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Femtosecond fluorescence upconversion study of rigid dendrimers containing peryleneimide chromophores at the rim

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Abstract

The kinetics of a newly synthesized series of a first generation of polyphenylene dendrimers in which one phenyl in a dendritic arm was *para*-substituted by a peryleneimide chromophore are reported. One such peryleneimide chromophore is attached to 1, 3 or 4 arms. The results are compared to a series of polyphenylene dendritic compounds, which are identical except for the substitution at a *meta*-position of a phenyl ring. The *para*-substitution yields a better spatial definition of the peryleneimide units relative to one another and the influence of this aspect on the kinetics is studied. Four different kinetic components were resolved for both groups of dendrimers. An ultra-short component varying from 500 fs to 2 ps and attributed to intramolecular vibrational redistribution (IVR) is identical for both series. The decay time of a second component, which is comprized of the vibrational relaxation and a singlet–singlet annihilation process observed in both substituted dendrimer series, is shorter in the *para*-substituted dendrimers compared to the *meta*-substituted ones. It is also shown that the annihilation process, which is only present in the multi-chromophoric compounds of both the series and resolved with an excitation energy dependent study, has definitely a larger contribution in the partial amplitudes for the *para*-substituted compounds. This is related to the relative orientation of the transition dipoles of the chromophores in both the series. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Dendrimers; Kinetics; Fluorescence spectroscopy; Time resolved spectroscopy; Singlet–singlet annihilation; Energy transfer

1. 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 [4–10].

Within the research group, dendrimers consisting of a polyphenylene core and decorated with peryleneimide chromophores at the rim have been investigated at *single molecule* [11,12] and *ensemble* levels [13–18]. In first instance, dendritic systems with a biphenyl core were studied [17,18] by performing femtosecond fluorescence upconversion and transient absorption measurements. To obtain a better control over the positioning of the chromophores and their interaction in the excited state, it is desirable to have them distributed on a spherical surface. Hence, a series of first generation peryleneimide dendrimers with rigid tetrahedral central core [19] was synthesized. These dendrimers possess pentaphenylbenzene units, and as a result of the "interlocking" of twisted phenyl rings, are shape persistent and more closely packed, thus allowing for a more systematic study of possible energy transfer processes between the chromophores. Furthermore, by way of synthesis, one can control the number of peryleneimide chromophores attached to the surface of the nanoparticles from 1 to 4 [20–22]. In these molecules, the peryleneimide chromophores were attached in *meta*-position of the pentaphenylbenzene units. These rigid peryleneimide dendrimers were studied by time resolved single photon counting spectroscopy [15] and femtosecond fluorescence upconversion, and several decay components could be resolved [13]. One of the interesting results in the upconversion study was the observation of an excitation intensity dependent component. As a result of the *meta*-substitution in these compounds, it was shown that for some of the structural isomers, conformations exist in which some of the peryleneimide chromophores spatially overlap leading to an excimer-like fluorescence component [15].

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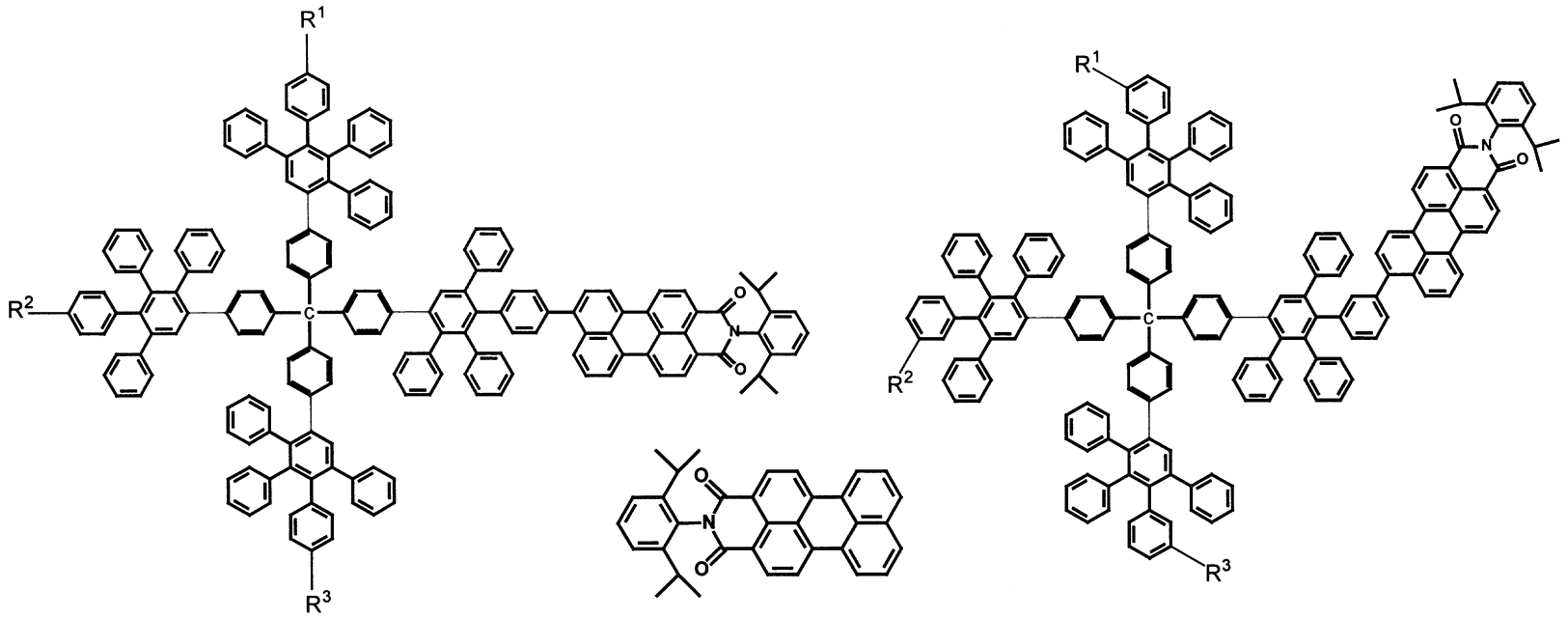

