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Direct proof of electron transfer in a rigid first generation triphenyl amine core dendrimer substituted with a peryleneimide acceptor †

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The combination of nanosecond transient absorption experiments and single photon timing experiments proved the occurrence of an electron transfer process in the triphenyl amine core dendrimer, $N1P_1$, by demonstrating the presence of an ion-pair absorption for $N1P_1$ in solvents of medium polarity. By means of femtosecond transient absorption measurements the rise time of this ion-pair absorption dominated by the radical anion absorption could be determined, resulting in a value of 180 ps in MeTHF and 138 ps in THF. Furthermore, in femtosecond fluorescence upconversion as well as in monochromatic femtosecond transient absorption, a few ps component was resolved which was assigned to a vibrational and solvent relaxation process of the locally excited singlet state of the peryleneimide.

Introduction

Electron transfer processes have already been investigated in a variety of covalently[1-4] and supramolecularly[5,6] linked electron donors and acceptors. Within the research group, dendrimers consisting of a rigid central sp^3-carbon core substituted with peryleneimide chromophores at the rim were investigated by single-molecule[7] and time-resolved spectroscopy.[8-11] Upon excitation of the peryleneimide chromophore energy hopping[8] and singlet–singlet exciton annihilation[9] were observed. Substituting the central sp^3-carbon core with a terrylenediimide chromophore led to the observation of directional energy transfer[12,13] between a peryleneimide donor and a terrylenediimide acceptor. In order to investigate photo-induced charge separation and charge recombination processes in peryleneimide dendrimers, a dendrimer with a triphenyl amine core, acting as an electron donor and decorated with one peryleneimide chromophore, acting as an electron acceptor has been chosen. The triphenyl amine moiety is an important hole-transport material in electrographic and electroluminescent devices[14,15] and as such creates an opportunity to use this type of dendrimer as electronic material.

The occurrence of a photo-induced electron transfer process in a first generation dendrimer with a triphenyl amine core substituted with one peryleneimide chromophore at the rim ($N1P_1$, see Scheme 1A) in a solvent of medium polarity, has already been inferred from fluorescence decay measurements.[16] It should be pointed out that as a result of the synthesis, $N1P_1$ is present as a mixture of two constitutional isomers. However, to prove directly that the nanosecond or subnanosecond fluorescence quenching is related with the formation of a radical-ion-pair, monochromatic and polychromatic femtosecond transient absorption measurements were now performed in two solvents of different polarity.

For the attribution of the different kinetic components and spectral features, comparison with the model compound m-$C1P_1$[8,9] (see Scheme 1B) was made. This model compound has the same dendritic structure and substitution pattern of the peryleneimide chromophore as $N1P_1$, with the exception of the nitrogen core being replaced by an sp^3-carbon core.

The electron transfer process is monitored by steady state and nanosecond to femtosecond time-resolved spectroscopy. As the presence of oxygen modified the kinetics of the different photo-induced processes occurring on a nanosecond time scale in this dendrimer,[16] the measurements were performed on both deoxygenated and aerated solutions of $N1P_1$.

## Experimental

Synthesis and steady state measurements

The synthesis of the aminecore dendrimer ($N1P_1$) and the model compound (m-$C1P_1$) bearing one peryleneimide (PI) chromophore at the rim has been reported elsewhere.[17,18]

Steady state absorption and corrected fluorescence spectra were recorded with Lambda 40 (Perkin Elmer) and Fluorolog spectrophotometers, respectively. The solutions obtained by dissolving the dendrimers in two different solvents [tetrahydrofuran (THF) and 2-methyltetrahydrofuran (MeTHF): spectroscopic grade] had an optical density below 0.1 at the absorption maximum in a 1 cm cuvette which corresponds to a concentration of about 2.5×10^{-6} M. The fluorescence quantum yields have been determined using Rhodamine 101 and Cresyl Violet Perchlorate as a reference.[19]

Picosecond and femtosecond time-resolved experiments

The fluorescence decay times of this amine core dendrimer ($N1P_1$) in the two solvents have been determined by the single-photon-timing method (SPT) described previously in detail.[20] In brief, the second harmonic of a Ti : sapphire laser (Tsunami, Spectra Physics) has been used to excite the samples at 488 nm with a repetition rate of 4 MHz. The detection system consists of a subtractive double monochromator (9030DS, Sciencetech) and a microchannel plate photomultiplier (R3809U, Hamamatsu). A time-correlated single photon timing PC
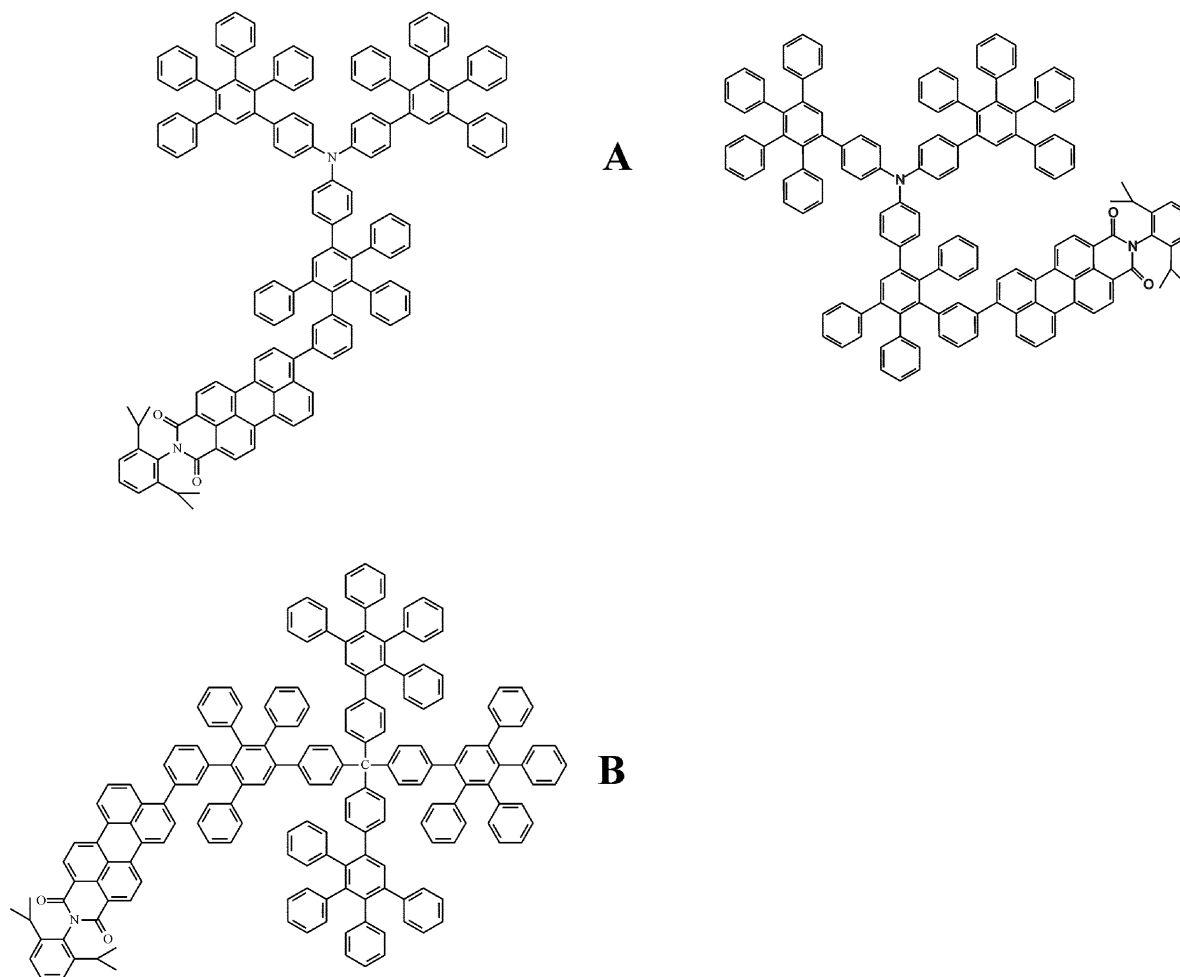
Scheme 1 Molecular structures of the two constitutional isomers of **N1P$_1$** (A) and the model compound **m-C1P$_1$** (B).

