Generation dependent singlet–singlet annihilation within multichromophoric dendrimers studied by polychromatic transient absorption †

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Intramolecular kinetic processes in a series of shape-persistent *meta*- and *para*-substituted polyphenylene dendrimers bearing different peryleneimide chromophores at the rim have been investigated using time-resolved polychromatic transient absorption measurements. The influence of the generation number and different substitution patterns upon these processes was revealed by comparing different compounds. In particular, in multichromophoric systems a singlet–singlet annihilation process was detected. The corresponding time constant was dependent on the generation number.

Introduction

Dendrimers are highly branched macromolecular systems whose structure can be defined on a molecular level^{1,2} and as such have been attracting a lot of attention not only from the synthetic point of view,³ but also from the point of view of their physical and chemical properties.^{4–21} Within our research group, different types of macromolecular systems have previously been investigated both at the single molecule and at the ensemble level.^{22–38} Recently, two series of first-generation dendrimers with an identical rigid central sp³-carbon core and substituted with peryleneimide chromophores at the *meta* and *para* position of the outer phenyl ring have been investigated in detail.^{22–25} Besides these, also *para*-substituted second-generation dendrimers were studied.²⁶ In addition to relaxation processes, a singlet–singlet annihilation process could be attributed in both generations of the dendrimers. This type of process, which can occur in multichromophoric systems, has been observed in many different compounds. Under appropriate conditions, two excitons existing at the same time can interact resulting in a first excited state and a ground state.³⁹ The efficiency of this two-photon process is strongly dependent on the excitation flux and, from the molecular system point of view, on the type, the number, the distance and the relative orientation of the chromophores involved. Thus, a detailed study of the singlet–singlet annihilation kinetics can also be used to investigate structural properties of the multichromophoric system. This has successfully been applied to various different systems such as J-aggregates,⁴⁰ pigment protein complexes^{41–45} polymers^{46,47} and others⁴⁸ and analyzed in the context of several theoretical approaches.^{39,41,49}

Whereas in all previous studies of the photophysical properties of the dendrimers time-resolved fluorescence techniques such as single photon timing (SPT) and fluorescence upconversion have been employed, in this publication, the complementary technique of polychromatic transient absorption is used to validate the presence of a generation dependent annihilation process and to evaluate the influence of generation number and the substitution pattern on the transient absorption

properties of these dendrimers. In general, this research fits into an in-depth investigation of fundamental photophysical processes going on in multichromophoric systems, in particular dendritic systems based on a rigid scaffold and having various chromophores at the rim.

Experimental

In this study, a total of six different compounds have been investigated (for the molecular structures see Scheme 1), which can be divided in three classes. First of all there is a class of *first*-generation dendrimers in which the peryleneimide chromophores are attached in the *meta* position to the outer phenyl ring. In a second class of *first*-generation dendrimers the peryleneimide chromophores are attached in the *para*-position to the outer phenyl ring. Finally, a third class consists of *second*-generation dendrimers in which the peryleneimide chromophores are also attached in the *para* position to the outer phenyl ring. An acronym of the type *a*-X_{*n*}Y_{*m*} will be used throughout this paper, where *a* denotes the way of attachment of the peryleneimide chromophore to the outer phenyl ring (*para/meta*), X denotes the core type of the sample (*e.g.* C: carbon), *n* = 0, 1, 2, the generation number of the dendrimer attached to it, and Y_{*m*} the type and number of chromophores at the rim of the molecules (P₃, *e.g.*, denoting three peryleneimides). The acronyms of the six studied compounds are thus *m*-C1P₁ and *m*-C1P₃ for the first class of dendrimers, *p*-C1P₁ and *p*-C1P₃ for the second class of dendrimers and *p*-C2P₁ and *p*-C2P₄ for the third class of dendrimers. The synthesis of these molecules has been reported before in detail.⁵⁰ The ground-state absorption spectra recorded by a spectrophotometer (Lambda 40 Perkin Elmer), and steady-state fluorescence spectra recorded with a fluorimeter (Spex) are shown in Fig. 1.