p-G1RX **PI** **m-G1RX**

	R^1	R^2	R^3
p-G1R1	H	H	H
p-G1R3	PI	PI	H
p-G1R4	PI	PI	PI

	R^1	R^2	R^3
m-G1R1	H	H	H
m-G1R3	PI	PI	H
m-G1R4	PI	PI	PI

Scheme 1. Molecular structures of all compounds investigated and discussed. *p*-G1R*X* ($X = 1, 2, 3, 4$), *para*-substituted first generation dendrimers; *m*-G1R*X* ($X = 1, 2, 3, 4$), *meta*-substituted first generation dendrimers; PI, peryleneimide chromophore.

To achieve an even better control over the spatial distribution of the chromophores at the periphery of the molecule, a new synthesis sequence was developed to connect the peryleneimide units in *para*-position of the pentaphenylbenzene units (Scheme 1). In this way, the spatial overlap between the peryleneimide chromophores is eliminated. A goal of this publication is to find out to what extent this will affect the early time photophysical behavior.

2. Experimental

In this study, three new compounds have been investigated whose molecular structures are shown in Scheme 1. These three compounds are all derivatives of a first generation dendrimer with a tetraphenyl-methane core. In order to study the influence of different number of chromophores in detail, it has been decorated with 1 (*p*-G1R1), 3 (*p*-G1R3) and 4 (*p*-G1R4) peryleneimide chromophores at the rim, all connected in *para*-position to the pentaphenylbenzene units (see Scheme 1).

All measurements on these three compounds were performed at room temperature in 1 mm optical path length cuvettes under magic angle polarization. All compounds were dissolved in toluene at a concentration that yielded an absorption of ca. 0.4 per millimeter at the excitation wavelength of 495 nm resulting in a concentration in the order of 10^{-5} M. Besides the measurements under these standard conditions, two more series of measurements were performed in which the concentration and excitation energy varied, respectively (see below).

The steady state absorption measurements were performed on a commercial Perkin-Elmer Lambda 40 spectrophotometer, while in the emission study, a SPEX fluorimeter was used. The integrity of the sample was checked thoroughly by means of these techniques before and after each set of fluorescence upconversion measurements.

The laser system has previously been described in detail [23]. In brief, a Nd:YVO_4 laser (Millennia V, Spectra Physics) is used to pump a Ti:sapphire laser (Tsunami, Spectra Physics). Its output seeds a regenerative amplifier (RGA, Spitfire, Spectra Physics). The output of the RGA (1 mJ, 100 fs, 800 nm) is split into two equal parts, one of which is used to pump an optical parametric generator/amplifier (OPA-800, Spectra Physics) and the second part is used as a gate pulse. The output wavelength range of the OPA is extended by harmonic generation using one or two BBO crystals, thus making a range of 300–900 nm accessible.

The fluorescence upconversion detection setup has also been described in detail in a previous publication [17]. Briefly, the fluorescence light emitted from the sample is collected and sent to an LBO crystal in which the sum frequency of this light and a gate pulse (800 nm, ca. 100 μJ) derived from the RGA is generated. The time resolved traces are then collected by detecting this sum frequency light while changing the relative delay of the gate pulse versus the sample excitation time. By detection of scattered light under otherwise identical conditions, the prompt response of this arrangement (including laser sources) was determined to be approximately 250 fs. This value was used in the analysis of all measurements for deconvolution of the data sets.

For all measurements performed here, the excitation wavelength was kept constant at 495 nm. Except for the series checking the excitation energy dependence (see below), all compounds were illuminated with an excitation energy of ca. 400 nJ. Each measurement consisted of 1024 delay positions, at each of which the fluorescence signal, the excitation laser intensity and the gate pulse intensity were recorded averaging over 5 s, thus resulting in a measurement time of ca. 5000 s per delay scan.

