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Comparative study of polychromatic transient absorption measurements for two generations of pyrene-terrylene dendrimers

Jasmeet Kaur

Department of Chemistry, Maharani Lal Kunwari Post Graduate College, Balrampur(U.P.), INDIA

ABSTRACT

The work presents time-resolved polychromatic transient absorption measurements for two generations of pyrene-terrylene dendrimers and was compared with those of three model compounds. The chemicals and solvents were of A.R. grade and used as such. As a solvent for all samples toluene (HPLC, Aldrich) was used without further purification. From the study it can be said that if there are multiple excitations within a molecule there will be most probably a competition between different kinetic processes. It seems that in T1P´$_4$ and in T2P´$_8$ there is a competition between the annihilation process and the energy transfer process. The outcome of this competition cannot be determined quantitatively since this will depend on the conformation of the molecule. A small difference could be related to the relative amount of donor acceptor chromophores and/or to the relative amount of energy transfer rate/singlet-singlet annihilation rates which can change by increasing the generation number.

Keywards: Pyrene-terrylene dendrimers, Fluorescence spectra, Femtosecond polychromatic transient absorption, donor-acceptor chromophores.

INTRODUCTION

Dendrimers[1] are complex, but well defined chemical compounds that can contain selected functions in predetermined sites of their tree-like multi-branched structure and host molecules or ions in their internal cavities. Because of such unique properties, dendrimers are currently attracting increasing attention for a wide range of potential applications in such different fields as medicine, biology, chemistry, physics and engineering. Dendrimers containing photoactive

components[2-15] are particularly interesting since (i) luminescence signals offer a handle to better understand the dendritic structures and superstructures (ii) cooperation among the photoactive components can allow the dendrimer to perform useful functions such as light harvesting, (iii) changes in the photophysical properties can be exploited for sensing purposes with signal amplification, and (iv) photochemical reactions can change the structure and other properties of dendrimers.

Ultrafast kinetic processes and single molecule properties of polyphenylene dendrimers containing peryleneimide chromophores at the rim were investigated in detail previously[16-28]. Recently, different generations of dendrimers containing a terrylenediimide acceptor chromophore in the center and decorated with pyrenylimide chromophores at the rim have been investigated by single molecule and time resolved spectroscopy[29]. Energy transfer processes in dendrimers are of current interest to several spectroscopy groups[30-32]. However, most of the investigated dendrimers are based on a flexible scaffold[33-36] where conformational mobility often leads to undesired chromophore interactions such as aggregation, excimer formation and dye self-quenching[37, 38].

In this paper, I present time resolved polychromatic transient absorption measurements for two generations of pyrene-terrylene dendrimers and were compared with those of three model compounds.

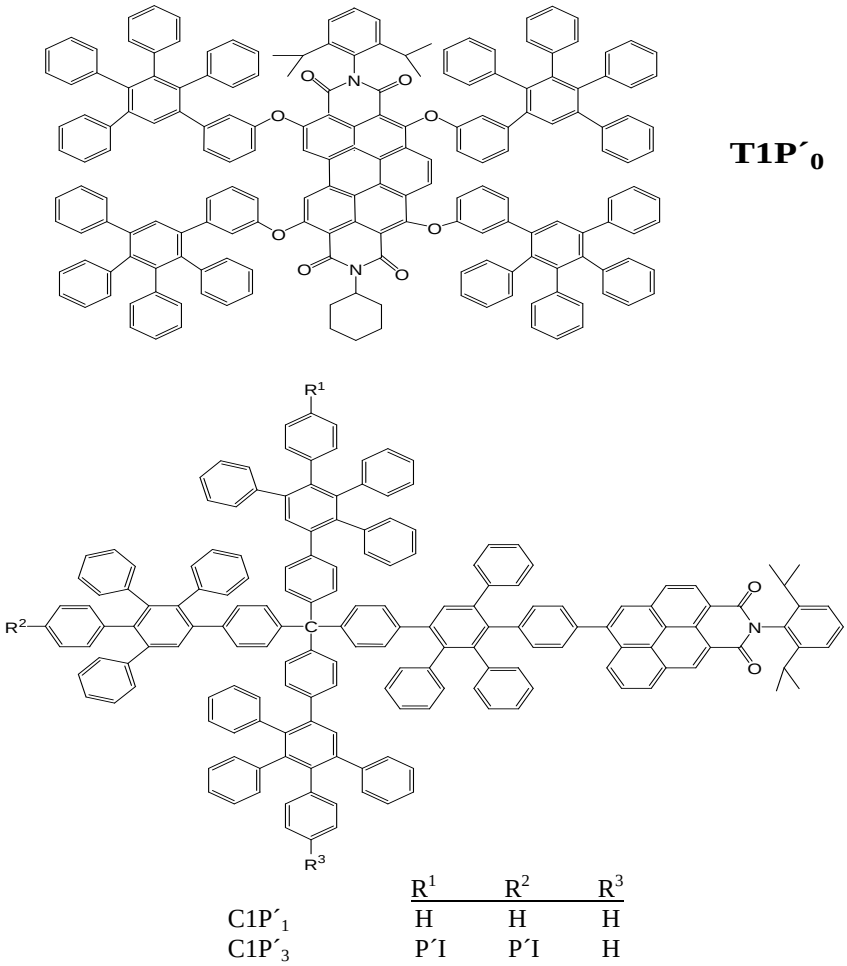
EXPERIMENTAL SECTION

The chemicals and solvents were of A.R.grade and used as such. As a solvent for all samples toluene (HPLC, Aldrich) was used without further purification. Five different compounds have been investigated, the molecular structures of which are shown in the above Chart 1(a) and 1(b). Two generations of pyrenylimide-terrylenediimide chromophore in the core, polyphenyl side arms and dependent on the generation number four ($T1P'_4$) or eight ($T2P'_8$) pyrenylimide chromophores at the rim.