Femtosecond polychromatic transient absorption measurements

The amplified femtosecond laser system has been described in detail previously.⁵¹ In brief, a Nd:YVO₄-pumped Titanium Sapphire laser (Millenia and Tsunami, Spectra Physics) was regeneratively amplified giving pulses of 1 mJ at 800 nm, *ca.* 120 fs pulse length at a 1 kHz repetition rate. One half of this energy was used to pump an optical parametric amplifier

† This paper is dedicated to Professor Fred Lewis on the event of his 60th birthday.

Scheme 1 Molecular structures of the six investigated compounds: the first-generation *para*-substituted dendrimers *p*-C1P₁ and *p*-C1P₃, the first-generation *meta*-substituted dendrimers *m*-C1P₁ and *m*-C1P₃ and the second-generation *para*-substituted dendrimers *p*-C2P₁ and *p*-C2P₄.

Fig. 1 Steady-state absorption and emission spectra of the investigated compounds. *p*-C1P₁, *p*-C1P₃, *p*-C2P₁, *p*-C2P₄ (solid lines —), *m*-C1P₁ (short dashes - - -) and *m*-C1P₃ (long dashes ---).

(OPA-800, Spectra-Physics). The output wavelength range of the OPA is extended by harmonic generation using one or two BBO (β -BaB₂O₄) crystals, thus making a range of 300–900 nm 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 femtosecond white light continuum for probing the absorption changes, which was generated in a 3.1 mm 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 (SP300i, Acton Research).

The transient signal of the samples was derived from a sequence of measurements: at each delay position, four spectra

were recorded with the CCD-camera. By selectively blocking the pump and/or white light beam, the transient absorbance signal (A) was determined as:

$$A(\lambda) = \log \left(\frac{S_A(\lambda) - S_D(\lambda)}{S_{EA}(\lambda) - S_E(\lambda)} \right) \quad (1)$$

where S_E denotes the spectrum recorded while only the excitation pulse was interacting with the sample yielding the correction for the fluorescence, S_{EA} is the spectrum while both the excitation pulse and the probe pulse were present at the sample position ("signal"), S_A is the spectrum while only the probing white light was present ("reference") and S_D is the spectrum while both the excitation pulse and the probe pulse were blocked before reaching the sample ("dark count signal"). At a fixed delay position, this set of measurements was repeated and averaged to improve the signal to noise ratio. This was done for 512 equally distant delay positions in time windows of 5, 50, 400 and 1500 ps.

To investigate possible multiphotonic processes, the intensity of the exciting laser beam was decreased by a factor of about three to seven in an additional series of measurements. These measurements were performed at detection wavelengths of 530 and 650 nm. To improve the signal to noise ratio, these single wavelength measurements were not performed using the CCD-camera detection setup. Instead, the probing white light continuum was passed through a monochromator and detected using a photomultiplier tube (R1527p, Hamamatsu). The electrical signal from the multiplier tube was gated by a boxcar averager (SR 520, Stanford Research Systems) and detected by a lock-in amplifier (SR 830, Stanford Research Systems).

In all measurements reported here, all samples were excited at wavelengths of 485 or 495 nm. In general, by appropriate

filtering of the white light continuum, the probe wavelength range was reduced to 450–740 nm. Besides this, all other experimental conditions were kept constant: all measurements were performed at room temperature in 1-mm optical path length cuvettes under magic angle polarization conditions. All compounds were dissolved in toluene (HPLC/Aldrich) at a concentration that yielded an absorbance of *ca.* 0.4 per mm at the excitation wavelength. By measuring the cross correlation between 495 nm excitation light and 600 nm probe light (derived from the continuum using appropriate filters) the prompt response of this setup was determined to be about 280 fs.