To capture all kinetic components potentially present in the excited state dynamics as precisely as possible, a measurement as described above was then repeated using three different channel widths for the detection. This results in three different time windows of 6.7, 50 and 450 ps for all 1024 measured channels. This set of three measurements was performed for each compound throughout its complete emission spectrum at 15 different fluorescence detection wavelengths from 530 to 670 nm at intervals of 10 nm, thus resulting in a set of 45 measurements.

In order to investigate possible multiphoton processes, an additional series of measurements was performed varying the laser energy exciting the compound in a systematic way while keeping all other conditions constant. This was done in a range from 400 nJ (maximum laser output available) down to 40 nJ which turned out to be at the detection limit. One measurement under these extreme conditions had to last about 20 h to yield data sets that could still be analyzed.

Finally, in a separate measurement sequence, the dependence of the ultrafast kinetics on the dendrimer concentration between 10^{-5} and 10^{-6} was investigated. In order to do this, the standard concentration used in all other sets was reduced by a factor of 10.

The data analysis was performed independently for each molecule but in an identical fashion. All 45 decay curves measured in all the three time windows were put together into a common data set which was analyzed globally using a nonlinear least square fit routine from a commercial software package. As part of the analysis, the data sets were also deconvoluted using information from system prompt response measurements that were routinely recorded during each measurement session.

For all dendrimers, a sum of four exponentials with time constants $\tau_1 \ldots \tau_4$ and amplitudes $a_1 \ldots a_4$ has been found necessary to fit the data sets properly as judged by minimization of χ^2 values and visual inspection of residual plots. The longest component (τ_4, a_4) is in the range of a few nanoseconds and thus cannot be determined precisely in the time windows used here. Instead, the actual values were taken from measurements performed and reported independently using a single photon timing detection setup

[16]. During the fits, τ_4 was fixed to 4 ns, however, the corresponding amplitude a_4 was a free fit parameter.

3. Results

3.1. Polyphenylene dendrimers substituted in para-position with peryleneimide chromophores

The steady state absorption (A) and emission spectra (B) for the *para*-substituted peryleneimide *p*-G1R*X* dendrimers (*p*-G1R1, □; *p*-G1R4, △) are shown in Fig. 1. The absorption spectra for all compounds under investigation are completely identical within the experimental error. Also the emission spectra taken at an excitation wavelength of 495 nm which is close to the absorption maximum are not showing pronounced differences. No spectral shift or broadening could be observed upon varying the number of chromophores. The only small variation that occurred was a slight change of the shoulder at 596 nm.

In order to reveal properties that are independent of potential chromophore–chromophore interactions, *p*-G1R1 was used as a model compound, since it contains only one chromophore, so it was investigated in a first series of measurements. Fig. 2 shows a typical result for *p*-G1R1 at two different detection wavelengths excited at 495 nm showing first a clear wavelength dependence from the fluorescence decay and second a complex non-mono-exponential decay consisting of several components. Especially in the first picoseconds, there is a clear wavelength dependence. These short decay components and their differences are in the focus of the investigation reported here. In a second series of measurements, the dendrimers containing 3 and 4 peryleneimide chromophores at the rim are studied and compared to the results obtained for the mono-chromophoric compound.

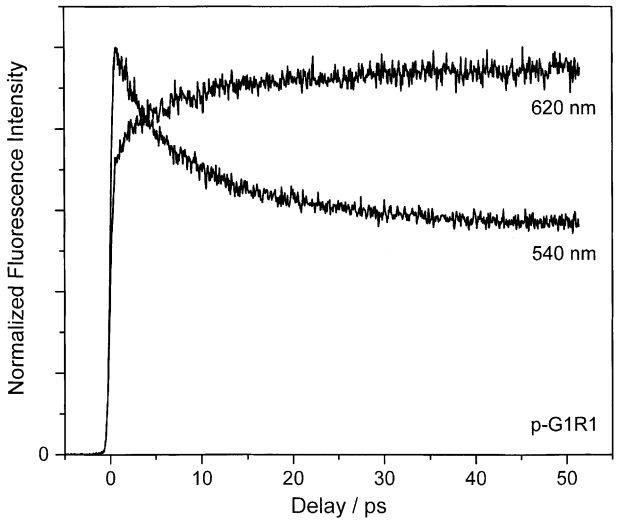

Fig. 2. Time resolved fluorescence intensity I of *p*-G1R1 detected at 540 and 620 nm as indicated.

The resulting time constants obtained by the described analysis procedure for the various compounds are summarized in Table 1. The results for τ_1 are not found constant throughout the spectrum, so these decay times could not be analyzed globally. The second component (τ_2, a_2) exhibits a fast time constant in the order of few picoseconds for all compounds and is representing 15–40% of the total

