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Photoinduced Electron Transfer in a Rigid First Generation Triphenylamine Core Dendrimer Substituted with a Peryleneimide Acceptor

Marc Lor, Jan Thielemans, Lucien Viaene, Mircea Cotlet, Johan Hofkens,
Tanja Weil, Christine Hampel, Klaus Müllen, Jan W. Verhoeven,
Mark Van der Auweraer, and Frans C. De Schryver*

*Contribution from the Department of Chemistry, Katholieke Universiteit Leuven,
Celestijnenlaan 200 F, 3001 Heverlee, Belgium, and Max-Planck-Institut für Polymerschung,
Ackermannweg 10, 55218 Mainz, Germany*

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Abstract: The electron-transfer process of a first generation dendrimer with a triphenylamine core substituted with one peryleneimide chromophore at the rim (**N1P1**) was investigated by steady-state and time-resolved spectroscopic techniques in two different solvents of medium and low polarity. Single photon counting experiments showed a fast charge separation and a thermally activated back reaction, which is uncommon for a polyaryl bridge or long-distance through-space electron transfer. The four exponential fluorescence decay can be traced to the presence of two subsets of molecules, which are constitutional isomers of **N1P1**. Although formally **N1P1** resembles a donor-bridge-acceptor compound, detailed analysis of the data shows that the electron transfer occurs by a through-space mechanism. This amine core dendrimer has peculiar and unique characteristics resulting in the observation of efficient back transfer and delayed peryleneimide fluorescence in diethyl ether at 293 K and very long-lived charge recombination luminescence at 77 K.

Introduction

A large number of covalently[1−40] and supramolecularly[41,42] linked electron donors and acceptors has been investigated with the aim to explore fundamental aspects of (photoinduced) electron transfer and/or to obtain efficient and long living charge

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* To whom correspondence should be addressed. E-mail: frans.deschryver@chem.kuleuven.ac.be.

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separation. To induce rigidity[1−11,19,35] and/or to obtain a better electronic coupling[43−51] between electron donor and acceptor, flexible alkane chains linking donor and acceptor were replaced by oligophenyl,[19,20,22,23,26,27,29−31] oligobenzyl,[32−35] anthryl,[37] or phenanthrolyl[24,25] moieties. The recent synthetic developments in the field of *meta*- and *para*-oligophenylenes[52] allowed for the preparation of dendrimers with chromophores at the edges.[53,54] While those dendrimers showed the formation of intramolecular excimer-like states[54,55] or intramolecular singlet−singlet exciton annihilation,[56,57] substituting them by energy donors and acceptors allowed us to observe the intramolecular energy transfer.[58,59] As the peryleneimide moiety can act as an electron acceptor in the excited state,[60] a dendrimer with a peryleneimide[54] moiety at the edges and an electron-donating core was synthesized. As electron donor, a triphenylamine moiety was chosen because of its importance as a hole transport material in electrophotographic and electroluminescent devices.[61−67] On the other hand, the large (photo)chemical stability makes the peryleneimide an interesting acceptor.

These polyparaphenylene dendrimers are highly rigid and thus conformationally well defined as the steric hindrance of the polyphenylene branches limits the number of stable conformations of each of the branches drastically.[68] On the time scale of the singlet decay (nanoseconds), those conformations will, for the molecules studied in this contribution, behave as a limited number of atropo-isomers characterized by an identical through-bond[14,43−44,47−48,50−51,69] and through-space distance[69,70] between electron donor and acceptor. Hence, this rotational conformational inhomogeneity will only have a limiting influence[7,11,71] on the solution photophysics of the donor−acceptor substituted dendrimers. However, in the present case, the synthesis route, based on a Diels−Alder addition, leads to the formation of two constitutional isomers (see Chart 1) characterized by an identical through-bond distance and a different through-space distance between electron donor and acceptor. The presence of the constitutional isomers can therefore be expected to influence the solution photophysics of donor−acceptor substituted dendrimers. The possible link to electronic materials, as well as the fundamental information that can be extracted from monitoring the photoinduced charge separation and charge recombination in dendrimers with a triphenylamine core, led to the investigation of the steady-state and time-resolved fluorescence of those molecules in two solvents of different polarity.