module (SPC 630, Picoquant) was used to obtain the fluorescence decay histogram in 4096 channels. The fluorescence decays were recorded with 10,000 counts in the peak channel in two different time windows and analyzed globally with a time resolved fluorescence analysis (TRFA) software[21] based on iterative reconvolution with the pulse. The full width at half-maximum (FWHM) of the IRF was typically in the order of 40 ps. The quality of the fits has been judged by the fit parameters χ^2 (< 1.2), $Z \chi^2$ (< 3) and the Durbin Watson parameter (1.8 < DW < 2.2) as well as by the visual inspection of the residuals and autocorrelation function.[22] All measurements were performed in 1 cm optical path length cuvettes on solutions of **N1P$_1$** in THF and MeTHF at an optical density of *ca.* 0.1 at the excitation wavelength 488 nm, which is very close to the absorption maximum. Deoxygenating was done by consecutive freeze–pump–thaw cycles.

In order to achieve a sufficient time resolution to extract complete information on the different kinetic processes in these dendrimers, femtosecond fluorescence upconversion experiments were performed. The fluorescence upconversion detection setup has also been described in detail in a previous publication.[23] 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 *ca.* 250 fs. This value was used in the analysis of all measurements for deconvolution of the data sets. The measurements were performed in

1 mm optical path length cuvettes and the optical density of the solutions was *ca.* 0.4 per mm at the excitation wavelength of 495 nm.

Nanosecond transient absorption and delayed fluorescence experiments

All measurements were performed in 1 cm optical path length cuvettes. The optical density of the solutions was *ca.* 1.0 at the excitation wavelength of 532 nm. Deoxygenation of the solutions was performed by bubbling argon for 30 min. The setup has been described previously in detail.[24,25] In brief, a Spectra physics DCR 3 pulsed Nd : YAG laser was used as an excitation source. Using a SHG-2 Harmonic Generator the fundamental of 1064 nm (10 Hz, 8 ns) was frequency doubled to 532 nm. A non-focused laser pulse of 20 mJ was used to excite the sample. For the transient absorption measurements an intense and relatively flat pulse of the analytical light with a duration of 1–10 ms was generated using a pulsed 450 W xenon lamp (Müller Elektronik-Optik SVX 1450 with MSP 05 pulsing unit). By means of OMA III system[26] (EG&G) the spectrum is analysed simultaneously over the whole wavelength region (350–750 nm). The delay between the laser pulse and the recording of the spectrum can be varied using a high-voltage pulse generator (model 1302 with 10 ns gate) and an intensified silicon photodiode array detector (model 1420).

Femtosecond monochromatic and polychromatic transient absorption measurements

The amplified femtosecond double OPA laser system has been described in detail previously.[27] 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 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: where at one delay position, four spectra were recorded with the CCD-camera consecutively. 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 with only the excitation. 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 ratio. This was done for 60 equally distant delay positions in four different time windows.

The single wavelength measurements were performed by passing the probing white light continuum through a monochromator while using a photomultiplier tube (R1527p, Hamamatsu) as detector. 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).

By appropriate filtering the probing wavelength was reduced to the range between 475 and 660 nm in the monochromatic transient absorption measurements. All measurements were performed at room temperature in 1 mm optical path length cuvettes under magic angle polarization conditions. All compounds were dissolved in THF and MeTHF at a concentration that yielded an absorption of *ca.* 0.4 per mm at the excitation wavelength of 495 nm. To avoid photodegradation of the compounds, the experiments were performed at low excitation fluxes ($< 1.2 \ \mu W \ mm^{-2}$).

Results and discussion

Stationary measurements

The normalized steady-state absorption and emission spectra of **N1P₁** and **m-C1P₁** in toluene, THF and MeTHF are displayed in Fig. 1A and 1B, respectively. The quantum yield of fluorescence in aerated solutions of **N1P₁** decreases from 1 in toluene to 0.08 in MeTHF. For the emission spectra a bathochromic shift of 10 nm in MeTHF and 15 nm in THF compared to toluene is observed. This bathochromic shift is also observed for the model compound, which indicates that the excited state dipole moment of the peryleneimide is slightly larger than that of the ground state.

The quantum yield of fluorescence of the model compound is within experimental error 1 in toluene, THF and MeTHF.

Single photon timing

The fluorescence decays of the aerated and deoxygenated solutions of **N1P₁** in THF and MeTHF were determined by single photon timing (SPT) and femtosecond fluorescence upconversion experiments. To capture the different kinetic components as precisely as possible, the measurements were performed in a long (130 ns) and a short (24 ns) time window for SPT experiments in the MeTHF solution of **N1P₁**, and a 130 ns and 12 ns time window for the THF solution of **N1P₁**. The short time window corresponds to 6 ps ch⁻¹ and 3 ps ch⁻¹ for the solutions of **N1P₁** in MeTHF and THF, respectively.