An acronym of the type X_nY_m is used where X denotes the core type of the sample (*e.g.* terylenediimide), n = 0, 1, 2, 3 the generation of the dendrimer attached to it and Y_m the type and number of chromophores attached to the rim of the molecules (P'_3, *e.g.*, denotes three pyrenylimides). Besides these two dendrimers, three model compounds were also studied. Two model compounds were dendrimers with an sp^3-carbon atom core and the same polyphenyl side arms containing pyrenylimide chromophores. They had respectively one ($C1P'_1$), and three ($C1P'_3$) pyrenylimide chromophores connected to the rim. The third model compound ($T1P'_0$) was the same molecule as the first generation dendrimer but without the four pyrenylimide chromophores connected to it. The synthesis of these molecules has been reported previously[39, 40].

2.2. Instrumentation

2.2.1. Steady state fluorescence spectra: The ground state absorption spectra were recorded on a Lambda 40 spectrophotometer (Perkin Elmer). The steady state fluorescence spectra were recorded with a SPEX fluorimeter.



	R^1	R^2	R^3
C1P´$_1$	H	H	H
C1P´$_3$	P´I	P´I	H

Chart 1(a): The first generation terrylenediimide core model compound T1P´$_0$ and two first generation carbon core model compounds C1P´$_x$ with one (x = 1) and three (x = 3) pyrenylimide chromophores attached.

2.2.2. Femtosecond polychromatic transient absorption measurements: The amplified femtosecond double optical parametric amplifier (OPA) laser system has been described in detail previously[41]. In short, an $NdYVO_4$-pumped titanium Sapphire laser *(Millenia and Tsunami, Spectra Physics)* was regeneratively amplified giving pulses of 1mJ at 800 nm, *ca.* 120 fs pulse length and 1 kHz repetition rate. One half of this energy was used to pump an optical parametric amplifier (OPA-800, Spectra-Physics). The output wavelength range of the OPA is extended by harmonic generation using one or two barium borate (BBO) crystals, thus making a range of 300nm to 900nm accessible.

While one half of the output of the regenerative amplifier was used in one OPA to generate the excitation pulse of the appropriate wavelength the other half served for generation of a fs white light continuum for probing the absorption changes. This fs white light continuum was generated in a 1mm sapphire plate. The actual detection was done by a 256-lines CCD camera (EEV 30, Princeton Instruments) mounted at the exit of a 30 cm spectrograph (SP 300i, Acton Research).

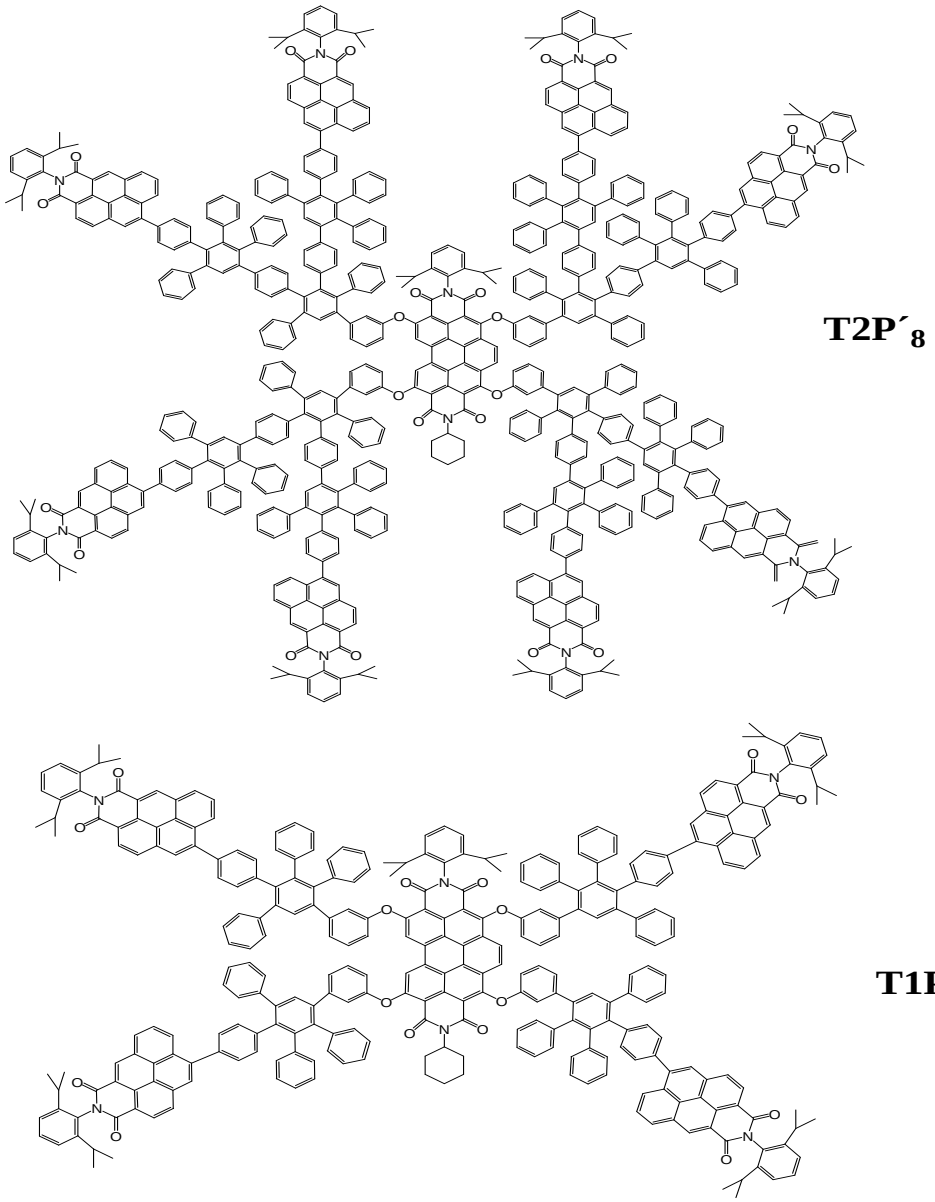


Chart 1(b): Molecular structures of the first and second generation dendrimers T1P´$_4$ and T2P´$_8$ respectively.