Experimental Section

Synthesis. The detailed synthesis of the amine core dendrimer bearing one peryleneimide chromophore (**N1P1**) at the rim (Chart 1) is reported elsewhere.[72] Diels−Alder cycloaddition of perylenemonoimide substituted cyclopentadienones to the triphenylamine core leads to two constitutional isomers indicated in Chart 1 as para-meta-meta isomer and para-para-meta isomer. This indicates the connectivity between the amine core and the chromophore in the two dendrimer isomers. As the two-dimensional representation of the molecules does not properly indicate the spatial distance between donor and acceptor, molecular modeling (see Chart 2) has been done. In the para-meta-meta isomer, the donor−acceptor distance is about 2 Å smaller than that in the para-para-meta isomer. The distance between the amine core and the center of the dye (**PI**) has been measured on the three-dimensional structures obtained by Merck molecular force field calculations.[73]

Steady-State Measurements. Steady-state absorption and corrected fluorescence spectra were recorded with Lambda 40 (Perkin-Elmer) and Fluorolog (SPEX) spectrophotometers, respectively. The solutions obtained by dissolving the dendrimers in two different solvents (toluene and diethyl ether, 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 a peryleneimide meta-substituted polyphenylene dendrimer (***m*-G1R1**) as a reference.[54] This reference has the same structure as **N1P1**, except the nitrogen core is replaced by a sp^3-carbon core.

Picosecond Time-Resolved Experiments. The fluorescence decay times and time-resolved fluorescence spectra of this amine core dendrimer (**N1P1**) in the two solvents have been determined by the

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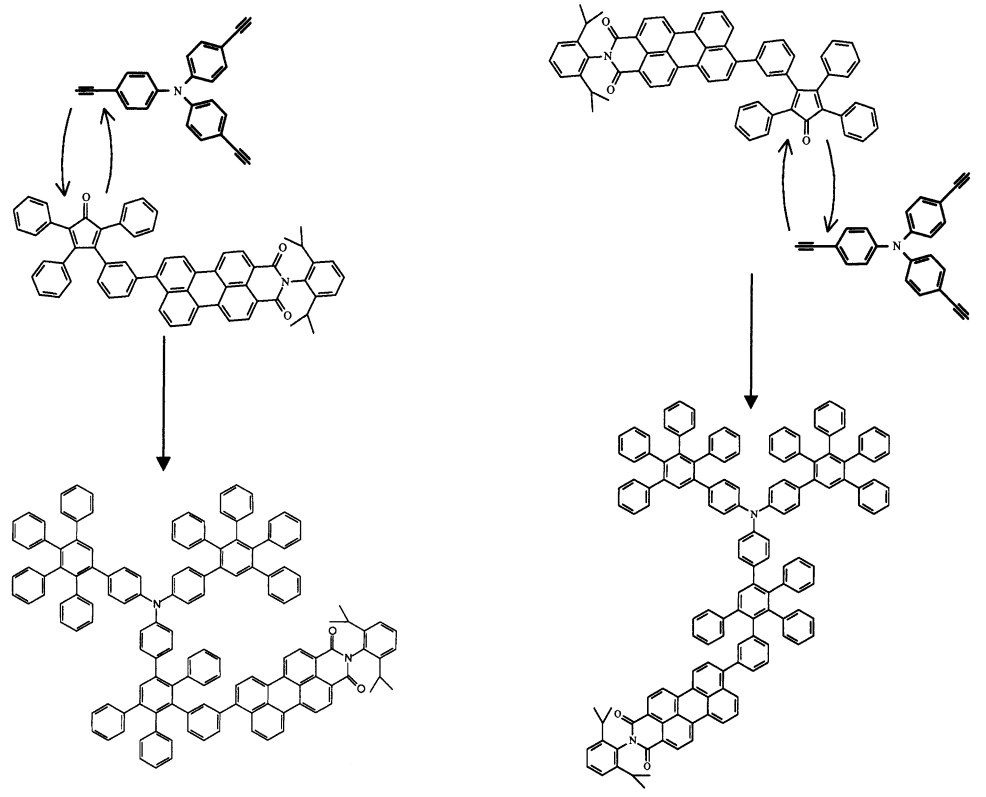
Chart 1