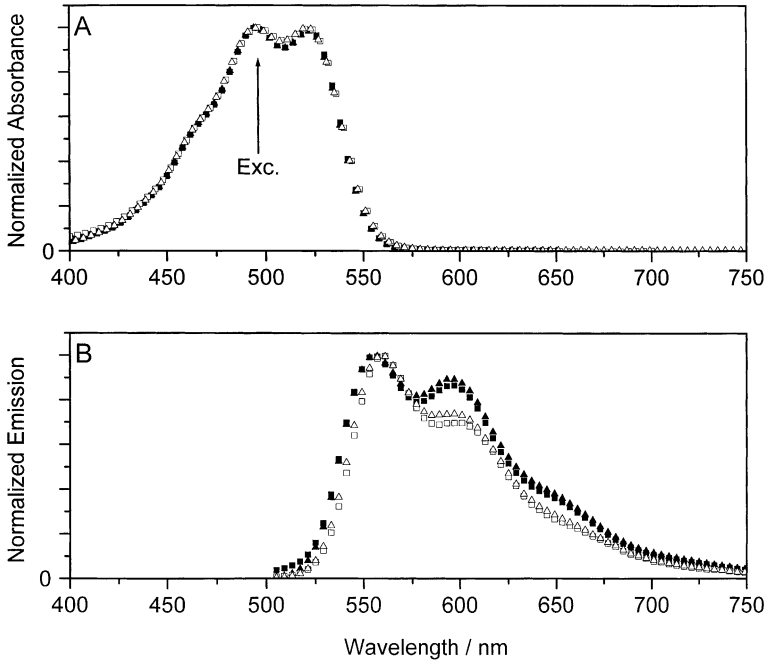

Fig. 1. Normalized steady state absorption (A) and emission spectra (B) for the *para*-substituted *p*-G1R*X* (*p*-G1R1 (□); *p*-G1R4 (△)) and *meta*-substituted dendrimers *m*-G1R*X* (*m*-G1R1 (■); *m*-G1R4 (▲)). The emission spectra were excited at a wavelength of 495 nm as indicated by the arrow.

Table 1
Decay times resulting from global analysis for all compounds investigated

Compound	N^a	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_4 (ps)[b]
p-G1R1	1	0.5–2[c]	6.3	110	4000
p-G1R3	3	0.5–2[c]	4.6	45	4000
p-G1R4	4	0.5–2[c]	4.0	45	4000
m-G1R1	1	0.5–2[c]	10.0	188	4200
m-G1R3	3	0.5–2[c]	8.0	137	4200
m-G1R4	4	0.5–2[c]	7.5	83	4200

[a] Number of chromophores per molecule.
[b] Fixed during the fit procedure (see text).
[c] Varying with fluorescence detection wavelength (for details, see text).

amplitude depending on the wavelength and the compound. The third component is contributing at the most 10%, and in most cases, even less to the total amplitude, however, it is found necessary to obtain good fits. The largest part of the amplitude, however, is found in the nanosecond component 4 (τ_4, a_4) for all compounds.

Fig. 3A shows the partial amplitudes for *p*-G1R*X* for the ultra-fast decay component as a function of the detection wavelength. Considering the behavior of this decay component, it is the only decay time out of the four resolved in our analysis that is wavelength dependent, all others could be kept constant. The change that can be observed in Fig. 3C for *p*-G1R3 is a clear increase of the decay time with increasing fluorescence detection wavelength. This shortest time constant can be seen at the shortest detection wavelength and has a value of about 500 fs evolving as shown in Fig. 3C to ca. 2 ps ranging from shorter to longer wavelengths. As a result, the time constant could not be kept constant in the global analysis although the values obtained for the partial amplitudes are still the result of the global analysis procedure which contains all decay parameters. A second observation that can be made for this decay component is that it has negative partial amplitudes at all detection wavelengths above 540 nm. This means a growing in of the decay curves at the early times after excitation originating from the formation of a fluorescing state [24]. For all compounds *p*-G1R1, *p*-G1R3 and *p*-G1R4, a similar behavior concerning partial amplitudes and decay times can be observed at the detected fluorescence wavelengths (Fig. 3A). This behavior of the negative partial amplitudes, the order of magnitude and change in decay time depending on detection wavelength is typical for an intramolecular vibrational redistribution (IVR) process in the electronically excited state of the chromophore [24,25]. So this component found in all compounds under investigation in the mono- and the multi-chromophoric dendrimers can be attributed to this IVR process. A time constant of ca. 1 ps has been reported before in literature [26–28] for various chromophores of similar size in toluene solution. The observation of increasing time constants for this process upon increasing detection wavelength is also in line with literature [29] and consistent with the attribution to an IVR process. Previously obtained results [17] from