Table 1 Decay times of the fluorescence decays measured between 600 and 635 nm with λ_{exc} = 488 nm for the deoxygenated and aerated solutions of **N1P₁** in MeTHF (time increment = 6 ps, long decay times determined in 130 ns time window). The variation of the pre-exponentials is given in Fig. 2

	Aerated	Deoxygenated
τ_1/ns	36	15
τ_2/ns	4.5	4.4
τ_3/ns	0.21	0.19
τ_4/ns	0.07	0.06

Table 2 Fit parameters of the fluorescence decays measured at 580 nm with λ_{exc} = 488 nm for the deoxygenated and aerated solutions of **N1P₁** in THF (time increment = 3 ps)

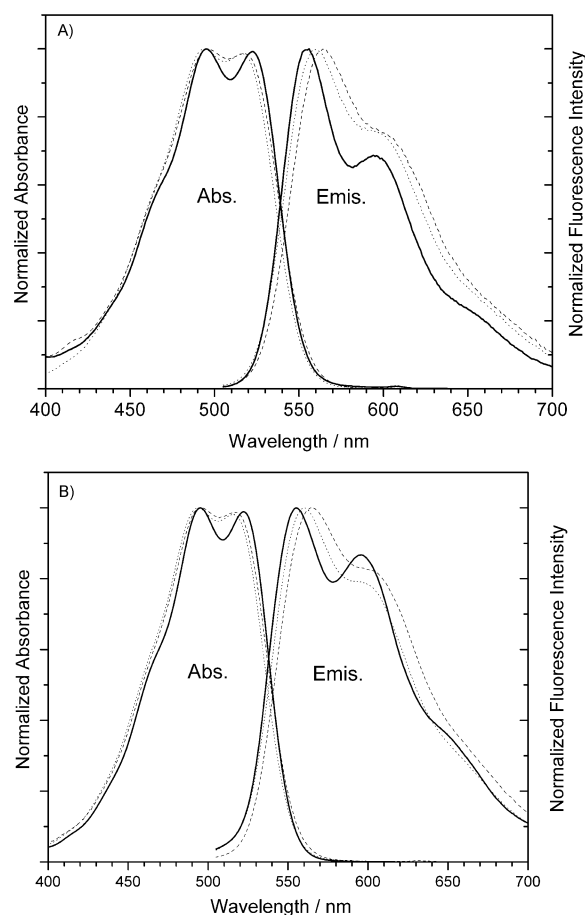|	Aerated	Deoxygenated
τ_1/ns	5.1	4.4
τ_2/ns	0.20	0.18
τ_3/ns	0.09	0.08
$^a a_1$	0.007	0.02
$^a a_2$	0.55	0.64
$^a a_3$	0.44	0.34

a Relative amplitude.

Fig. 1 Normalized steady-state absorption and emission spectra for **N1P₁** (A) and **m-C1P₁** (B) in toluene (line), MeTHF (dot) and THF (dash). The emission spectra were excited at a wavelength of 495 nm.

Global analysis of the single photon decay traces required a four-exponential decay for **N1P₁** in MeTHF and only a three-exponential decay for **N1P₁** in THF. The results are depicted in Tables 1 and 2.

The wavelength dependence of the amplitudes of the four decay components for **N1P₁** in deoxygenated MeTHF is shown in Fig. 2.
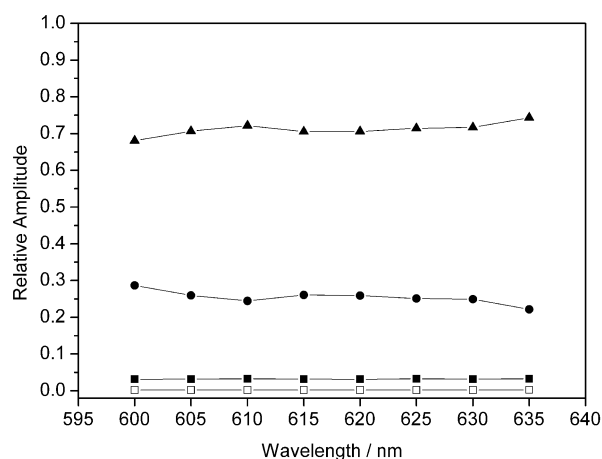
Fig. 2 Wavelength dependence of the partial amplitudes of the decay times of the deoxygenated solution of **N1P$_1$** in MeTHF determined by SPT. 70 ps component (●), 210 ps component (▲), 4.5 ns component (■), 36 ns component (□).

The relative amplitudes of the different components of the decay are identical over the whole wavelength region of the emission band. As discussed in a previous publication,[16] the four decay times are related to the presence of two constitutional isomers, each displaying a biexponential fluorescence decay. The biexponential fluorescence decay of each isomer was interpreted as evidence for intramolecular charge separation from an excited state to an ion-pair state and subsequent thermally activated repopulation of the excited initial state, leading to a prompt and a delayed fluorescence component[28–30] (Scheme 2).
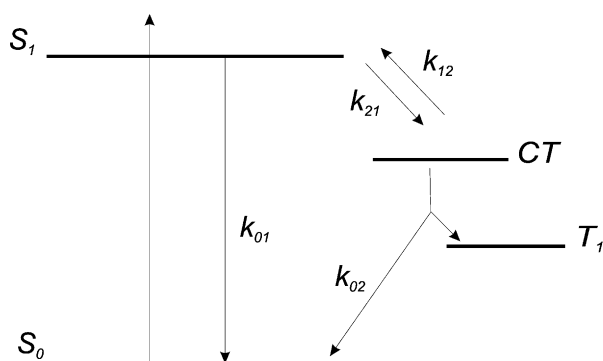
Scheme 2 Kinetic scheme of the different photophysical processes with corresponding rate constants occurring in **N1P$_1$**.

The observation of three instead of four components for **N1P$_1$** in THF can be explained by the impossibility to resolve the two decay times related to the delayed fluorescence due to a small difference between both decay times and/or their small amplitudes (0.7 and 2% in deoxygenated and aerated solutions, respectively). The relative contribution of the long ns decay times of **N1P$_1$** in both THF and MeTHF has decreased, compared to their contribution in the less polar solvent diethylether.[16]

For the different possible combinations of decay times, one can calculate[28,29,31,32] the rate constants of charge separation (k_{21}), charge recombination (k_{12}) and the rate of recombination to the ground state or a triplet state (k_{02}) as well as the free enthalpy change of the charge separation (ΔG_{CS}). The results of these calculations for the deoxygenated and aerated solution of **N1P$_1$** in MeTHF are presented in Table 3 and 4.

The calculations have been done using a value of 2.27×10^8 s^{-1} (2.38×10^8 s^{-1}) for k_{01} corresponding to the inverse decay time of 4.4 ns (4.2 ns) obtained in deoxygenated (aerated) MeTHF for **m-C1P$_1$** (see Table 5).