Para,meta,meta isomer

Para,para,meta isomer

single photon counting method (SPC) described previously in detail.[74] 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 4.09 MHz. The detection system consists of a subtractive double monochromator (9030DS, Sciencetech) and a microchannel plate photomultiplier (R3809U, Hamamatsu). A time-correlated single photon counting PC module (SPC 630, Picoquant) was used to obtain the fluorescence decay histograms in 4096 channels. In combination with the stepper motor controller device SM (STP 240, Picoquant GmbH), which sets the monochromator wavelength, the SPC card enables us to record time-resolved emission spectra on the picosecond to microsecond time scale. The fluorescence decays were recorded in two different time windows and analyzed globally with a time-resolved fluorescence analysis (TRFA) software.[75] The quality of the fits has been judged by the fitting parameters such as χ^2 (<1.2), $Z\chi^2$ (<3), and the Durbin Watson parameter ($1.8 < \mathrm{DW} < 2.2$), as well as by the visual inspection of the residuals and autocorrelation function.[76] All measurements were performed in 1 cm optical path length cuvettes and dissolved in the two solvents at an optical density of ca. 0.1 at the excitation wavelength 488 nm. Deoxygenating was done by consecutive freeze−pump−thaw cycles.

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 532 nm. Deoxygenation of the solutions was performed by bubbling argon for 30 min. The setup has been described previously in detail.[77,78] In brief, a Spectra physics DCR 3 pulsed Nd:YAG laser was used as an excitation source. Using a SHG-2 Harmonic Generator, we frequency doubled the fundamental of 1064 nm (10 Hz, 8 ns) to 532 nm. The nonfocused laser pulse of 20 mJ was used to excite the sample. For the transient absorption measurements, an intense and narrow (1−10 ms) pulse of the analytical light 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[79] (EG&G), the spectrum is analyzed 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).

Results and Discussion

The steady-state absorption and emission spectra of **N1P1** in toluene and diethyl ether are depicted in Figure 1. A small hypsochromic shift is observed in diethyl ether as compared to toluene. The quantum yield of fluorescence in *aerated* solutions decreases with increasing polarity of the solvent from 1 in toluene to 0.6 in diethyl ether. This suggests the occurrence of electron transfer in the more polar solvent because the fluorescence quantum yield of the peryleneimide chromophore itself equals 1, independent of the solvent. Amazingly, however, degassing the ether solution of **N1P1** increases the fluorescence quantum yield from 0.6 for the *aerated* diethyl ether solution to virtually 1 for the *deoxygenated* solution. At first sight, this might suggest that no electron transfer occurs in the absence of oxygen, which would be very unusual. As will be shown below,