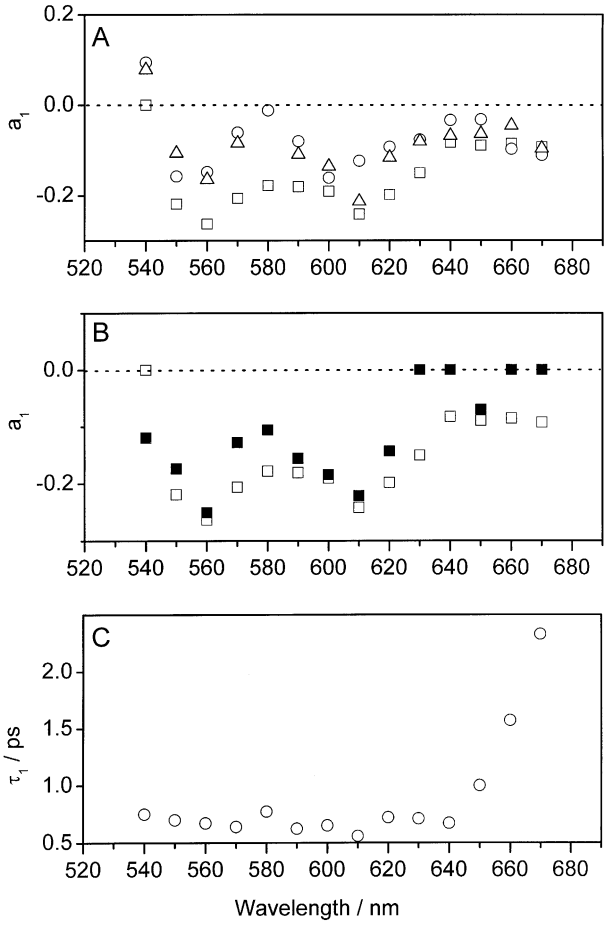

Fig. 3. Dependence of the IVR component amplitude a_1 from the detection wavelength: (A) for the *p*-G1R*X* dendrimers (*p*-G1R1 (□); *p*-G1R3 (○); *p*-G1R4 (△)) and (B) comparison of *p*-G1R1 (□) and *m*-G1R1 (■), and (C) time constant τ_1 of the IVR component as a function of the detection wavelength for *p*-G1R3.

ultra-fast studies of similar dendrimers containing identical chromophores are also supporting an attribution of this type. In view of the time resolution of ca. 250 fs of the setup used here, it cannot be excluded, however, that this IVR component is actually a combination of various processes resulting from the static and dynamic response of the environment of the chromophore [30]. Also, a fast vibrational relaxation of highly excited levels of the first singlet excited state in the peryleneimide cannot totally be excluded as a part of this component [31].

The second decay component that could be found in the *para*-substituted dendrimers has a decay time of 6.3–4 ps, depending on the compound (Table 1). Fig. 4A shows the partial amplitudes of *p*-G1R*X* for this component as a function of the detection wavelength. First, looking at only the mono-chromophoric compound with a τ_2 of 6.3 ps, a change of sign of the partial amplitude can be observed. Taking into account the shape and the positive/negative amplitude behavior of this kinetic component, it is attributed to a vibrational relaxation in the electronically excited state

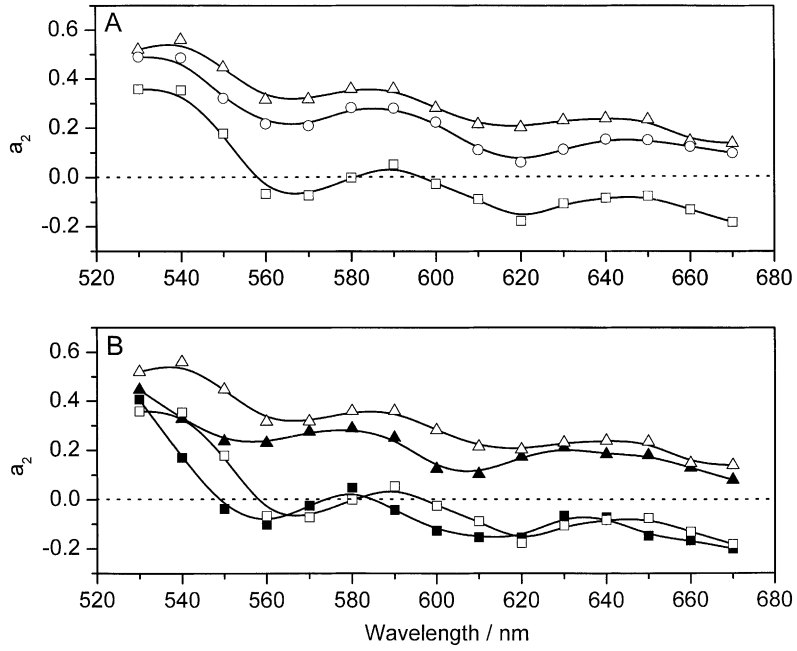

Fig. 4. Wavelength dependence of the amplitude a_2 of the second component (A) for the *p*-G1R*X* dendrimers (*p*-G1R1 (□); *p*-G1R3 (○); *p*-G1R4 (△)) and (B) comparison of *p*-G1R1 (□) versus *m*-G1R1 (■), and *p*-G1R4 (△) versus *m*-G1R4 (▲).

of the peryleneimide chromophore. This process is coupled to a relaxation and reorganization of the solvation shell around the chromophore, as the solvent molecules have to accommodate for the newly populated S_1 state of the peryleneimide [32]. At fluorescence detection wavelengths close to the excitation, this will be seen as a fast decay component, whereas at longer wavelengths the fluorescence is detected from a state that first has to be populated with the time constant resolved. In the kinetic analysis, this is found as a rise term with the corresponding time constant. Thus, it can be concluded that this kinetic component is related to the single chromophore itself and its interaction with the surrounding solvent toluene molecules. The finding of a 6.3 ps component and its attribution is in line with literature where an ultra-fast stimulated transient absorption spectroscopy setup [33] was used to determine a vibrational relaxation time in the same order of magnitude for perylene in toluene solution. In many other investigations [34–39], time constants of a few picoseconds were found and attributed to a vibrational relaxation process for various chromophores in toluene and other solvents.