The transient signal of the samples was derived from a sequence of measurements: at one delay position, four spectra were recorded with the CCD camera. By selectively blocking the pump and/or white light beam, the absorbance was determined as:

$$A = \log (S_A - S_D)/ (S_{EA} - S_E) \qquad (1)$$

where S_E denotes the spectrum recorded while only the excitation pulse was interacting with the sample. This gave the correction for the fluorescence. S_{EA} was the spectrum while both the excitation pulse and the probe pulse were present at the sample position. S_A was the spectrum while only the probing white light was present and S_D was the spectrum while both the excitation pulse and the probe pulse were blocked before reaching the sample. At a fixed delay position, this

set of measurements was repeated and averaged to improve the signal to noise ration. This was done for 512 equally distant delay positions in time windows of 5 ps, 50 ps, 400 ps and 1500 ps.

To investigate possible multiphotonic processes, the intensity of the exciting laser beam was decreased by a factor of about ten in an additional series of measurements. These measurements were performed at two different detection wavelengths: 525 nm and 645 nm. To improve the signal to noise ratio, the probing white light continuum was passed through a monochromator and detected using a photomultiplier tube (R 1527p, Hamamatsu). The electrical signal from the multiplier tube was gated by SR 520 Standard Research systems and detected by SR 830 Stanford Research Systems. For all measurements performed here, the excitation wavelength was kept constant at 490 nm with the only exception of the measurements of $T1P'_0$ where 620 nm was employed. By appropriate filtering the probing wavelength range was reduced to 445 nm-735 nm. Besides this, all other experimental conditions were kept constant: all measurements were performed at room temperature in 1mm optical path length cuvettes under magic angle polarization conditions. All compounds were dissolved in toluene at a concentration that yielded absorption of *ca.* 0.3 per mm at the excitation wavelength. By measuring the cross correlation between 490 nm excitation light and 595 nm probe light (derived from the continuum using appropriate filters) the time resolution of this setup was determined to be about 278 fs.

RESULTS AND DISCUSSION

3.1. Steady state spectroscopy:

The steady state absorption and fluorescence spectra of all investigated compounds are shown in Figure 1. The absorption spectrum of the dendrimers is a superposition of the absorption spectra of the model compounds. The only difference between the absorption spectra of the two generations is the ratio of the pyrenylimide to terrylenediimide absorbance, which is explained by the relative amount of both chromophores which is 4:1 in the first generation and 8:1 in the second generation respectively.

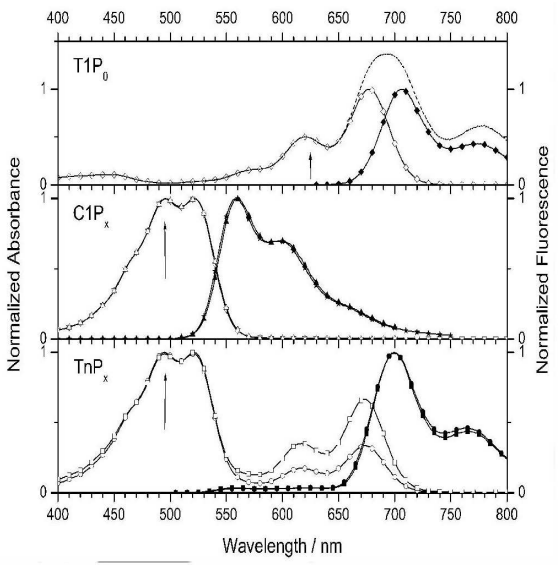


Figure 1: Steady state absorption and emission spectra of the investigated compounds. *Top*: $T1P'_0$ (♦) and the calculated transient spectrum as a sum of the contribution of ground state bleaching and stimulated emission (-), *Middle*: $C1P'_1$(6) and $C1P'_3$ (7), *Bottom*: $T1P'_4$ (□) and $T2P'_8$ (.).

Since the presence of both chromophores within the same molecule does not lead to the appearance of a new band or to differences in the ground state absorption spectrum, it can be concluded that there are no interactions between the chromophores in the ground state. However, when the pyrenylimide chromophores are excited at 490 nm within these dendrimers, the fluorescence of these pyrenylimide chromophores is almost completely quenched compared to the model compound C1P´$_1$. Instead, the fluorescence of the dendrimers at longer wavelengths almost completely resembles the emission spectrum of the model compound T1P´$_0$. This feature is a strong indication that within these dendrimers the excitation energy is efficiently transferred from the pyrenylimide chromophore to the terrylenediimide chromophore.

3.2. Time resolved polychromatic transient absorption measurements:

3.2.1. Model compound T1P´$_0$: Transient absorption spectra of T1P´$_0$ were obtained at an excitation wavelength of 620 nm. The results are shown in Figure 2, top left. At positive delay times the signal is decaying on a nanosecond time scale and it has a negative value throughout the complete spectral range except between 445 nm and 545 nm where the signal is positive.

For the interpretation of these spectra and their positive or negative values it must be considered that in general there are three contributions to a pump-probe signal: excited state absorption (positive) and both stimulated emission and ground state bleaching (both negative). From previous studies,[31] it is known that T1P´$_0$ has a fluorescence quantum yield of almost unity and a fluorescence lifetime of 3.0ns. Since the excited state absorption observed decays on a nanosecond time scale it is attributed to an S_1-S_n absorption of the terrylenediimide chromophore.

