state and higher states is larger than between the excited state and the ground state.

![Figure 6.2 Pump/probe measurements of TPY aggregates in a polycarbonate matrix at 1.5 K. The top trace was recorded at a wavelength for pump and probe of 680 nm, the middle trace at 670 nm. The bottom trace (dashed) is the pulse autocorrelation.](image)

The two time constants, 45 ps and 3.5 ns are present in all decays at different wavelengths. This statement does of course not hold for the respective zero-crossing points, but the growth dynamics of the signal at 670 nm in Fig. (6.1) can definitely be fitted with the same time constants as the decay at 680 nm.

The main portion of the experiments was performed at a temperature of 80 K. At this temperature $kT$ is in the order of 55 cm$^{-1}$, which might influence the dynamics. However, the experiments that were performed at 4.2 K gave the same results for the kinetic constants, showing that the observed processes are not energy activated. One difference must be noted: the zero crossing point for the transient absorption shifted to somewhat longer wavelengths (3 to 4 nm). This observation can be explained by thermal population of ground state levels at higher temperatures.
Figure 6.3 Relative bleaching as function of the wavelength of the probe pulse. (△) is the fast 45 ps component, and (○) is the 3.5 ns component. Note that a negative bleaching is the same as an increased absorption.

In the femtosecond laser lab a series of experiments on TPY was performed [18], using a colliding pulse modelocked (CPM) laser, which has a pulsewidth of 50 fs. Fast transients were found but turned out to be very intensity dependent. Analysis in terms of biexcitonic annihilation model [21] proved to be fruitful. Apparently too many excitations are made on one aggregate, and "collisions" can take place. The remedy for this problem is the lowering of the peak intensity of the pulses used, at the expense of the signal-to-noise ratio. The pulse intensities used in the femtosecond experiments, about 300 to 6000 μJ/cm² per pulse, are about two orders of magnitude higher than the picosecond pulse intensities of 5 to 20 μJ/cm². The intensity dependence of the picosecond pump/probe transients was checked, and no effect was found. Besides the 45 ps transient no fast transients which can be assigned to free excitons were found using CPM laser laser pulses.

6.3.3 Homogeneous lineshape

From the transient spectrum depicted in Fig. (6.3) it can be inferred that a pulse with a well determined wavelength bleaches the whole band. Such a time-resolved holeburning experiment shows that the "homogeneous" lineshape is very broad (~1000 cm⁻¹) at 80 K. No narrow zero phonon line (ZPL) feature is present, because either when pump and probe pulses have the same wavelength or when wavelengths differing about 5 nm are used, the holedepth is the same. Experiments performed at liquid helium temperatures give the same results. This behavior resembles that of some chromophores in glasses [17], where the chromophore transition and the
motions of the matrix are coupled strongly. In these systems most absorption is found in phonon-coupled transitions. In a standard steady state holeburning experiment no permanent hole was found. This could mean that the efficiency for permanent holeburning is very low. However, the wide band must be bleached as a whole, therefore only a very small effect is expected at the burn wavelength.

In Fig. (6.4) a stochastic accumulated echo trace is shown, together with the autocorrelation trace. The intensity used in the experiments was ten times smaller than in the pump/probe experiments. The strength of the accumulated signal is large, so large that reliable pump/probe measurements around $t=0$ could only be made with the traveling wave modulator in one of the beams (see Sect. (3.3)). The echo response (top trace of Fig. (6.4)) resembles the field correlation (bottom trace of Fig. (6.4)). This observation leads to the conclusion that the dephasing time $T_2$, must be much shorter than the field-correlation width of the exciting light pulses. Otherwise the echo trace should show a decaying tail at $t>0$.