Results

Steady-state spectroscopy

The steady-state absorption and fluorescence spectra of all investigated compounds are depicted in Fig. 1. Within experimental error the absorption spectra are identical for all compounds. In the emission spectra, however, a 10 nm bathochromic shift and a small broadening of the *para*-substituted compounds spectra relative to those of the *meta*-substituted compounds can be seen. Moreover, a change in the intensity ratio between the two vibronic maxima is also visible. For the *meta* compounds, the vibronic maximum at 595 nm is relatively more pronounced as compared to that for the *para* compounds. The *para* coupling leads to a better conjugation of the π -electrons of the peryleneimide over the aromatic phenyl ring of the branch. This better conjugation lowers the excited-state energy leading to a bathochromic shift of the emission spectrum. The quantum yield for fluorescence was determined to be 0.98 ± 0.05 for all compounds under investigation.

Time-resolved polychromatic transient absorption measurements

Compound *p*-C1P₁. For the measurements of the transient absorption spectra of *p*-C1P₁, the excitation wavelength was set to 495 nm. The wavelength dependent absorption changes are presented in Fig. 2 for a number of different delay times after excitation. At positive times two different parts in the transient spectrum can be seen: a negative signal extending from 450 to 600 nm and second, a positive signal beyond 600 nm with a maximum at approximately 660 nm. Both features appear instantaneously after the excitation and decay on a nanosecond time scale.

Fig. 2 Transient absorption spectra of *p*-C1P₁ at different delay times: –10 ps (■), 1 ps (●), 2 ps (▲), 5 ps (▼), 10 ps (◆) and 30 ps (◄). *Insert bottom right*: detailed display of the 520–580 nm region.

Since the signal in the transient absorption spectrum above 600 nm is positive, it can unambiguously be attributed to an excited-state absorption (ESA). From previous studies^{23,24} it is known that *p*-C1P₁ has a fluorescence quantum yield of almost

unity and a fluorescence lifetime of 4.2 ns, thus the ESA found here can be attributed to a S_1 – S_n absorption within the peryleneimide chromophore.

From the facts that the steady-state absorption spectrum is negligible above 560 nm and that the fluorescence spectrum extends from 510 to 750 nm, the negative signal in the transient spectrum cannot solely be attributed to ground-state bleaching. It seems reasonable to believe that ground-state bleaching dominates the signal between 450 and 510 nm. Above 510 nm, however, both ground-state bleaching and stimulated emission are responsible for the negative signal, whereas the signal in the range between 560 and 600 nm is dominated by stimulated emission. There is no reason to believe that stimulated emission would only occur in the very blue part of the fluorescence spectrum so it must be considered that there is also a contribution of stimulated emission above 600 nm. It seems, though, that the absolute value of the cross section for excited-state absorption at these wavelengths exceeds the stimulated emission, since the netto result of transient absorption and stimulated emission yields a large positive signal in this wavelength range.

As stated above, the transient signal mainly decays on a nanosecond time scale. However, a detailed decay analysis of the transient absorption intensities as a function of delay time for different wavelengths reveals an additional picosecond relaxation process which can clearly be seen in the inset of Fig. 2. Within the first 20 ps, the transient absorption intensity drops at a wavelength of 530 nm, at about 555 nm the intensity remains constant while at 570 nm it rises. This relaxation process has been described before in detail⁵² and is interpreted as a combination of vibrational and solvent relaxation. This feature, where the intensity decays at a given wavelength and rises at another wavelength with an identical time constant (6.3 ps) had been found previously in fluorescence upconversion experiments.²⁴ In the transient absorption data reported here, the same feature can be observed, however, the signs of the amplitudes are of course reversed.

Compound *p*-C1P₃. Another series of experiments was performed on *p*-C1P₃, which contains three peryleneimides at the rim. Also for these measurements the excitation wavelength was set to 495 nm. Comparing the transient absorption spectra of this compound (see Fig. 3, top) to *p*-C1P₁ (Fig. 1, and for better comparison repeated in Fig. 3, bottom) one can see that the general shape is identical. Since the same chromophore is involved the attribution of the signals in *p*-C1P₃ is the same as in *p*-C1P₁.