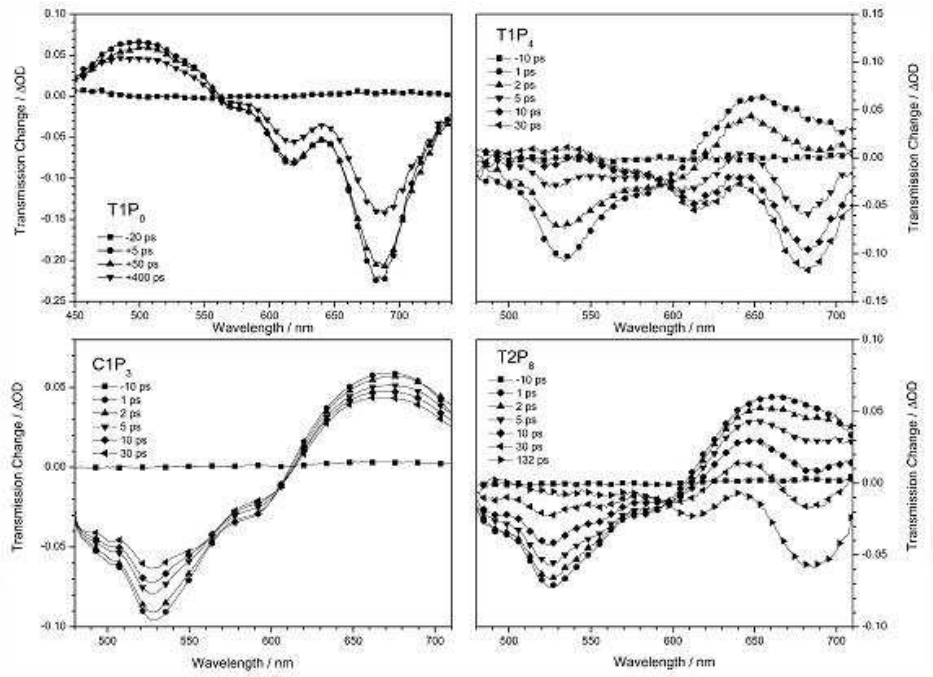


Figure 2: Transient absorption spectra of the model compounds T1P´$_0$ (*top left*) and C1P´$_3$ *(bottom left)* and the dendrimers T1P´$_4$ (*top right*) and T2P´$_8$ (*bottom right*) at different delay times.

When the ground state absorption spectrum of this model compound is compared with its transient spectrum after 50 ps it is observed that in the former two absorption maxima are situated at 615 nm and 670 nm with an intensity ratio of 1:2. In the latter, a band at 615 nm is found, however the second band is 8nm red shifted and the intensity ratio between the two bands has changed to 1:3.

These differences can be explained in the following manner. The steady state spectra of T1P´$_0$ (Figure 1) shows that the ground state absorption ends at 735 nm, whereas the fluorescence spectrum covers the spectral region from 645 nm to beyond 845 nm. It is known from previous experiments that there is a very small spectral shift of the fluorescence spectrum within about 5ps after excitation. This means that if there is stimulated emission after 20 ps, it can only contribute to the signal starting from 645 nm. As a result, the negative signal in the spectral region between 525 nm and 645 nm is fully dominated by ground state bleaching. Hence, the transient absorption band at 615 nm perfectly matches the ground state absorption band at 615 nm.

Since at 615 nm only ground state bleaching is contributing to the transient signal and the molar absorption coefficient, ε, of the ground state absorption is known, it is possible to calculate the concentration of the excited states. Based on this information an ε-value of the S_1-S_n absorption band of the central terrylenediimide can be calculated to be about 33000 $Lmol^{-1}$ at 495 nm, the maximum of the S_1-S_n absorption band in toluene. At the red edge of the transient spectrum of 20 ps, (*e.g.* at 725 nm), the intensity of the negative transient signal is comparatively larger as compared to the one at 615 nm. However, the ground state absorption at 725 nm is almost completely non-existent as compared to that at 615 nm. Thus a considerable amount of stimulated emission must contribute to the transient signal at 725 nm. This stimulated emission is contributing to the signal in the complete fluorescence range.

If one takes the two negative contributions (ground state bleaching and stimulated emission) into account it is clear that the transient spectrum beyond 645 nm is thus a sum of two transient spectra, one of the ground state bleaching and one of the stimulated emission. It is possible to calculate the theoretical negative spectrum with the information from the steady state absorption and the fluorescence spectra. For this, one has to account for the fact that the Einstein coefficient for stimulated emission scales with the Einstein coefficient for spontaneous emission corrected with the third power of the frequency and that the integral of the transition probability for ground state absorption and stimulated emission has to be the same.

It is also possible to get kinetic information by observing the intensity of the transient absorption signal as a function of time at fixed wavelength. It is seen that the intensity drops on a nanosecond time scale. However, from 650 nm to 730 nm two additional processes can be determined with time constants in the order of 8 ps and 98 ps with amplitudes which both go negative, starting from zero at 640 nm, crossing the zero line to positive and decreasing again. The presence of these kinetic processes and their wavelength dependence was discussed earlier when this model compound was investigated with the fluorescence up conversion and single photon timing technique. A vibrational relaxation process with a time constant of 5ps and a structural relaxation process of the central terrylenediimide chromophore were detected with a time constant of 115 ps.

3.2.2. Model compound C1P´$_1$: For the measurement of the transient absorption spectra of C1P´$_1$, the excitation wavelength was set to 490nm. The results are shown in Figure 3. At positive times two different parts in the transient spectrum can be observed, a negative signal reaches from 475nm to 595nm with a maximum at about 535nm and second, a positive signal beyond 595nm with a maximum at approximately 650nm. Both features can be seen instantaneously after excitation and decay on a nanosecond time scale.

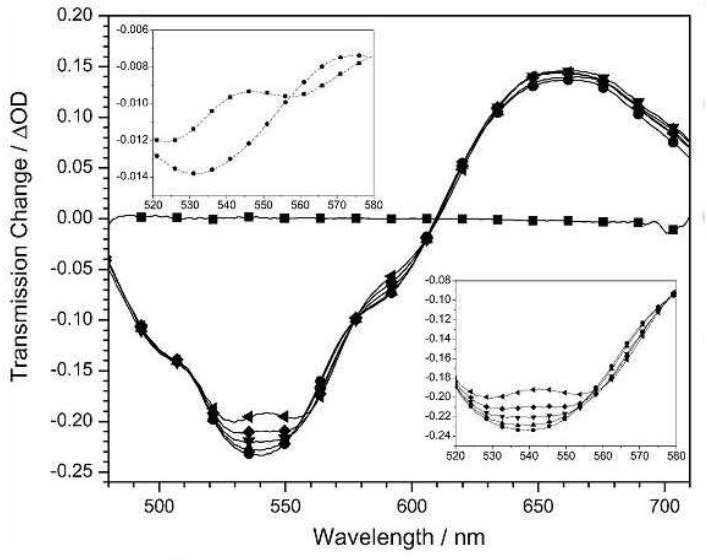


Figure 3: Transient absorption spectra of the model compound C1P´$_1$ at different delay times: 10 ps, ( ), 1 ps (•), 2 ps (Δ), 5 ps (∇), 10 ps (ɜ) and 30 ps ( ). *Insert top left*: detailed display of the 520 nm-580 nm region of the calculated (-) transient spectra from the normal ( ) and the 5 nm blue shifted (•) fluorescence spectra. *Insert bottom right*: detailed display of the 520 nm to 580nm region.