![Figure 6.4 Response of TPY aggregates at 1.5 K to stochastic excitation (top). The center wavelength of the exciting light was 680 nm, the field correlation is shown in the bottom trace. The width of the intensity correlation in this experiment was about 20 ps.](image)

The absence of a decaying echo signal shows that the oscillator strength is dispersed over phonon-coupled states. The echo decay reflects the Fourier transform of the lineshape: the very fast decay is related to a very broad "homogeneous" line. If some of the oscillator strength is present in the zero phonon line, a component with a normal decay can also be observed. Actually, for some dye molecules complex beating decays are observed, in which case the decay traces can be Fourier transformed to the quasi-homogeneous lineshape [17].
6.3.4 Monomer properties

In Sect. (6.3.1) the absorption and emission spectra were presented. The radiative lifetime of the TPY monomer can be determined from the absorption spectrum using the Strickler-Berg relation [20]. Dulmage et al. [12] calculated a value of 8 ns for the radiative lifetime from the absorption spectrum. Nonradiative processes are expected to shorten the fluorescence lifetime to less than 8.0 ns.

In our previous publication on aggregates of TPY, [19] some preliminary time resolved fluorescence results with nanosecond resolution were presented. These preliminary photon counting measurements on TPY monomers yielded a 1.5 ns decay time [19]. The reinvestigation with the new time resolved fluorescence setup showed that the radiative dynamics is more complicated. The fluorescence decays turned out to be concentration dependent, and strongly nonexponential. However, in low concentration samples TPY in PMMA, the decay was exponential with a 4 ns time constant. Low concentration TPY samples in glycerol showed a 3.5 ns decay time. The quantum yield for radiative emission can be deduced from the ratio of the fluorescence lifetime and the purely radiative lifetime, and is about 0.5.

For concentrated samples transfer of energy between monomers occurs. For example, a concentration dependent red-shift of the emission, and concentration dependent decays are observed. In those concentrated samples a 300 ps pump/probe transient was detected [19]. We tentatively assigned the discrepancy of absorption recovery and emission lifetime to dipolar relaxation of the matrix around the excited molecule. However, on the basis of the better fluorescence data, the 300 ps decay must be assigned to energy transfer. It presents an average of the transfer time of the excitation. The signal-to-noise ratio of the pump/probe data is not good enough to allow for biexponential fitting, so a real match to the emission data is hard.

I conclude that the radiative lifetime of the TPY monomer is 8 ns. In PMMA and glycerol the emission lifetime is 4 ns, leading to a quantum yield of 0.5. I assume that these numbers also hold for TPY in polycarbonate.

6.3.5 Time Correlated Single Photon Counting results

In Fig. (6.5) three fluorescence decay traces are shown, recorded at wavelengths corresponding to three different positions in the fluorescence spectrum of TPY aggregates. The top trace is representative for the broad structureless emission detected from 600 to 700 nm. The middle trace belongs to the short wavelength side of the band centered at 750 nm, while the bottom trace was detected at the long wavelength side of the 750 nm band. On inspection, it is clear that the traces shown present totally different regimes.

The emission band from 600 to 700 nm originates from residual monomer in the aggregated samples. The time-resolved data show the same fluorescence decay time of 3.5 ns in the wavelength region from 600 to
6. TPY-aggregates: Excitons and Polaron

700 nm. This long lifetime and the high yield for emission exclude the possibility of vibronic emission of aggregates. The emission spectrum matches that of the monomer, and the lifetime is close to 4 ns found for TPY monomer in PMMA. When the excitation wavelength was varied while monitoring the emission at 700 nm, the relative weight of the 3.5 ns component decreased from 0.17 with 585 nm excitation to 0.05 with 650 nm excitation. This shows that the slow emission in the specified wavelength region follows that of the monomer.

![Fluorescence decays of TPY aggregates at 80 K at three different wavelengths indicated in the figure. See text for explanation.](image)

Figure 6.5 Fluorescence decays of TPY aggregates at 80 K at three different wavelengths indicated in the figure. See text for explanation.

A small component with a very short lifetime (about 30 ps) is observed at 690 nm, a wavelength corresponding to the onset of the emission band centered at 750 nm. At longer wavelengths the weight of the fast component rapidly increases, relative to the 3.5 ns component. Upon scanning to longer wavelengths the average initial decay constant gets larger. The word "average" has to be used because the initial decays are strongly nonexponential. Since the fluorescence decay traces appear to be the sum of many (more than three) exponentials I will not stress the quantitative results too much.