Table 3 Calculated rate constants, equilibrium constant of charge separation (K_{CS}) and free enthalpy change of charge separation (ΔG_{CS}) of the deoxygenated solution of **N1P$_1$** in MeTHF

	τ_1 and τ_3	τ_2 and τ_4	τ_1 and τ_4	τ_2 and τ_3
$k_{01}/10^7$ s^{-1}	23 ± 1	23 ± 1	23 ± 1	23 ± 1
$k_{21}/10^7$ s^{-1}	450 ± 10	1230 ± 20	1360 ± 10	430 ± 50
$k_{12}/10^7$ s^{-1}	1.2 ± 0.1	130 ± 30	8.1 ± 0.2	20 ± 1
$k_{02}/10^7$ s^{-1}	2.7 ± 0.2	22 ± 1	2.7 ± 0.2	22 ± 1
K_{CS}	375	9.3	165.8	21.9
ΔG_{CS}/kcal mol^{-1}	−3.5	−1.3	−3.0	−1.8

Table 4 Calculated rate constants, equilibrium constant of charge separation (K_{CS}) and free enthalpy change of charge separation (ΔG_{CS}) of the aerated solution of N1P$_1$ in MeTHF

	τ_1 and τ_3	τ_2 and τ_4	τ_1 and τ_4	τ_2 and τ_3
$k_{01}/10^7$ s^{-1}	24 ± 1	24 ± 1	24 ± 1	24 ± 1
$k_{21}/10^7$ s^{-1}	500 ± 10	1210 ± 10	1620 ± 10	480 ± 10
$k_{12}/10^7$ s^{-1}	1.0 ± 0.1	430 ± 10	24 ± 2	23 ± 1
$k_{02}/10^7$ s^{-1}	6.6 ± 0.2	22 ± 1	6.4 ± 0.2	23 ± 1
K_{CS}	501	2.8	68.6	21.1
ΔG_{CS}/kcal mol^{-1}	−3.7	−0.6	−2.5	−1.8

Two different combinations of decay times are possible for **N1P$_1$** in deoxygenated MeTHF: (i) the combination τ_1 with τ_3 and τ_2 with τ_4 and (ii) the combination τ_1 with τ_4 and τ_2 with τ_3. Both combinations yield positive rate constants. For both combinations the calculated rate constants k_{21} and k_{02} in MeTHF increase as compared to diethylether,[16] as expected on the basis of the higher polarity of MeTHF. However, for the first combination (τ_1 with τ_3 and τ_2 with τ_4), an increase in k_{12} is observed instead of the expected decrease of the back reaction rate. Therefore the combination τ_1 with τ_4 and τ_2 with τ_3 is the most likely one. The smaller solvent effect on k_{21} compared to k_{02}, which describe both exergonic processes, is due to the fact that while the exergonicity of the first process (charge separation) is situated in the "inverse" Marcus region ($\Delta G_{21} = -2 \pm 1$ kcal mol^{-1}), that of the second one (recombination to the ground state) is situated in the "normal" Marcus region ($\Delta G_{02} = -55 \pm 2$ kcal mol^{-1}).

For **N1P$_1$** in aerated MeTHF, again two different combinations of decay times are possible, both yielding positive rate constants: (i) the combination τ_1 with τ_3 and τ_2 with τ_4 and (ii) the combination τ_1 with τ_4 and τ_2 with τ_3. Also for **N1P$_1$** in aerated MeTHF the second combination (τ_1 with τ_4 and τ_2 with τ_3) has the highest probability for the same reasons as described above for **N1P$_1$** in deoxygenated MeTHF. When comparing the calculated rate constants of the aerated and deoxygenated solution of **N1P$_1$** in MeTHF, one can observe that within experimental error, little to no changes occur in k_{21}, k_{12} and K, as expected. For k_{02} a decrease is observed upon deoxygenating. An overview of the decay times has been accumulated in Table 5.

Femtosecond fluorescence upconversion

To reveal possible ultrafast processes occurring on a time scale less than 20 ps, femtosecond fluorescence upconversion measurements were performed on the aerated solution of **N1P$_1$** in THF. By global analysis, an additional short 4 ps component was revealed (see Table 5). The amplitudes of the different decay components are depicted in Fig. 3.

The 80 and 186 ps components, corresponding to the values found by SPT, are the decay times of the direct fluorescence of the two isomers of **N1P$_1$** quenched by intramolecular electron transfer. The shape and the positive/negative amplitude behavior of the 4 ps component is characteristic for a vibrational and solvent relaxation process in the electronically excited state of the peryleneimide chromophore.[9,33–36] Finally a

Table 5 Overview of the different spectroscopic techniques used and the measured decay times

Technique	Compound	Decay time
SPT	Deoxygenated **N1P1** in MeTHF	210 ps/70 ps 36 ns/4.5 ns
	Aerated **N1P1** in MeTHF	190 ps/60 ps 15 ns/4.4 ns
	Deoxygenated **N1P1** in THF	200 ps/90 ps 5.1 ns
	Aerated **N1P1** in THF	180 ps/80 ps 4.4 ns
	Deoxygenated *m*-**C1P₁** in MeTHF	4.4 ns
	Aerated *m*-**C1P₁** in MeTHF	4.2 ns
fs- Fluorescence Upconversion	Aerated **N1P1** in THF	186 ps/80 ps 4 ps 0.5 – 2 ps
fs- Transient Absorption	Deoxyg./Aerated **N1P1** in MeTHF	ns component 180 ps 4 ps
	Deoxyg./Aerated **N1P1** in THF	ns component 138 ps 2 ps
	Aerated *m*-**C1P₁** in MeTHF	ns component 4 ps
	Aerated *m*-**C1P₁** in THF	ns component 2 ps
ns- Transient Absorption	Deoxygenated **N1P1** in MeTHF	100 μs 37 ns
	Aerated **N1P1** in MeTHF	200 ns
	Aerated **N1P1** in THF	200 ns
ns- Delayed Fluorescence	Deoxygenated **N1P1** in MeTHF	33 ns
	Aerated **N1P1** in MeTHF	22 ns

Fig. 3 Wavelength dependence of the partial amplitudes of the decay times of the aerated solution of **N1P₁** in THF determined by femtosecond fluorescence upconversion. 4 ps component (Δ), 80 ps component (●), 186 ps component (▲).

Fig. 4 Three dimensional display of the transient absorption spectra for the model compound *m*-**C1P₁** in MeTHF (A) and THF (B).

fourth ultrashort component—not displayed in Fig. 3—varying from 500 fs at short fluorescence detection wavelengths to 2 ps at longer fluorescence detection wavelengths was observed. This ultrashort component bears the same characteristics as the ultrafast component encountered in the carbon core dendrimers[9–11] and can therefore be attributed to an intramolecular vibrational redistribution (IVR) process in the electronically excited state of the peryleneimide chromophore.[37,38]

Transient absorption

The femtosecond transient absorption spectra (polychromatic transient absorption.) were recorded at 60 delay positions in time windows of 5, 50, 420 and 1400 ps at a 495 nm excitation wavelength. More detailed kinetic information (monochromatic transient absorption) was obtained by measurements at 1024 delay positions. In the transient absorption spectra of the model compound (*m*-**C1P₁**) in MeTHF (Fig. 4A) and THF (Fig. 4B) two different bands can be observed.