However, the temporal evolution of the transient spectra of *p*-C1P₃ and *p*-C1P₁ is grossly different. It seems that the signal

Fig. 3 Transient absorption spectra of *p*-C1P₃ (top) and *p*-C1P₁ (bottom) at different delay times: –10 ps (■), 1 ps (●), 2 ps (▲), 5 ps (▼), 10 ps (◆) and 30 ps (◄).

Fig. 4 Excitation intensity dependent plot of the normalized transient absorption signals as a function of time at high (●,■,▼,▲) and low (○,□,▽,△) excitation power recorded at 530 nm (top) and at 650 nm (bottom) for the dendrimers *p*-C1P₃ (●,○), *p*-C1P₁ (■,□), *p*-C2P₄ (▼,▽) and *p*-C2P₁ (▲,△).

in the multichromophoric dendrimer decays faster when compared to *p*-C1P₁. This feature is demonstrated in Fig. 4 (left) where the transient absorption intensity as a function of time is plotted for *p*-C1P₃ and *p*-C1P₁ at detection wavelengths of 530 nm (top) and 650 nm (bottom).

In accordance with previous findings,^{24–26,38} this feature is attributed to a singlet–singlet annihilation process between two excited states within one dendrimer, leading to a first excited state and a ground state. In order to confirm this attribution, an additional series of experiments was performed in which the only varied parameter was the excitation intensity impinging on the sample, which was decreased by a factor of five. These measurements were performed at 530 nm (maximum of the negative part of the transient signal) and 650 nm (maximum of the positive part of the transient spectrum). The absorption changes were probed in the maxima of the corresponding negative and positive bands to maximize the signal to noise ratio. The results of these measurements are shown in Fig. 4 (left). The decays for *p*-C1P₁ are independent of the excitation intensity in contrast to those of *p*-C1P₃ which is a further strong support for the assumption of an annihilation process. At 530 nm the annihilation process reduces the number of excited peryleneimide chromophores, leading to a decrease both in stimulated emission and ground-state bleaching. At 650 nm it is detected as a decrease in the amount of peryleneimides in the excited state. This singlet–singlet annihilation process is the additional decay channel in the transient absorption measurements of *p*-C1P₃ compared to *p*-C1P₁.

Compound *p*-C2P₁. In order to reveal the influence of the generation number on the photophysical properties, the compound *p*-C2P₁ was studied. It is a monochromophoric second-generation dendrimer consisting of an interior building block and one peryleneimide chromophore attached in a *para* position to the outer phenyl ring at the rim. Compared to the first-generation dendrimer, the situation at the rim is very

similar, however the photophysically inert interior building block is bigger.

The time-dependent transient absorption spectra ($\lambda_{\text{ex}} = 485 \text{ nm}$) are shown in Fig. 5 (bottom). At positive times two different parts in the transient spectrum can be seen: a negative signal which reaches from 450 to 600 nm with different maxima at about 500 nm, and second, a positive signal beyond 600 nm with a maximum at approximately 660 nm. Both features appear instantaneously after excitation and decay on a nano-second time scale. These general features are exactly the same as those observed for the first-generation monochromophoric dendrimer *p*-C1P₁. Since the chromophore involved, the steady-state spectra and quantum yields are identical, the above information leads to the identical attributions of the negative

Fig. 5 Transient absorption spectra of *p*-C2P₄ (top) and *p*-C2P₁ (bottom) at different delay times: -10 ps (■), 1 ps (●), 5 ps (▲), 20 ps (▼), 50 ps (◆) and 400 ps (◄).

signal to ground-state bleaching/stimulated emission and of the positive signal to S_1-S_n absorption as in the case of p -C1P₁. In the short wavelength part of the signal related to ground-state bleaching, however, we find a more intense signal as compared to the transient spectrum of p -C1P₁. This negative spectrum also resembles the ground-state absorption spectrum in a more precise way which seems reasonable assuming there is no excited-state absorption in this spectral region. This difference between p -C2P₁ and p -C1P₁ is related to an improvement of the stability of the white light continuum in the course of the investigation which allows to probe the transient absorption changes in this part of the spectrum more exactly.