At 700 nm the initial decay lengthens to 150 ps, and the weight increases as well. Upon shifting the detection to even longer wavelengths, the decay times get longer. This trend continues up to 775 nm where the initial decay is about 0.9 ns and the residual long component is 2.4 ns. The lengthening of the initial decay time indicates that transfer of energy towards aggregates absorbing at lower energy takes place. Energy transfer shows up from a longer risetime of the low energy emission. The first 500 ps of the aggregate emission detected at 800 nm was compared to the emission of Styryl 9 dye, in order to estimate
the risetime. The result is that the growth of the emission signal of the aggregates is slower than that of the dye. The time constant of the growth of the aggregate emission is about 50 ps. The nonexponentiality of the decays, together with incomplete knowledge of the instrument response of the detection, do not allow for more precise determination of the risetime.

As was mentioned earlier most cited data were taken at 77 K or a few degrees above. Fluorescence decay traces recorded at 4.2 K gave the same results. The onset of the fast component is also found at 690 nm, the values of the decay parameters with biexponential fitting are the same. Room temperature experiments give ambiguous results. The 3.5 ns component that is observed at low temperature is not present any more. The background decay has shortened very much leaving a combination of fast picosecond decays. I conclude that the dynamics are not temperature dependent up to 77 K. Above that temperature the dynamics change, possibly caused by increasing nonradiative relaxation.

To summarize the observations:
1) in the 600 to 700 nm region a 3.5 ns decay process cause by residual monomers is observed,
2) beyond 690 nm a fast aggregate decay is present which starts off with a 30 ps decay time at 690 nm and lengthens to about 1.5 ns (as an average for the biexponential decay) at 800 nm.

6.4 Discussion

In this section I will first discuss the physical shape of the aggregates of TPY. Thereafter I will show that the spectroscopy of TPY aggregates can be explained on the basis of a model involving strong exciton-phonon which leads to self-trapping of the delocalized excitation.

The physical structure of the aggregate of TPY has been studied by Dulmage et al., using X-ray diffraction. They prepared single crystals of TPY mixed with a compound that resembles the repeating unit in the polymer polycarbonate. The most simple way of describing the structure of the model system is that layers of TPY are separated by layers of polymer precursor. Neighboring TPY layers are connected via an inversion operation, which means that the center of a stack of layers is a center of symmetry. The separate layers of TPY consist of strings of molecules stacked side-to-side.

Frequency doubling experiments performed by Wang showed strong enhancement caused by aggregation of TPY in polycarbonate. Since no frequency doubling is possible in inversion symmetric media, the X-ray structure of the model seems to be in conflict with the structure of the aggregate in polycarbonate. However, it is possible that the larger disorder in the real aggregate allows for some enhancement of the doubling efficiency. Small regions of single layers or odd number TPY stacks could contribute strongly to the frequency doubling.

The layered aggregate model was also used by Marchetti et al. [15] to explain their DC Stark effect experiments. In those experiments the energy changes which are the result of the interaction of an external
The close resemblance of the spectra of TPY aggregates in polycarbonate and TPY aggregates in the polymer precursor is convincing evidence that the aggregate consists of layers of molecules. However, the extension of the ordered region in the TPY aggregate cannot be deduced directly. The microscope photographs presented by Wang [11] indicate long-range (\( \mu \)) structural order. Photographs of the samples used in this work show much less structure. The aggregates are barely resolvable in optical microscopy, and can be seen as beady grains. Apparently, the addition of large quantities of plasticizer in the samples of Wang changes the aggregation process. Marchetti et al. [15] noted that aggregates also exist in the "homogeneous phase", which means that the aggregates are smaller than can be observed using optical microscopes.