Both bands can be seen instantaneously after excitation and decay on a nanosecond time scale. The negative band has con-
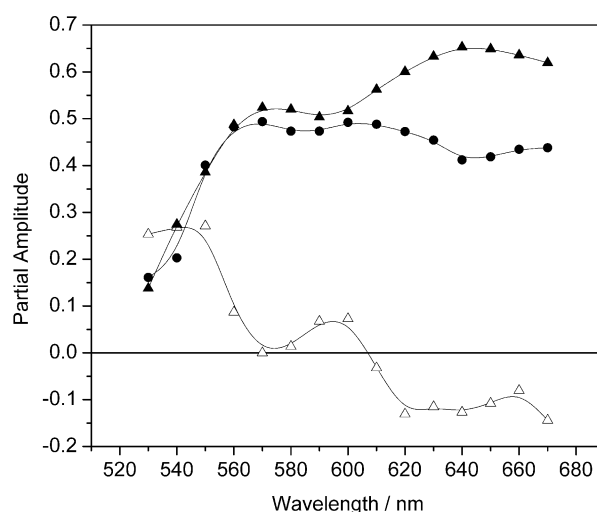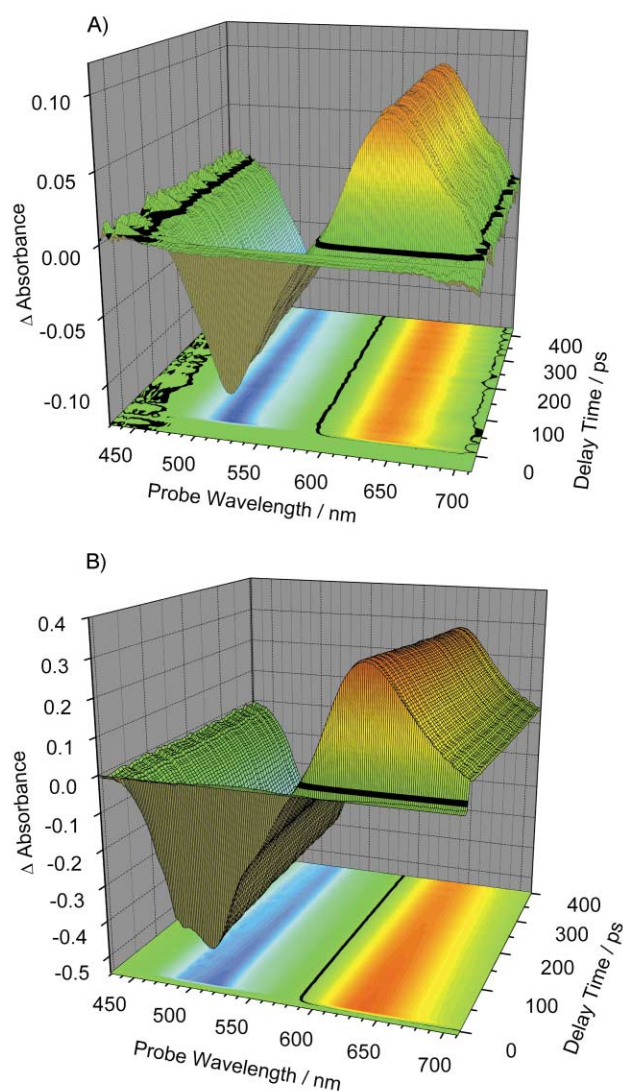
tributions from the ground-state depletion and stimulated emission. The positive band can be attributed to a S^1–S^n absorption band of the peryleneimide chromophore. The high fluorescence quantum yield excludes the occurrence of any intermediates. In

the model compound no change occurs in the S^1–S^n absorption band over time.

The transient spectra of the triphenyl amine core dendrimer **N1P1** in deoxygenated toluene, presented in Fig. 5, display the same features as its model compound, indicating that no electron transfer occurs in toluene.
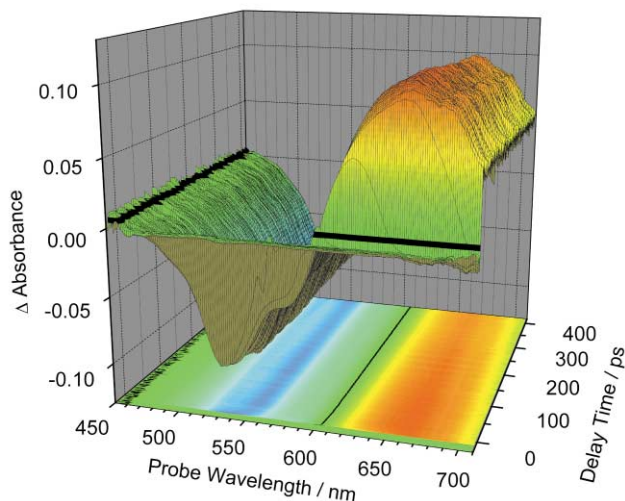

Fig. 5 Three dimensional display of the transient absorption spectra for the deoxygenated solution of **N1P1** in toluene.

The transient spectra of **N1P1** in deoxygenated MeTHF, depicted in Fig. 6B, however, show clearly different features. Here we observe on a picosecond time scale a decrease of the S^1–S^n absorption band of the peryleneimide chromophore and an increase of a new absorption band, displayed in detail in Fig. 6A, situated hypsochromic of the S^1–S^n absorption band. This new absorption band has its absorption maximum at 620 nm.

The radical anion absorption band of the peryleneimide is characterized by an absorption maximum at 600 nm.[39] The observation of this maximum at longer wavelengths of this radical anion could be due to the overlap with the absorption band of the triphenylamine radical cation with absorption maxima at 400, 700 and 770 nm,[40,41] as discussed in a previous publication.[16] Hence, this new absorption band observed in fs-T.A. spectrum of **N1P1** in MeTHF can be attributed to the radical anion absorption band of the peryleneimide. This band corresponds to the absorption band observed in ns-transient absorption measurements (insert in Fig. 7).

The growing in of this radical anion absorption band, as shown in Fig. 8, is also observed for **N1P1** in THF.

To estimate the rise time of the ion-pair absorption band, the positive absorption band was Gauss-deconvoluted in two bands. One of these two bands rises in function of time, the other one decays in function of time. The numerical fit of the band which increases in intensity yielded a rise time of 147 ps in THF and 165 ps in MeTHF (Fig. 9).

To obtain more accurate information on the rise time of the peryleneimide radical anion absorption band, monochromatic transient absorption experiments were performed at different wavelengths throughout the positive absorption band observed by polychromatic transient absorption experiments. These monochromatic T.A. experiments were performed on the aerated and deoxygenated solutions of **N1P1** in MeTHF (Fig. 10A) and THF (Fig. 10B) and compared to the model compound **m-C1P1** (see Table 5).

As described previously,[16] a long ns component found in the SPT-experiments can be attributed to delayed fluorescence, arising from the back reaction from the charge separated state to the locally excited state and has been kept fixed in the global analysis of the monochromatic T.A. decay traces.