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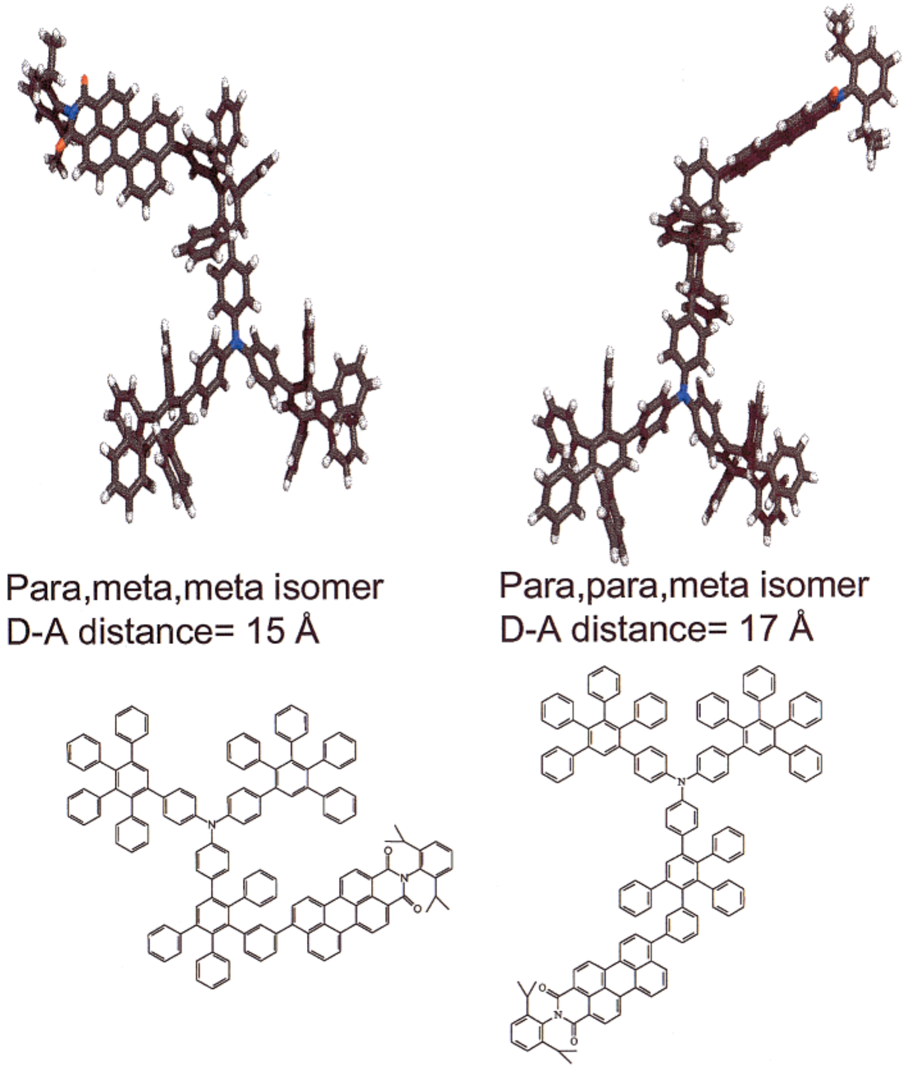
Chart 2



however, electron transfer is not at all impeded by deoxygenation, but instead this leads to the occurrence of delayed local fluorescence to such an extent that the overall fluorescence quantum yield reaches almost unity.

To investigate the properties of the fluorescent states for the dendrimer more closely, the fluorescence decays were determined in *aerated* solutions of toluene and *aerated* and *deoxygenated* solutions of diethyl ether. In toluene, the fluorescence decay of **N1P1** can be analyzed as a single-exponential decay with a decay time of 4.1 ns. A very different behavior is observed when the fluorescence decays are measured in a solvent of higher polarity such as diethyl ether. To capture the different kinetic components precisely and correctly, the measurements were repeated in a long (130 ns) and a short (<60 ns) time window corresponding to 6 ps/ch and 12 ps/ch for the *deoxygenated* and *aerated* solutions, respectively. Global analysis of the single photon counting decay traces obtained at different time scales and emission wavelengths required a four-exponential decay for **N1P1** in diethyl ether. The fitting parameters are given in Table 1. Typically, there are two subnanosecond components and two nanosecond ones. In the *aerated* dendrimer solution, the latter are significantly shorter than the *deoxygenated* equivalents as shown in Table 1. The two subnanosecond components display little oxygen sensitivity and are much shorter than the decay time of the peryleneimide chromophore itself (4.2 ns in *aerated* and 4.7 ns in *deoxygenated* diethyl ether). The observation of decay times longer than that of the peryleneimide suggests a reversible excited-state reaction leading to delayed fluorescence. This process has been observed