The aggregation energy shift is large indicating that the coupling of the molecular states is large. Despite the large coupling no strong motional narrowing effect of the exciton absorption line is observed. If one realizes that a part of the width of the monomer absorption line must be assigned to vibronic activity, hardly any narrowing is observed. Clearly, the narrowing is counteracted by another effect. The packing of the TPY molecules in the layers leads to chains of molecules with relatively small distances in one direction. A one dimensional character of the resulting aggregate excitation can therefore be anticipated. Spectra of the model system [13] showed that all oscillator strength should be assigned to the lower \( k=0 \) state of the exciton band. This would imply that individual transition dipole moments are oriented head-to-tail.

A one dimensional exciton can show a strong enhancement of the radiative rate. The delocalization of the exciton can lead to resonant emission. In TPY aggregates no resonant emission is found: the aggregate emission shows a large shift relative to the absorption. Together with the observation of very short dephasing times, and the bleaching of the whole absorption band in pump/probe spectra, the large shift shows that the delocalized aggregate excitation is strongly coupled to the lattice. Pure exciton states are not observed in any of the experiments. The fact that an strongly shifted aggregate band is observed, however, proves that a delocalized aggregate state exists.

The zero-order description of the aggregates excitation is not an exciton in a well defined \( k \)-state but an exciton coupled to lattice modes. This coupled state is red shifted with respect to the monomer, because of the intermolecular coupling. The \( k=0 \) oscillator strength is dispersed over many mixed exciton-phonon modes, leading to a large "homogeneous" width, which is found in transient spectra and accumulated echo experiments. The initially formed optical excitation is best described as a polaron. The large shift of the emission relative to the absorption shows that the local deformation term of the aggregate Hamiltonian is dominant (see Sect. (2.3)).

From DC Stark effect experiments an interaction between dye layers, which are separated by a polymer layer, of 450 cm\(^{-1} \) was inferred. This
coupling is very large when compared with the estimated 700 cm\(^{-1}\) coupling between molecules within a single layer (B). The displacement of the spectrum of the exciton–phonon state relative to the pure exciton used in their analysis, could explain the large value of the interlayer coupling.

The time resolved results must be interpreted in terms of the polaron model. From pump/probe spectroscopy it is clear that two kinds of dynamics are present. On one hand, a fast (45 ps) temperature transient is observed. On the other hand we see an approximately 3.5 ns transient. The spectrally resolved responses of the fast decaying species and the slow decaying species (Fig. (6.3)) are very similar except for a shift of 5 nm (120 cm\(^{-1}\)). The similarity of the spectral response shows that the excited states involved have the same absorption spectrum. This fact suggests that the two species represent different states on one energy potential. The time resolved fluorescence traces show no resonant 45 ps component caused by direct emission of a extended (superradiant) polaron. Throughout the 600 to 700 nm region a 3.5 ns component is observed, which is caused by residual monomers in the aggregated samples. A very fast (±30 ps) component can be seen at 690 nm, at the edge of the absorption, but no fast emission is seen that is resonant with the absorption. The fast emission at 690 nm must originate from a phonon relaxed state.

The absence of a resonant 45 ps component indicates that no superradiant extended state exists, like the one found in PIC aggregates. It is possible that a small fraction of the fast emission around 700 nm arises from the remnant of such a state. It does however only represent a very small fraction of the total emission.

Since the total rate out of the initially formed state (this rate is observed in pump/probe responses and is (45 ps)\(^{-1}\)) is:

\[
k_{\text{total}} = k_{\text{transfer}} + k_{\text{superradiant}} \quad ,
\]

and the superradiant emission yield is:

\[
\phi_{\text{superradiant}} = \frac{k_{\text{superradiant}}}{k_{\text{total}}} = \frac{\tau_{\text{pump/probe}}}{\tau_{\text{superradiant}}} \quad ,
\]

the emission yield of a superradiant state is proportional to the ratio of the nonradiative transfer time to the radiative lifetime. The emission yield of the fast polaron emission is negligibly small so the "superradiant" decay time has to be large. The conclusion can be drawn that no direct polaron emission is seen in the fluorescence spectra of TPY aggregates. The observed 45 ps dynamics are totally determined by the transfer rate out of the initially prepared delocalized aggregate state.