To study the influence of more than one chromophore attached on this second component, also the multi-chromophoric compounds *p*-G1R3 and *p*-G1R4 were studied. As can be seen in Fig. 4A, the typical shape and wavelength dependence of the partial amplitude is persistent for all three dendrimers, but a positive shift can clearly be observed. Increasing the number of chromophores results in a bigger shift. So there clearly is an indication for having more than one process contributing to this second decay component, meaning a more complex attribution for this second component compared to the one in the mono-chromophoric compound. Thus, for the interpretation of these results two different contributions 2a and 2b to this kinetic component are assumed, which are related to different processes. They both exhibit time constants that are very close to each other and because of this cannot be separated by the global analysis. First, component 2a is present in all compounds and can be attributed to the vibrational relaxation, responsible for the typical shape and wavelength dependence and appearing purely only in the analysis of the mono-chromophoric compound. The second component 2b can only be observed if there is an intramolecular interaction possible between two or more chromophores. It is superimposed on the wavelength dependent component 2a and is almost wavelength independent and increasing in amplitude with the number of chromophores. A possibility to separate these two processes can be found in excitation energy dependent measurements. When the photon flux available in the laser focus at the sample position is calculated, a value of several tens of photons per chromophore and per laser pulse can be found, so a dependence can be expected. The estimated distance obtained by means of molecular modeling between two chromophores is about 29 Å [16]. The combination of this estimated distance and the fact that more chromophores can get excited at the same time in one molecule yields a possibility for an intramolecular singlet–singlet annihilation of two excited chromophores resulting eventually in a first excited state and a ground state [40]. This annihilation process has been reported and investigated in literature theoretically [40,41] and has been the experimental topic in different investigations in various systems like pigment–

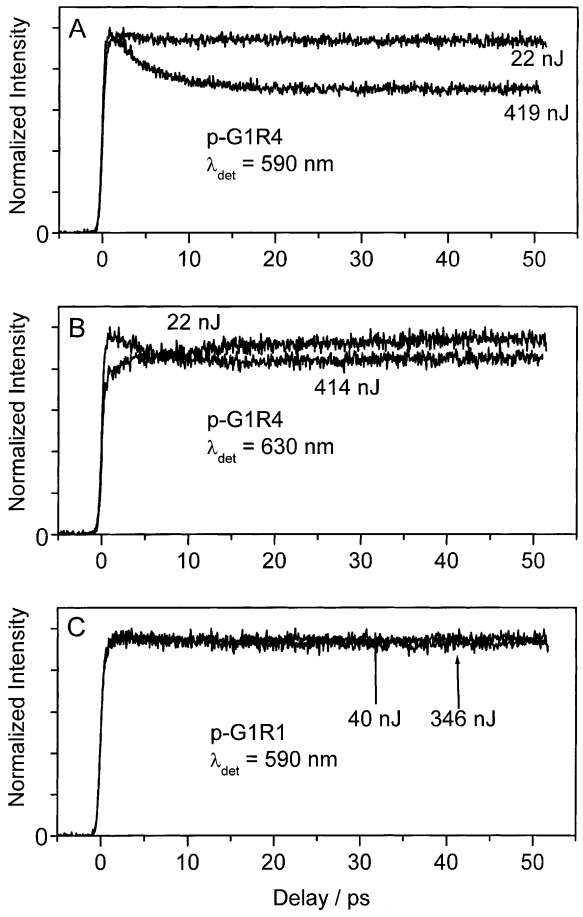

Fig. 5. Comparison of the time resolved fluorescence intensity I recorded at low and high excitation energy (as indicated): (A) multi-chromophoric compound *p*-G1R4 detected at 590 nm; (B) multi-chromophoric compound *p*-G1R4 detected at 630 nm; (C) mono-chromophoric compound *p*-G1R1 detected at 590 nm.

protein complexes [42–45], polymers [46] and J-aggregates [47,48].