As can be seen in Fig. 10A and B, a new kinetic component is observed in **N1P1** compared to the model compound.
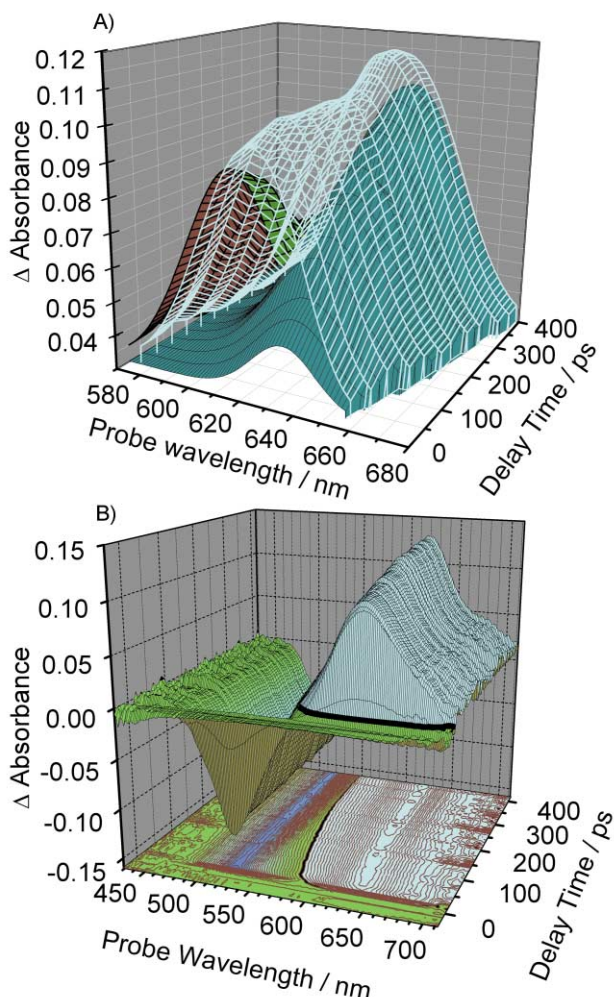
Fig. 6 Three dimensional display of the transient absorption spectra for the deoxygenated solution of **N1P1** in MeTHF (B) and close-up of the positive band (cyan) (A) S^1–S^n absorption band (green), peryleneimide radical anion absorption band (dark gray) and the sum of the two absorption bands (cyan).

This 180 ps component—in MeTHF—can therefore be attributed to the formation of the radical anion absorption band. At short wavelengths, this component has a large negative amplitude, due to the small amplitude of the S^1–S^n absorption band at short wavelengths. At long wavelengths a positive amplitude for this 180 ps component is observed due to the dominance of the S^1–S^n absorption band at these wavelengths. In the more polar solvent THF, a shorter rise time of 138 ps has been found. Deoxygenating the **N1P1** solutions has in this case little to no influence on the wavelength dependency of the amplitude and decaytime of the electron transfer component. Because of the existence of two **N1P1** isomers this electron transfer (180 ps in MeTHF/138 ps in THF) component is in fact a combination of two electron transfer components each belonging to a separate **N1P1** isomer. The 180 ps and 138 ps component are average rise times over the two constitutional isomers. By analyzing the transient absorption decays with a four-exponential fit function, two electron transfer components of 100 ps and 200 ps emerge in MeTHF (see Fig. 11), consistent with both subnanosecond fluorescence decay times found by SPT measurements.

The short component of 4 ps found for **N1P1** and the model compound (**m-C1P1**) in MeTHF, has a negative amplitude over the whole wavelength region studied of which the absolute value diminishes at longer probe wavelengths. The short 2 ps component observed for **N1P1** and the model compound in THF has a negative amplitude at short wavelengths and a positive amplitude at longer wavelengths (Fig. 10B and 12). The negative/positive amplitude behaviour is more pronounced in
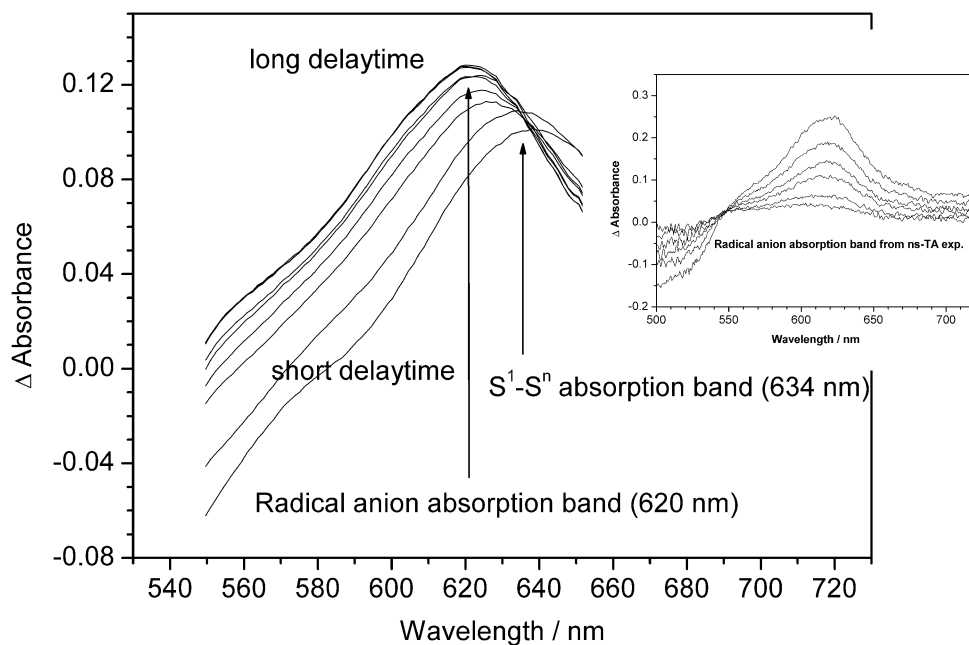
Fig. 7 Radical anion absorption band of the deoxygenated solution of **N1P₁** in MeTHF demonstrated by femtosecond and nanosecond (insert) transient absorption experiments.
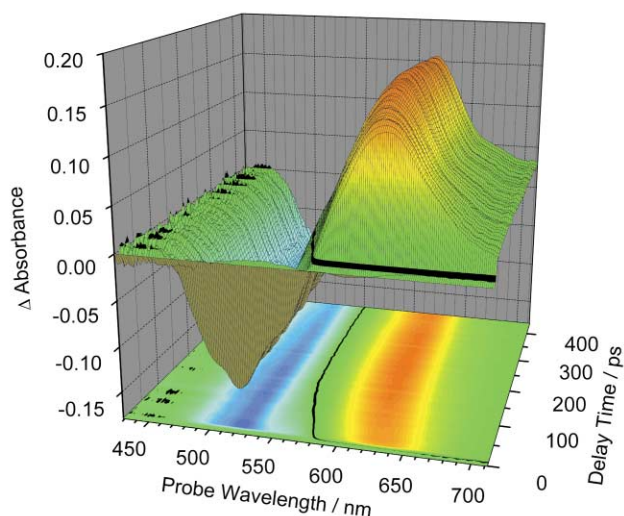