Also in this molecule, a relaxation process can be seen during the first 20 ps. Exactly as in p -C1P₁, the transient absorption intensity drops at a wavelength of 530 nm, stays constant at about 555 nm, and rises at 570 nm. In view of the presence of exactly the same chromophore and the very similar environment as compared to the situation in p -C1P₁ these findings are as expected.

Compound p -C2P₄. Another series of experiments was performed on p -C2P₄, which contains four peryleneimides at the rim. Also for these measurements the excitation wavelength was set to 485 nm. The time-dependent transient absorption spectra are displayed in Fig. 5 (top). Comparing the transient absorption spectra of p -C2P₄ to those of p -C2P₁ Fig. 5 (bottom), one can see that the general shape is identical, thus the attribution of the signals in p -C2P₄ can be the same as in p -C2P₁. The temporal evolution of the spectra, however, is different. The change is completely analogous to that reported above for the comparison of first-generation mono- to multi-chromophoric dendrimers. In order to check the presence of multiple excited chromophores within the same molecule at the same time in p -C2P₄, a series of measurements was performed in which the excitation intensity was varied. These measurements were performed at detection wavelengths of 530 and 650 nm while the laser intensity was varied by a factor of about six.

The results of these excitation intensity dependent measurements are depicted in Fig. 4 (right). It can be seen that the time-dependent transient absorption change is independent of the excitation intensity for the monochromophoric dendrimer p -C2P₁ while there is a clear dependence for p -C2P₄. So also in this case a singlet–singlet annihilation process is responsible for the presence of this specific feature. In previous investigations it was evidenced by careful analysis of measurements conducted at many different excitation intensities, that there were two intensity dependent annihilation processes, one of those with a time constant of 40 ps and by far the main component and a second, minor amplitude process with a time constant of about 5 ps. In the measurements reported here, only two different excitation intensities were investigated from which we can neither exclude nor claim the presence of a second minor annihilation component. The occurrence of more than one annihilation process relates to the presence of different isomers resulting in a broad distribution of rate constants which under certain conditions can be analyzed as two annihilation processes.⁵³

Compound m -C1P₁. The only difference to the compound p -C1P₁ is that in the molecule m -C1P₁ the peryleneimide chromophore is connected in *meta* position to the phenylring of the branch as compared to *para* in p -C1P₁.²⁴ The results of the measurements on this molecule, in which an excitation wavelength of 495 nm was used, are depicted in Fig. 6 (bottom). Albeit that small differences are observed (*vide infra*) the data sets can be interpreted identically and thus lead to the same attributions. In the inset of Fig. 6 (bottom), the same excited-state relaxation process can be seen as already was described for the *para* compound. As a small difference the maximum of the

Fig. 6 Transient absorption spectra of m -C1P₃ (top) and m -C1P₁ (bottom) at different delay times: -10 ps (■), 1 ps (●), 2 ps (▲), 5 ps (▼), 10 ps (◆) and 30 ps (◄).

positive transient absorption band for the compound m -C1P₁ is about 5 nm shifted to the blue and also the zero crossing point is shifted from 610 nm in the case of p -C1P₁ to 602 nm for m -C1P₁.