Since the signal in the transient absorption spectrum above 595 nm is positive, it can be attributed to an excited state absorption. From previous studies it is known that C1P´$_1$ has a fluorescence quantum yield of almost unity and a fluorescence lifetime of 4.0 ns, thus the excited state absorption found in the measurements shown here can be attributed to a S_1-S_n absorption within the pyrenylimide chromophore.

From the fact that the steady state absorption spectrum ends at 550 nm and the fluorescence spectrum extends from 505 nm to 745 nm, the negative signal in the transient spectrum cannot completely be attributed to ground state bleaching. It seems that ground state bleaching dominates the signal between 475 nm and 505 nm. From 505 nm both ground state bleaching and stimulated emission are responsible for the negative signal whereas between 555 nm and 595 nm stimulated emission dominates. However since the steady state fluorescence spectrum extends upto 745 nm it must be considered that there is also a contribution of stimulated emission beyond 555 nm.

The maximum of the negative signal is situated around 535 nm. However, this is neither the maximum of the ground state absorption band nor the maximum of the steady state fluorescence. This can be rationalized by following the same arguments as stated for the model compound T1P´$_0$. The spectrum for model compound C1P´$_1$ is as shown in Figure 4.

The differences between this calculated spectrum and the actual measured spectrum can be attributed to excited state absorption. It is possible to calculate it by subtracting the calculated theoretical negative spectrum from the actual measured spectrum. The result of this calculation is shown in Figure 4. In the transient absorption spectrum two maxima can be seen, one at 475nm and another at 643nm.

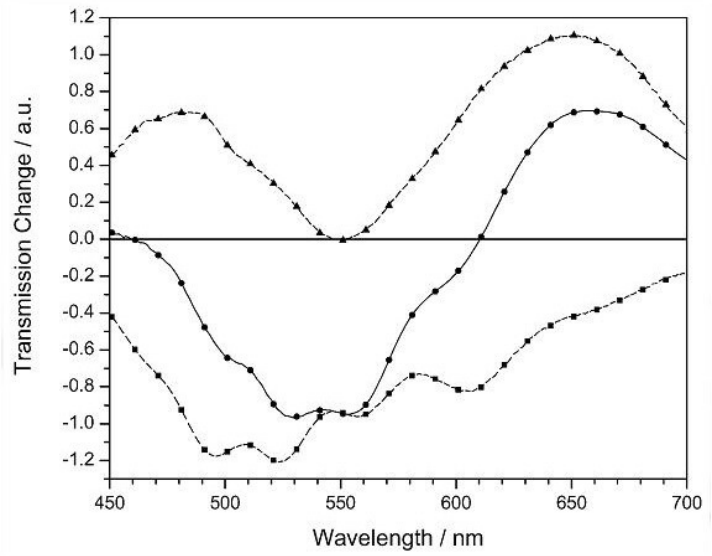


Figure 4: Full spectral region display of the calculated (-) theoretical negative ( ) transient absorption spectrum and the measured (●) transient absorption spectrum after 28 ps of the model compound C1P´$_1$. (Δ) is the calculated (-) S_1-S_n transient absorption spectrum of this model compound.

A kinetic analysis of the transient absorption intensities in function of delay time for different wavelengths reveals an additional picosecond relaxation process. This process can be seen in the inset of Figure 3. It seems that the band with a maximum at 535 nm becomes broader and after 28 ps shows two distinctive maxima, one at 525 nm and one at 550 nm. As reported earlier this relaxation leads to a small red shift of the fluorescence spectrum of about 5nm within 8 ps.

3.2.3. Model compound C1P´$_3$: Another series of experiments was performed on C1P´$_3$, which contains three pyrenylimides at the rim. Since the chromophore is the same, also for these measurements the excitation wavelength was set to 490 nm. Comparing the transient absorption spectra of C1P´$_3$ with C1P´$_1$, one can see that the general shape is identical thus the attribution of the signals in C1P´$_3$ can be the same as in C1P´$_1$.

However, the temporal evolution of the transient spectra of C1P´$_3$ and C1P´$_1$ is grossly different. It seems that the signal in the multichromophoric dendrimer decays faster when compared to C1P´$_1$. This feature is demonstrated in Figure 5. In accordance with previous findings, this feature is attributed to a singlet-singlet annihilation process. This is confirmed by an additional series of experiments performed at 525 nm and 645 nm in which the only varied parameter was the excitation intensity, which was decreased by a factor of four. The results of these measurements are shown in Figure 6. The decays for C1P´$_1$ are independent of the excitation intensity in contrast to those of C1P´$_3$ which strongly supports annihilation process. Thus at 525 nm, the annihilation process shows up by removing excited pyrenylimide chromophores from the excited state, leading to a decrease in stimulated emission from the excited state and a decrease in ground

state bleaching. This singlet-singlet annihilation process is the additional decay channel in the transient absorption measurements of C1P´$_3$ compared to C1P´$_1$.

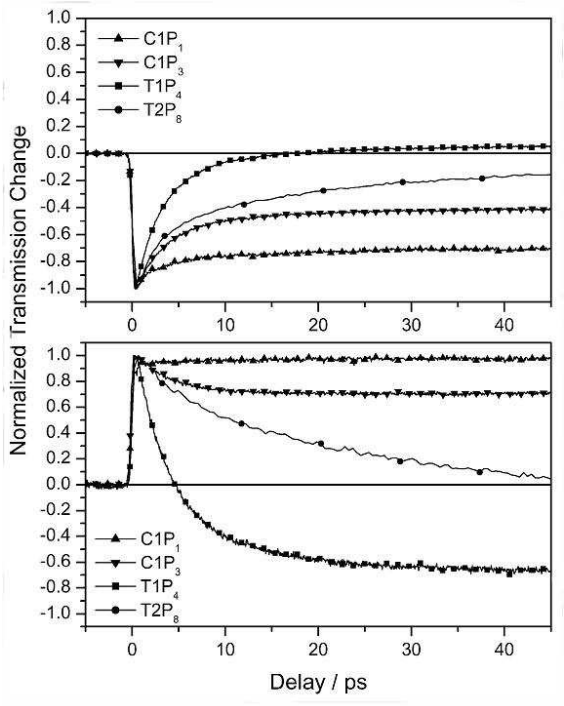


Figure 5: Plot of the transient absorption signal as a function of time recorded at 525nm (*top*) and 645 nm (*bottom*) for C1P´$_1$ (Δ), C1P´$_3$ (∇), T1P´$_4$ ( ) and T2P´$_8$ (•) upon excitation at 490 nm.