Fig. 8 Three dimensional display of the transient absorption spectra for the deoxygenated solution of **N1P₁** in THF.
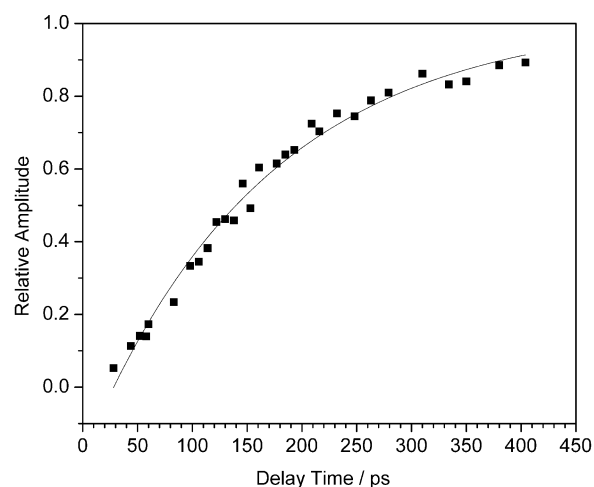

Fig. 9 Mono-exponential fit of the Gaussian bands at different delay times of the radical anion absorption band for the deoxygenated solution of **N1P₁** in MeTHF. The resulting decay time from the fit has a value of 165 ps.
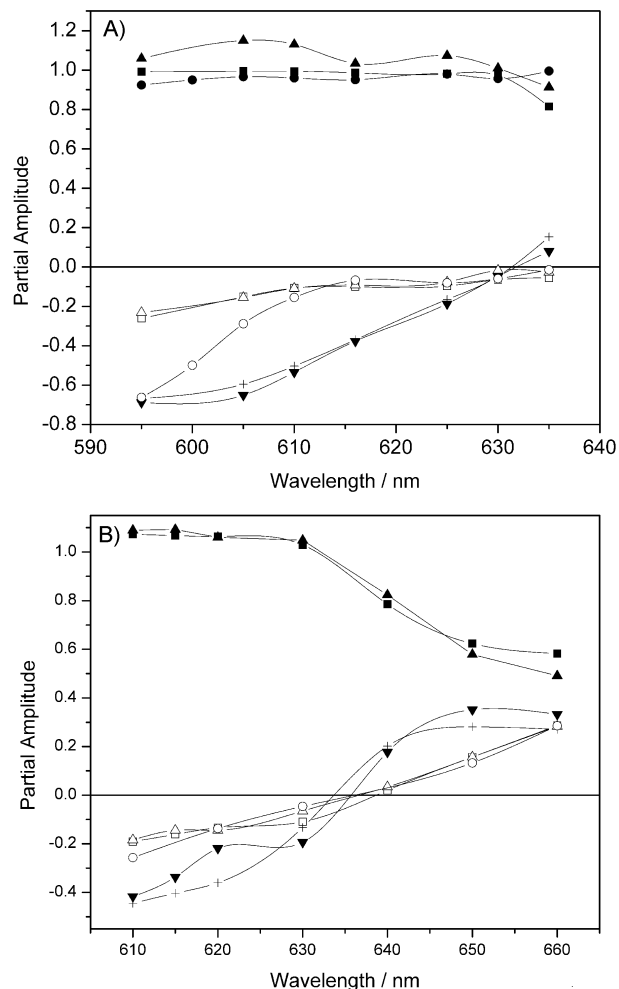

Fig. 10 Wavelength dependence of the partial amplitudes of the decay times of the aerated and deoxygenated solution of **N1P₁** in MeTHF (A) and THF (B) determined by femtosecond transient absorption. Aerated solution of **N1P₁** in MeTHF (THF): ns component (▲), 4 ps (2 ps) component (△), 180 ps (138 ps) component (▼); deoxygenated solution of **N1P₁** in MeTHF (THF): ns component (■), 4 ps (2 ps) component (□), 180 ps (138 ps) component (+); *m*-**C1P₁** in MeTHF (THF): ns component (●), 4 ps (2 ps) component (○).
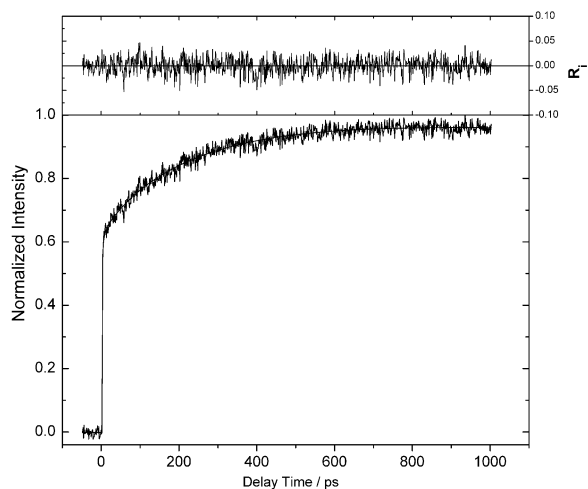
Fig. 11 Four-exponential fit of the monochromatic transient absorption trace of the deoxygenated solution of **N1P$_1$** in MeTHF, probed at 616 nm. The upper panel shows the distribution of weighted residuals (R_i).
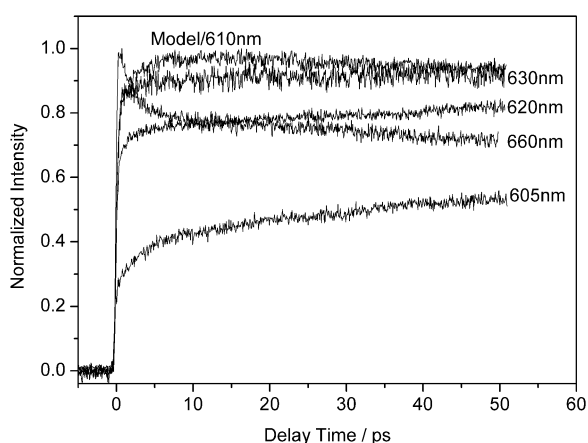

Fig. 12 Monochromatic transient absorption traces of the deoxygenated solution of **N1P$_1$** in MeTHF at 605 nm/630 nm probe wavelength and THF at 620 nm/660 nm probe wavelength and the model compound **m-C1P$_1$** in THF at 610 nm, as indicated in a 50 ps time window. The traces are normalized to their value in the 420 ps time window.

THF compared to MeTHF. It is not related to electron transfer as it gives identical decay times and similar evolution of the amplitudes for **N1P$_1$** and **m-C1P$_1$** (Fig. 10A/B and 12).

The amplitude of this short component is under the experimental conditions independent of the energy of the impinging excitation laser pulse and is therefore not related to biphotonic processes. It can be assigned to the solvation dynamics for a number of reasons. The decreasing magnitude of the decay time of this component with polarity[42] and the −/+ amplitude behavior[9,10] are characteristic features for components arising from vibrational relaxation coupled with a relaxation and reorganization of the solvent shell around the peryleneimide chromophore. In the literature, time constants of the same order of magnitude for solvent relaxation in macromolecular systems have been reported.[43] A difference in short decay time obtained by fs-transient absorption (2 ps) and fs-fluorescence upconversion (4 ps) measurements is observed for **N1P$_1$** in THF. The explanation for this discrepancy is that the 2 ps component retrieved by fs-transient absorption consists of a combination of the ultrashort I.V.R. component and the vibrational/solvent relaxation component. The same discrepancy is observed when comparing the results of the fs-transient absorption and fs-fluorescence upconversion measurements of the model compound **m-C1P$_1$**.