In order to distinguish and separate these two kinetic decay channels 2a and 2b present in the multi-chromophoric dendrimers, an excitation energy dependent study was performed on the mono- and the multi-chromophoric *para*-compounds. The excitation energy imposed onto the sample systematically varied between 40 and 400 nJ and a clear dependence of the amplitude of the second component could be observed. Fig. 5 shows the decay curves for *p*-G1R4 at two different well chosen wavelengths, namely 590 (5A) and 630 nm (5B) at two different excitation energies. These detection wavelengths were selected because of the magnitude of the partial amplitude for the second component (Fig. 4A) at these wavelengths. For the mono-chromophoric compound, the amplitude at 590 nm is close to zero, while at 630 nm, it has a clear negative value. Contrary, to the multi-chromophoric compounds the amplitudes are positive and substantially larger at these selected wavelengths. From the importance of the annihilation process, 2b should decrease as the excitation energy diminishes, the partial amplitudes as a function of wavelength of component 2 of the multi-chromophoric compounds should resemble the one for the *p*-G1R1 compound (2a) at low excitation energies. This means that the amplitude of this second decay component should turn from a positive into a negative value with decreasing excitation energy when detection is done at 630 nm, and this is exactly what is observed (Fig. 5B). Also at 590 nm, there is clear decrease of the contribution of the annihilation process at the lower excitation energy. Since its partial amplitude is almost zero at 590 nm detection, no decay can be observed anymore (Fig. 5A). In order to cross-check these findings, a similar energy series has also been performed for the mono-chromophoric compound *p*-G1R1. The results shown in Fig. 5C (bottom frame) are as expected; in contrast to the multi-chromophoric compound measured at this detection wavelength, there is no detectable excitation energy dependence within the measured range. Thus, at all excitation intensities, the partial amplitudes a_2 are constant which is a clear indication that in this mono-chromophoric compound the component 2b is nonexistent.

Fig. 6 shows the partial amplitude a_2 for *p*-G1R1 (□) and *p*-G1R4 (△) at the two selected detection wavelengths (Fig. 6A at 590 nm and Fig. 6B at 630 nm) as a function of the excitation energy. For the multi-chromophoric dendrimers (*p*-G1R4 shown), the typical dependence for an annihilation process is observed [13,41]. As a reference, also the mono-chromophoric *p*-G1R1 was measured in an identical way (Fig. 6A and B). For this compound, no dependence on the excitation energy at the two detection wavelengths was observed over the range studied. This is a clear indication that in this mono-chromophoric compound, the second and the shortest component 2b is not present and that the amplitude spectrum is showing only the 2a component of 6.3 ps, attributed to the vibrational relaxation of the chromophore.

Looking at decay times for this component 2 (Table 1), one can observe a decrease in decay time upon increasing the number of chromophores. This can be explained by the fact that the decay time determined by the analysis is a weighed combination of these two separate decay times τ_{2a} and τ_{2b} of the vibrational relaxation and the annihilation process as shown in the previous paragraph. Since the relaxation process is the slowest one of these two processes, the more the chromophores are added, the more likely the annihilation becomes and the shorter the overall decay times.

The third kinetic component that could be found back for all *para*-substituted peryleneimide dendrimers at all detection wavelengths has a time constant in the order of 100 ps and a relatively low partial amplitude. By checking a possible concentration effect between 10^{-5} and 10^{-6} M on the different kinetic components by diluting the samples, this was the only one that was dependent on the concentration. For this reason, this component is not further discussed and attributed to an intermolecular process.

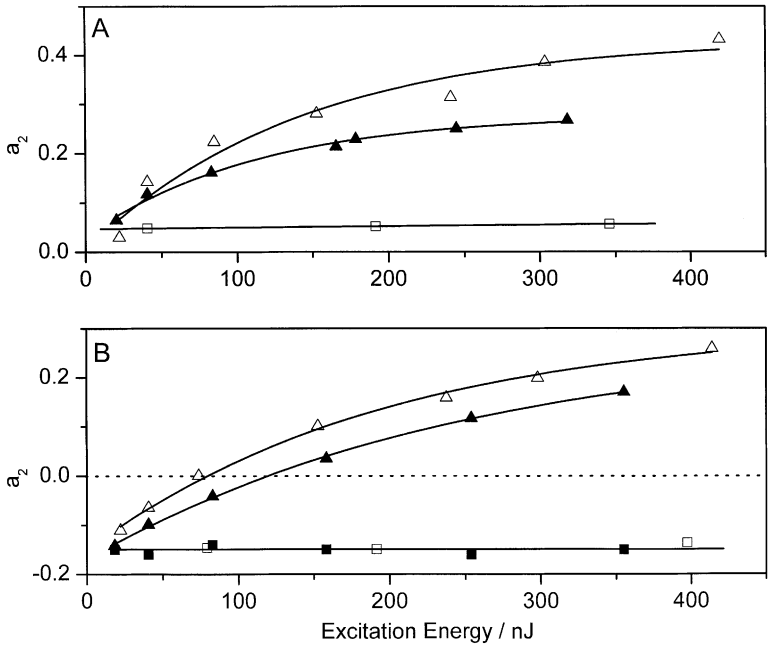

Fig. 6. Dependence of the partial amplitude a_2 of the second component from the laser excitation energy for the *para* *p*-G1R*X* (*p*-G1R1 (□); *p*-G1R4 (△)) and *meta*-substituted peryleneimide dendrimers *m*-G1R*X* (*m*-G1R1 (■); *m*-G1R4 (▲)). (A) Detection done at 580 nm (*meta*-substituted compounds) and 590 nm (*para*-substituted compounds). (B) Detection done at 620 nm (*meta*-substituted compounds) and 630 nm (*para*-substituted compounds).