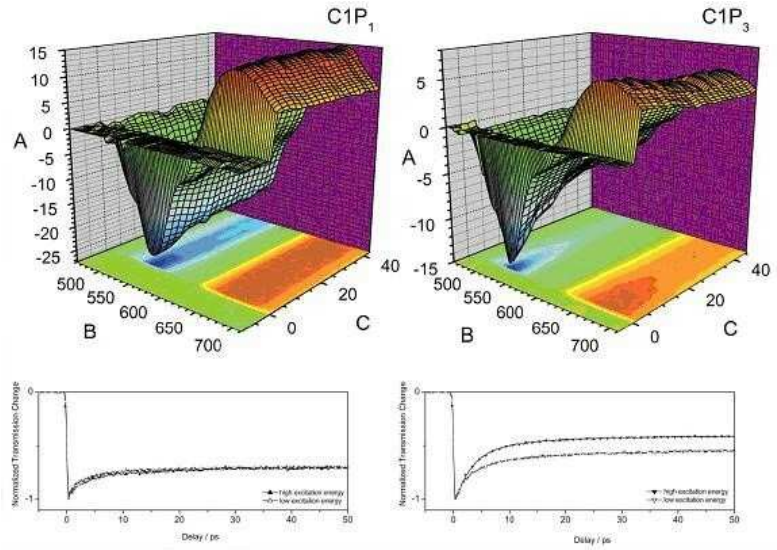


Figure 6: Three dimensional display of the transient absorption intensity (6OD*10^{-2}, A) as a function of wavelength (nm, B), and time (ps, C) for C1P´$_1$ (*top, left*) and C1P´$_3$ (*top, right*). Excitation energy dependent plots of the transient absorption signals as a function of time at high (Δ,∇) and low (Δ,∇) excitation energy recorded at 525 nm for C1P´$_1$ (*bottom, left*) and C1P´$_3$ (*bottom, right*) upon excitation at 490 nm.

3.2.4. First generation dendrimer T1P´$_4$: For the transient absorption spectra of T1P´$_4$ the excitation wavelength was set to 490 nm. The transient spectrum is completely identical to that

found for the model compound C1P´$_1$. At time delays longer than 28 ps the transient spectrum of the dendrimer is exactly the same as T1P´$_0$. This time evolution of the transient spectrum can be explained as followed. At time origin, the 490 nm excitation pulse promotes a pyrenylimide chromophore from its ground into the S_1 state. This excited pyrenylimide chromophore transfers its energy to the central terrylenediimide chromophore in its ground state yielding a pyrenylimide chromophore in the ground state and a terrylenediimide chromophore promoted from the ground state to the S_1 state which is detected as a bleaching signal in the transient absorption spectrum. A temporal view of this dataset is shown in Figure 7, bottom, for a detection wavelength of 645 nm which is the maximum of the positive signal in the transient spectrum of the model compound C1P´$_1$. The decay times which were determined were 2 ps, 28 ps and a nanosecond component. This is in accordance with previously reported fluorescence up- conversion data.

3.2.5. Second generation dendrimer T2P´$_8$: The results for the second generation dendrimer are shown in Figure 2, bottom right. The transient spectrum immediately after excitation perfectly resembles that of C1P´$_1$. During the following 68 ps it temporally evolves into a spectrum which perfectly coincides with the transient spectrum of T1P´$_0$. Also in this case, the energy transfer process occurring between the excited pyrenylimide donors and the terrylenediimide acceptor is responsible for the kinetics albeit at a slower rate constant as can be seen in Figure 7, top. This decrease in energy transfer rate was also reported before using fluorescence and upconversion measurements. Within the framework of the Forster formulation an effective interaction radius R_0 can be calculated from the steady state spectra and the fluorescence quantum yield of the donor chromophore (ϕ_D) as 5.7 nm assuming κ^2 =2/3. The donor-acceptor center-to-center distances within the dendrimers depend on the conformation of the dendritic arms. From molecular modelling representative values of 2.1 nm for T1P´$_4$ and 2.9 nm for T2P´$_8$ are obtained which are well within the Forster radius, indicating the presence of an efficient energy transfer process. From these donor acceptor distances and the Forster radius R_0, inversed rate constants of energy transfer of 12 ps and 82 ps are calculated for the first and second generation, respectively.

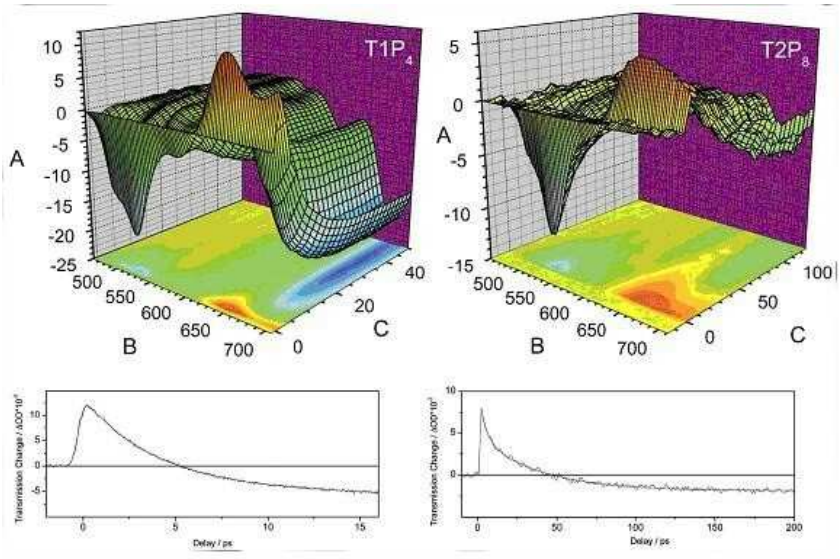


Figure 7: Three dimensional display of the transient abosorption intensity (6OD*10^{-2}, A) as a function of wavelength (nm, B), and time (ps, C) for T1P´$_4$ (*top, left*) and T2P´$_8$ (*top, right*) upon excitation at 490 nm. Plot of the transient absorption signals as a function of time recorded at 645 nm for the dendrimers T1P´$_4$ (*bottom, left*) and T2P´$_8$ (*bottom, right*) upon excitation at 490 nm.