The presence of this short lifetime component in both **N1P$_1$** and **m-C1P$_1$** in THF and MeTHF is also observed when probing in the ground-state depletion band. The results of **N1P$_1$** and **m-C1P$_1$** in MeTHF are depicted in Fig. 13. The short component appears as a rise time when probing in the ground-state depletion band, reflecting the temporal changes in the occupation of the vibrational states in S^1.
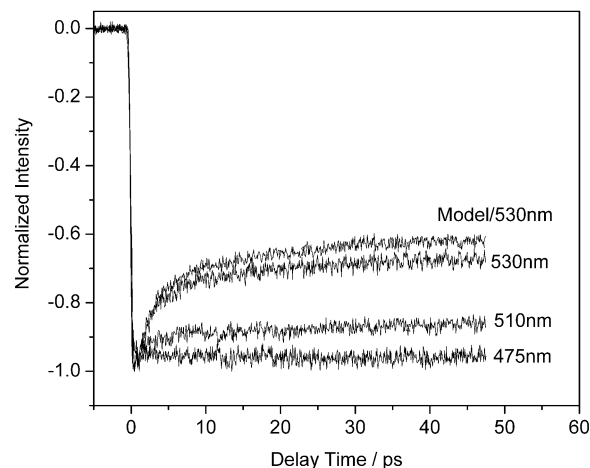

Fig. 13 Monochromatic transient absorption traces of the deoxygenated solution of **N1P$_1$** in MeTHF probed in the ground-state depletion band at 475, 510 and 530 nm and **m-C1P$_1$** in MeTHF probed at 530 nm.

The absolute value of its amplitude diminishes at shorter probe wavelengths, leading to an almost horizontal trace at 475 nm probe wavelength suggesting that the molar extinction coefficient of the S^1- S^n absorption of the peryleneimide and of the radical anion absorption are very similar at this wavelength.

From these observations it is clear that the electron transfer process occurs from the relaxed local singlet excited state.

By ns-T.A. experiments a rate constant of 2.7×10^7 s^{-1} (corresponding to a decay time of 37 ns) has been found for the decay of the peryleneimide radical anion absorption band (Table 5 and Fig. 14) of the deoxygenated solution of **N1P$_1$** in MeTHF.
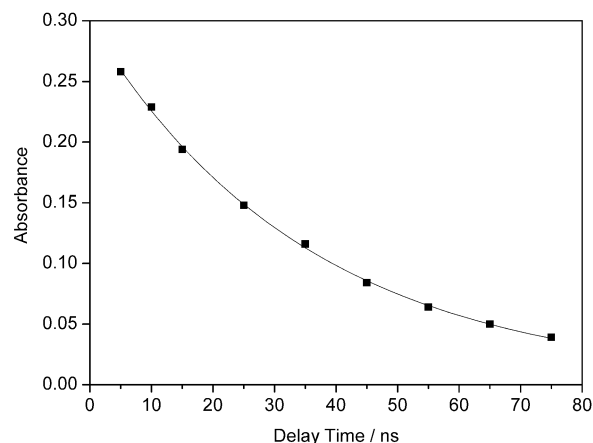

Fig. 14 Plot of the decay of the radical anion absorption band as a function of the delay time for the deoxygenated solution of **N1P$_1$** in MeTHF, determined by nanosecond transient absorption experiments.

The formation and decay of a peryleneimide radical anion absorption band for **N1P$_1$** in THF could not be monitored by ns-transient absorption experiments, indicating a decay of the radical anion on a time scale faster than the resolution of the experimental setup. This corresponds to the SPT experiments suggesting a decay time of 5.1 and 4.4 ns (deoxygenated and aerated, respectively) for the intermediate formed by quenching of the S^1-state of the peryleneimide chromophore. The small amplitude of the slowest two fluorescence decay components

suggests that the back reaction k_{12} is relatively unimportant and hence that the inverse long decay time approaches k_{02}. In the ns-T.A. spectra of the aerated solutions of **N1P₁** in MeTHF and THF, triplet–triplet absorption bands of the peryleneimide are observed (data not shown). The decay time of this triplet in aerated THF and MeTHF is *ca.* 200 ns. In deoxygenated MeTHF the decay of the triplet is *ca.* 100 µs. The formation of a locally excited triplet is already discussed previously[16] and is not the focus of this paper.

Performing ns delayed fluorescence experiments resulted in a mono-exponential decay process (Fig. 15).
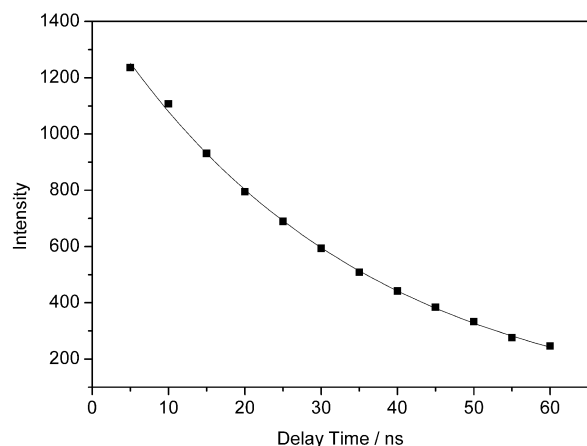

Fig. 15 Plot of the decay of the emission as a function of the delay time for the deoxygenated solution of **N1P₁** in MeTHF, determined by nanosecond delayed fluorescence experiments.

The ns-time resolved emission spectra have the same spectral characteristics as the peryleneimide fluorescence. A rate constant of 3.0×10^7 s^{-1} (corresponding to a decay time of 33 ns) for the deoxygenated **N1P₁** solution in MeTHF and a rate constant of 4.6×10^7 s^{-1} (corresponding to a decay time of 22 ns) for the aerated **N1P₁** solution in MeTHF is obtained (see Table 5). These results correspond well with the results obtained by SPT-experiments and the decay time of peryleneimide radical anion absorption band (*vide supra*).

Conclusions

Polychromatic femtosecond transient absorption measurements have revealed a new transient absorption band in the triphenyl amine core dendrimer **N1P₁**, not present in the corresponding carbon core dendrimer ***m*-C1P₁**. By means of monochromatic femtosecond transient absorption measurements the formation time of this new process could be determined. The process could be identified as an electron transfer process between the triphenyl amine core and the perylenimide chromophore at the periphery. A short decay component found back in **N1P₁** and the model compound ***m*-C1P₁** could be linked to a vibrational relaxation process coupled with solvent relaxation. The electron transfer process appears to start from the relaxed S^1 state of the peryleneimide chromophore.

By calculating the rate constants of charge separation and charge recombination from the SPT data, faster charge separation and recombination to the ground state (or triplet state) has been demonstrated in a more polar solvent.

Acknowledgements

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