In the region of 750 to 800 nm a biexponential decay is observed, with components of 0.9 ns and 2.4 ns. These times indicate that the relaxed state is not superradiant, but resemble the 3.5 ns monomer emission. I propose that this slow decay process should be interpreted in the polaron model. After optical absorption a polaron state is formed. From the absence of direct emission one can infer that this delocalized state relaxes strongly. The relaxation inhibits the fast emission that would be expected from a delocalized polaron. After 45 ps the delocalized polaron is self–trapped at a lattice site. The observation of equal trapping
times at 4 and 77 K suggests that the trapping is not activated, and is either the result of tunneling or a barrierless transition.

In some molecular systems like pyrene and α-perylen [6] self-trapping occurs caused by molecular excimer formation. Such an excimer formation process is special case of self-trapping. Very short-lived delocalized polaron emission is observed, together with much longer lived self-trapped emission. Recently evidence for self-trapping was reported for a quasi one dimensional platinum salt [7]. In this last case Stokes shifted self-trapped emission is observed together with small quantities of free exciton emission. This assignment was substantiated by time-resolved data. The authors claim that in this case the formation of the self-trapped state is barrierless. No barrier is expected for true electronic one- or two-dimensional self-trapping processes [2]. TPY aggregates show the same nonactivated emission behavior.

In the spectral range from 690 nm to 775 nm a distribution of emission lifetimes is observed. The wavelength and concentration dependent decay constants indicate excitation transfer, caused by hopping of the trapped excitation towards lower energy. The formed trapped state can communicate with many sites around it, and energy transfer occurs, until no more sites are available. The transfer rate obeys the Förster equation:

$$k_{en, tr} \propto \frac{1}{r^6} \int f_d(\nu) e_a(\nu) \, d\nu$$

(6.4)

where $f_d(\nu)$ represents the fluorescence profile of the donor, $e_a(\nu)$ is the absorption profile of the acceptor, and $r$ is the distance between donor and acceptor. The energy transfer rate is proportional to $r^{-6}$, so only molecules at short distances contribute. In the highly concentrated TPY samples many molecules are available at short distances. The initially excited molecule located at the high energy side of the emission band rapidly transfers the excitation to a lower energy molecule. The result is lifetime shortening at the high energy side and lifetime lengthening at the low energy side of the band, together with a slowing of the rising edge of the fluorescence time profile. These effects can be observed both in TPY monomer and TPY aggregate in polycarbonate samples. It is clear however, that the interpretation of the aggregate emission is complicated by the energy transfer.

The transfer of the self-trapped excitation to other sites also explains the striking difference of depolarization found in pump/probe and fluorescence experiments. In the pump/probe experiments no initial depolarization is observed whereas the emission shows rapid depolarization. The pump/probe response consists solely of a transfer to a self-trapped state. The emission in contrast comes from the trapped state after several hops to other sites have taken place. In the hopping process the polarization memory is lost.

In this chapter I have shown that the optical excitation in TPY aggregates is an example of strong coupling of the exciton exciton and phonons. The initially formed state is better described by a new quasi-particle called polaron. The experimental results show that the extended polaron states evolves into a localized state. This can be explained on the basis of self-trapping of self-trapping of the
excitation. The initially formed delocalized state rapidly relaxes, without showing radiative relaxation. The delocalized state is self–trapped with a time–constant of 45 ps. The trapped state has a lifetime of about 2 ns. Further investigations should focus on either smaller aggregates, in order to separate energy–transfer effects, or on different host systems for the TPY–aggregate.

Acknowledgments

I thank Wim van Veenen for the preparation of the aggregate samples. Mr. Meiborg was so kind to spend some time on the phase–contrast microscopy, and produced some excellent photographs. The TPY dye was kindly donated by Océ–van der Grinten N.V.

References