Another finding is the difference between the transient spectra of T1P´$_4$ and T2P´$_8$ after completion of the energy transfer. The transient spectrum of T1P´$_4$ completely resembles the transient spectrum of T1P´$_0$ including the small positive contribution below 555 nm. In contrast, the transient spectrum of T2P´$_8$ does not become positive in this spectral region. To investigate this difference, excitation energy dependent measurements were performed at a detection wavelength of 525 nm. The excitation intensity was decreased by a factor of about five. The results of these measurements are shown in Figure 8.

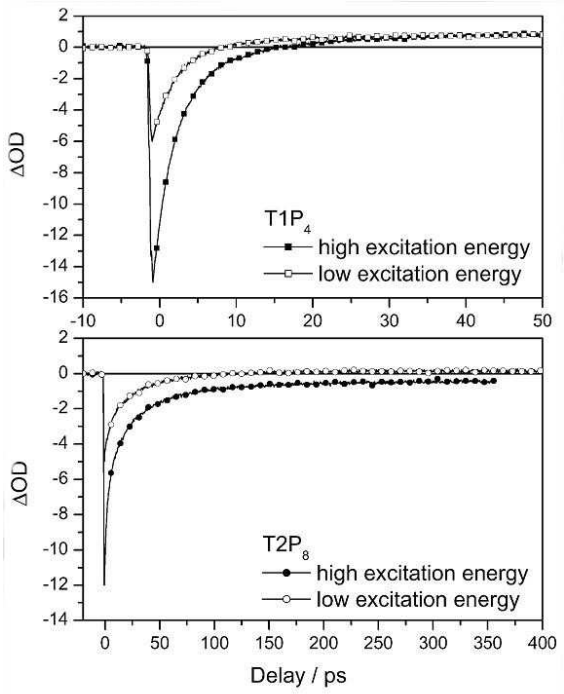


Figure 8: Excitation energy dependent plot of the transient absorption signals (6OD*10^{-2}) as a function of time at high (. , •) and low (□, .) excitation energy recorded at 525 nm for the dedrimers T1P´$_4$ (*top*) and T2P´$_8$ (*bottom*) upon excitation at 490 nm.

3.3. Energy transfer and singlet-singlet annihilation:

3.3.1. Energy transfer rate is faster than singlet- singlet annihilation rate: In this case, if more than one pyrenylimide chromophore is excited at the same time, one of them will transfer its energy to the central terrylenediimide chromophore leading to one excited terrylenediimide chromophore and (atleast) one excited pyrenylimide chromophore. The latter cannot transfer its energy anymore ("closed" ET-system) before the former has returned to its ground state. Thus, if there are three or more pyrenylimides excited, a relatively slower annihilation process would be going on in parallel with a relatively faster energy transfer process.

3.3.2. Singlet-singlet annihilation rate is faster than energy transfer rate: In such a case, if more than one pyrenylimide chromophore is excited initially the annihilation process will occur, leading to a situation with only one excited pyrenylimide. Then this single excited pyrenylimide chromophore transfers its energy to the central terrylenediimide acceptor leading to a molecule with an excited terrylenediimide chromophore only. In order to calculate the amount of photons available per molecule in the illuminated area of the laser spot, some parameters have been considered. The diameter of the laser beam at the position of the sample was determined to be

about 78 μm. Using this and the concentration of the molecules, it is possible to calculate the amount of molecules in the excitation spot volume of the sample. Together with this information and the excitation energy measured at the sample position, 1.3 photons are estimated to be available for each chromophore in the illuminated volume. Thus, it can be concluded that there is a possibility of exciting more than one chromophore with one molecule.

Another consideration which has to be made is the dependence of the rate of energy transfer and the rate of singlet-singlet annihilation upon the distance and the orientation of the chromophores involved. It is known that the rate of energy transfer within the dendrimers is related to the conformation of the side arms which are connected to the central terrylenediimide chromophore which result in a spread of energy transfer rate constants. Rate constants for energy transfer were reported to be 2 ps and 23 ps in T1P´$_4$ and 20 ps and 66 ps in T2P´$_8$. There is also a spread on the rate constant of singlet-singlet annihilation between the pyrenylimide chromophores at the periphery of the molecule. This will be more pronounced, especially in the case of T2P´$_8$ since in this molecule two pyrenylimide chromophores are connected to the same side arm which can give a much smaller distance than between pyrenylimide chromophores on side arms across the molecule. This phenomenon was reported previously where rate constants of singlet-singlet annihilation of 3 ps and 38 ps were obtained. The reported average distance between pyrenylimide chromophores was estimated to be 3.7 nm. Molecular modelling also indicated a spread in intramolecular pyrenylimide distances between 0.4 nm and 2nm for T1P´$_4$ and between 0.4 nm and 3.4 nm for T2P´$_8$.

3.4. Second generation dendrimer T2P´$_8$ at 525 nm:

For T2P´$_8$ the decays measured at 525 nm and two different excitation energies are shown in Figure 8, bottom. At high excitation energies, the signal remains negative at all times, whereas at low excitation energies the signal becomes positive after approximately 118 ps. At 525 nm, the measured signal is comprised of stimulated emission of pyrenylimides (negative), ground state bleaching of pyrenylimides (negative) and excited state absorption of the terrylenediimide (positive). If annihilation is faster than energy transfer in this molecule, the resulting state after energy transfer would comprise of only one excited terrylenediimide chromophore yielding a positive signal after energy transfer, as discussed above. These expectations are fulfilled by the results from low excitation energy measurements (Figure 8, bottom). However, at high excitation energies, the signal after energy transfer is negative. Thus, it can be concluded that there are still excited pyrenylimides present (besides the excited terrylenediimide) after the energy transfer process is completed.