The fourth and the longest component (τ_4, a_4) is in the range of a few nanoseconds and thus cannot be determined precisely in the time windows used here. Instead, the actual values were taken from measurements performed and reported independently using a single photon timing detection setup [15]. It is attributed to the intrinsic fluorescence lifetime of the peryleneimide chromophore of 4.0 ns.

4. Discussion

4.1. Comparison of para- and meta-substituted polyphenylene dendrimers

In a previous study performed in the research group [13], a similar set of measurements was performed on *meta*-substituted polyphenylene dendrimers (Scheme 1), containing also 1 (*m*-G1R1), 3 (*m*-G1R3) and 4 (*m*-G1R4) peryleneimide chromophores. By comparing these results and the newly obtained ones for the *para*-substituted compounds, the influence of the better spatial definition in the *para*-substituted dendrimers on the kinetic behavior can be studied.

While the absorption spectra (Fig. 1A) of both series of compounds are identical within the experimental error, the emission spectra (Fig. 1B) show a 10 nm bathochromic shift of the first maxima for the *para*-substituted compounds. The width at half height of the *meta*-substituted compounds is slightly larger compared to the one of the *para*-substituted dendrimers. In both series of dendrimers, the respective kinetics that could be resolved by fluorescence upconversion are showing a high degree of similarity.

First of all, a very short decay time τ_1 varying from about 500 fs to ca. 2 ps dependent on the detection wavelength can be found in the analysis of both series, and in the *para*- and in the *meta*-substituted compounds, this decay time increases as the detection wavelength increases and this occurs in both cases in an identical way. Fig. 3B shows the change of the partial amplitude of this short component as a function of the detection wavelength for *m*-G1R1 and *p*-G1R1. The shape and the negative sign of the amplitudes are completely identical, the only difference that can be observed is a small shift which is probably originating from the difference in the steady state emission spectra. Since this decay component is attributed to an IVR process, it is not surprising that this component is always identical, no matter how the chromophores are distributed in space and how they are attached to the central part of the dendrimer.

The second decay component that can be found in both series of dendrimers is the one that is consisting of two parts 2a and 2b not separable in decay time by the analysis. The attribution could be made by means of an excitation energy dependent study at the two different strategically chosen wavelengths making it possible to distinguish the vibrational relaxation that is independent and the annihilation process which is dependent on this parameter. Fig. 4B shows the partial amplitudes for this vibrational relaxation

component for the two mono-chromophoric compounds. Considering the dendrimers *m*-G1R1 and *p*-G1R1, the time constants obtained are 10 and 6.3 ps, respectively. It is clear that in these compounds only the vibrational relaxation contributes and not the annihilation process, since no chromophore–chromophore interaction is possible.

There is a clear drop in the vibrational relaxation decay time when the peryleneimide is *para*- instead of *meta*-substituted. This can be explained by the fact that the coupling in the *para*-substituted compounds to the polyphenylene core is more important resulting in a better redistribution of the energy over the vibrational modes and a shorter decay time. Except for the shift of about 10 nm, the two sets of partial amplitudes as a function of the wavelengths displayed are completely identical (Fig. 4B). The observed shift of the *meta*-substituted compared to the *para*-substituted dendrimers relates to the shift observed in the stationary emission spectra.

When the partial amplitude of this second component for the mono-chromophoric compounds (*m*-G1R1, ■; *p*-G1R1, □) is plotted as a function of the excitation energy at the two considered emission wavelengths, no dependence can be observed (Fig. 6A and B). So in both cases, only a contribution of the vibrational relaxation process 2a can be seen.

Comparing the τ_2 decay times of the multi-chromophoric compounds, again a decrease can be found (Table 1) in the same order of magnitude for both the *meta*- and *para*-substituted series of dendrimers. This means that in both types of molecules, *meta*- and also *para*-substituted, the singlet–singlet annihilation process 2b is present. The decrease of the overall decay time by adding more chromophores at the rim has been explained by the increase of the relative contribution of the annihilation compared to the vibrational relaxation. This is of course still valid in both series of dendrimers. Fig. 4B displays the partial amplitudes for the multi-chromophoric compounds *p*-G1R4 (△) and *m*-G1R4 (▲) as a function of the detection wavelength. Although it is clearly visible that the overall shapes are identical, two differences can be seen. First, the same shift of 10 nm of the *meta*-substituted compounds compared to the *para*-substituted ones can be observed again, as it was also the case in the mono-chromophoric dendrimers. Second, the positive amplitude is higher for the *p*-G1R4, comparing identical excitation energies. This effect can also be observed in Fig. 6A and B where the amplitude a_2 is displayed as a function of the excitation energy at the two detection wavelengths considered. At both detection wavelengths, the curve for *p*-G1R4 has a larger positive amplitude compared to *m*-G1R4. This means that due to the different substitution, the annihilation process is becoming more important. This can be explained by the fact that in the *para*-substituted series compared to the *meta*-substituted series, the better orientation of the transition dipoles of the peryleneimide chromophores results in a more efficient annihilation. A similar effect was observed for singlet energy hopping [16].

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