Compound m -C1P₃. Another series of experiments was performed on m -C1P₃, which contains three peryleneimides connected in *meta* position to the outer phenyl ring. Also for these measurements the excitation wavelength was set to 495 nm. The time-dependent transient absorption spectra are displayed in Fig. 6 (top). The interpretation of these measurements leads to exactly the same picture as derived from the comparison of p -C1P₃ to p -C1P₁. This includes the same general attribution of the transient bleaching and absorption signals as in m -C1P₁ and the presence of a singlet–singlet annihilation process in m -C1P₃, which is also evidenced by an additional excitation intensity dependent study here at a detection wavelength of 650 nm. The results of these additional measurements are depicted in Fig. 7.

Fig. 7 Excitation intensity dependent plot of the normalized transient absorption signals as a function of time at high (◆, ◄) and low (◇, ◊) excitation power detected at 650 nm for the dendrimers m -C1P₁ (◆, ◇ top) and m -C1P₃ (◄, ◊ bottom)

Discussion

The results of all these independent measurements can be compared to get insight into the influence of the generation number and the influence of the different substitution pattern. The former can be deduced by comparing the results of the second-generation dendrimers (p -C2P_{1,4}) to those of the first-generation dendrimers (p -C1P_{1,3}). In the monochromophoric compounds, no difference can be observed between the first and

second-generation dendrimer. The chromophore involved is the same and it is also connected in the same way (*para*) to the outer phenyl ring. Since they are monochromophoric, no intramolecular chromophore–chromophore interactions are possible.

In the multichromophoric dendrimers, a clear dependence of the annihilation process from the generation number can be observed. Although this process is seen in both generations (compare Fig. 4 left and right) the corresponding time scales are grossly different: while in *p*-C1P₃ the annihilation process relates to a decay time of 4.2 ps, it corresponds to a decay time of 53 ps for *p*-C2P₄. For *p*-C1P₃, (*p*-C2P₄), the decay times of the annihilation processes were determined as 4.6 ps (40 ps),^{24,26} respectively. In the measurements reported here, the analyzed decay times were 4.2 ps for *p*-C1P₃ and 53 ps for *p*-C2P₄, which corresponds well with the decay times reported using the fluorescence upconversion technique.^{24,26}

The differences in the photophysical properties due to the different substitution patterns can be determined by comparing the compounds (*m*-C1P_{1,3}) with the compounds (*p*-C1P_{1,3}). Already in the emission spectra a bathochromic shift of the *para*-substituted compounds can be observed while the ground-state absorption spectra are identical. Also the vibrational structure of the emission spectra becomes less pronounced in the *para*-substituted compounds. Differences can also be seen in the transient behavior of these compounds. The maximum of the positive transient absorption band for the compound *m*-C1P₁ is about 5 nm shifted to the blue and also the zero crossing point is shifted from 610 nm in the case of *p*-C1P₁ to 602 nm for *m*-C1P₁.

The influence of the different substitution pattern upon the fluorescence dynamics of these dendrimers has been studied previously in detail²⁴ using fluorescence upconversion detection. In that investigation, it had been concluded that changing the substitution pattern from the *meta* to the *para* leads to a better spatial definition of the peryleneimide chromophore and a stronger coupling to the outer phenyl ring. The transient absorption measurements reported here show exactly the same features, thus confirming the above interpretation. The *para* coupling leads to a better conjugation of the π -electrons of the peryleneimide over the aromatic phenyl ring of the branch. This better conjugation lowers the excited-state energy leading to a bathochromic shift of the emission spectrum. This is illustrated by the 5 nm shift of the zero crossing point of the transient spectrum from *m*-C1P₁ compared to *p*-C1P₁ (see Fig. 6).

Conclusions

Time resolved polychromatic transient absorption measurements have been performed on different rigid dendrimers containing peryleneimide chromophores at the rim. It is shown that the time dependence of the transient absorption spectra of the multichromophoric dendrimers completely differs from the monochromophoric dendrimers. This difference is attributed to singlet–singlet annihilation processes between the peryleneimide chromophores at the rim only present in the multichromophoric dendrimers. Besides this generation-number dependent singlet–singlet annihilation process, minor differences in photophysical properties as a result of the different substitution patterns were also observed.

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