3.5. First generation dendrimer T1P´$_4$ at 525 nm:

The contributions of the signal are the same as within the second generation dendrimer, thus a negative signal from the pyrenylimides and positive signal of the terrylenediimides. At high excitation energies, the transient signal at time zero is much larger than at low excitation energies as shown in Figure 8 top.

3.6. Comparison of T1P´$_4$ with T2P´$_8$:

After aboul 28 ps the signal in T1P´$_4$ is the same as at low excitation energies which is in contrast to T2P´$_8$. This means that the pyrenylimide chromophores which were excited additionally in T1P´$_4$ do not contribute to the signal after 28 ps, thus they do not transfer their energy to the

terrylenediimide. A possible reason could be that they lose their energy by singlet-singlet annihilation before or in competition with the energy transfer to the terrylenediimide.

The excitation intensity dependent measurements of T2P′$_8$ differ also by the fact that at high excitation energies, the signal of the T2P′$_8$ is negative while this is positive for T1P′$_4$. A fact to consider is that in T1P′$_4$, the relative amount of pyrenylimides to terrylenediimides is 4 to 1 while it is 8 to 1 in T2P′$_8$. The solutions of the two dendrimer generations were prepared to have an identical optical desity of about 0.4 at the excitation wavelength of 490 nm. This means that the same number of pyrenylimides is excited in both samples but the ratio of pyrenylimide: terrylenediimide is doubled in the second generation. This results in a larger dependence of the kinetics on the excitation intensity.

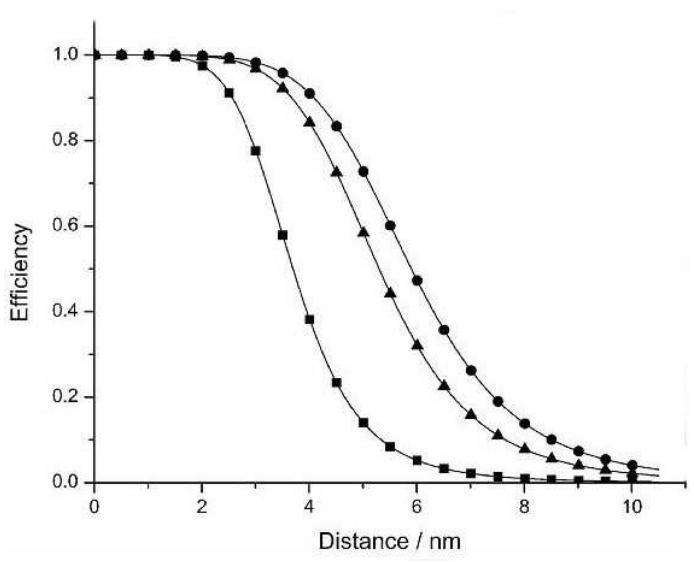


Figure 9: Plot of the efficiency of energy transfer as a function of interchromophoric distance for energy transfer between an S_1 state of pyrenylimide and an S_0 of terrylenediimide (•), annihilation between two S_1 states of pyrenylimide (Δ) and annihilation between an S_1 state of pyrenylimide and an S_1 state of terrylenediimide ( ).

Another explanation for the difference between T1P′$_4$ and T2P′$_8$ could be another possible excited state process which was not discussed earlier. The S_1-S_n absorption band of T1P′$_0$ has a maximum at 500 nm and it ranges to 550 nm. There is a small overlap between the fluorescence spectrum of the pyrenylimide chromophore and the S_1-S_n absorption of the terrylenediimide, thus excitation transfer between an exited state of pyrenylimide and an excited state of terrylenediimide cannot be excluded. This process will lead to pyrenylimide chromophores in the ground state and a terrylenediimide chromophore in the higher excited state (S_2). Since the spectrum and the ε-value of the S_1-S_n absorption band is known, it is possible to calculate an overlap integral and an R_0 value in the framework of Forster energy transfer. This calculation leads to an R_0 value of 3.5 nm for singlet-singlet annihilation between an S_1 state of pyrenylimide and an S_1 state of terrylenediimide assuming a random orientation between the chromophores involved (κ^2=2/3). For singlet-singlet annihilation between two excited pyrenylimide chromophores, an R_0 value of 5.1 nm is reported.[30] In Figure 9, the efficiency of energy transfer, which is defined as $E = R_0^6 / (R_0^6 + R^6)$ as a function of interchromophoric distance is displayed for three different processes which are: energy transfer between an S_1 state of pyrenylimide and

an S_0 state of terrylenediimide (eq.2) (R_0=5.7 nm), annihilation between two S_1 state of pyrenylimides (eq.3) (R_0=5.1 nm) and annihilation between an S_1 state of pyrenylimide and an S_1 state of terrylenediimide (eq.4) (R_0=3.5nm)

$$S^0_{P'I} + S^0_{TDI} \rightarrow S^0_{P'I} + S^0_{TDI} \quad (2)$$

$$S^0_{P'I} + S^1_{P'I} \rightarrow S^0_{P'I} + S^1_{P'I} \quad (3)$$

$$S^1_{P'I} + S^1_{TDI} \rightarrow S^0_{P'I} + S^1_{TDI} \quad (4)$$

It can be seen that for a given distance, the process of energy transfer between a pyrenylimide chromophore and a terrylenediimide chromophore always has the highest efficiency. The average distance between the central terrylenediimide chromophore and the pyrenylimide chromophores at the rim changes, from 2.1nm in the first generation to 2.9 nm in the second generation. This change in distance is somewhat responsible for the difference between the two generations in the intensity dependent measurements since the probability for annihilation between an S_1 state of pyrenylimide and an S_1 state of terrylenediimide decreases from 0.92 to 0.72.

CONCLUSION

The study concluded that if there are multiple excitations within a molecule there will be most probably a competition between different kinetic processes. It seems that in T1P´$_4$ and in T2P´$_8$ there is a competition between the annihilation process and the energy transfer process. The outcome of this competition cannot be determined quantitatively since this will depend on the conformation of the molecule. A small difference could be related to the relative amount of donor acceptor chromophores and/or to the relative amount of energy transfer rate/singlet-singlet annihilation rates which can change by increasing the generation number.

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