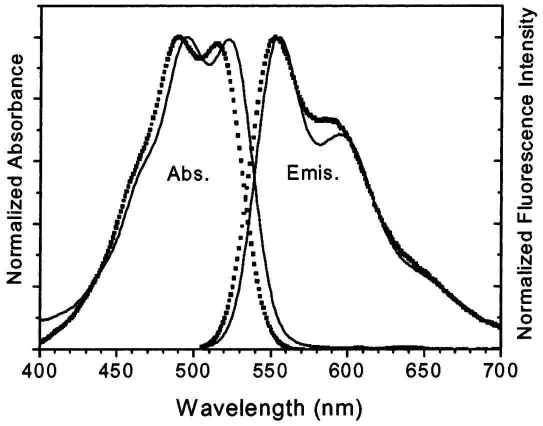


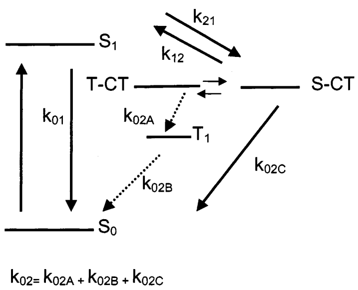
Figure 1. Normalized steady-state absorption and emission spectra for **N1P1** in toluene (−) and diethyl ether (■). The emission spectra were excited at a wavelength of 495 nm.

Table 1. Fitting Parameters of the Fluorescence Decays Measured between 540 and 620 nm with $\lambda_{exc} = 488$ nm for the *Deoxygenated* (A) and *Aerated* (B) Solutions of **N1P1** in Diethyl Ether[a]

	A	B
τ_1 (ns)	45.35	12.81
τ_2 (ns)	22.18	1.81
τ_3 (ns)	0.55	0.42
τ_4 (ns)	0.22	0.21
a_1	0.06	0.86
a_2	0.05	0.21
a_3	0.33	3.43
a_4	0.99	5.90

[a] The decay times and amplitudes are invariant over the whole wavelength region.

Scheme 1



for reversible inter- and intramolecular excimer[80] and exciplex[81,82] formation where it leads to a biexponential fluorescence decay of the locally excited state (LE). In this framework, the four decay times can be related to the presence of the two constitutional isomers differing 2 Å in donor−acceptor distance (Chart 2), each showing a biexponential fluorescence decay. These donor−acceptor distances were obtained by molecular modeling.[73] Each biexponential decay is interpreted in terms of a fast charge separation and a thermally activated back reaction from the charge-separated state to the locally excited state (LE), leading to a prompt and a delayed fluorescence component (Scheme 1) with identical spectral characteristics. In general, depending upon the relative values of the different rate constants, for each isomer the short decay time should then be attributed to the quenched direct fluorescence of the peryleneimide, the long decay time being related to the back transfer process (delayed fluorescence). A detailed analysis of the kinetics[80−82] shows that at least one of the decay times of each isomer must be shorter than that of the peryleneimide. It is not immediately evident upon inspection of the four decay components in Table 1 which short component is linked to which long component. Hence, we should consider two different sets of solutions: (1) the combination τ_1 with τ_3 and τ_2 with τ_4, and (2) the combination τ_1 with τ_4 and τ_2 with τ_3.

For each combination of decay times, it is possible to calculate the rate constants of charge separation k_{21}, of the back reaction k_{12}, as well as the rate of recombination k_{02} to the ground state or to a triplet state and the free energy change ΔG_{cs} of the charge separation. These parameters can be calculated from the decay times τ_i, τ_j, the ratio of the amplitudes a_i/a_j of the two components of the corresponding biexponential fluorescence decay, $I(t) = a_1 \exp(-\lambda_i t_i) + a_j \exp(-\lambda_j t_j)$, and the fluorescence lifetime τ_0 of the unquenched acceptor with the following set of equations[80−83] ($\lambda_i = 1/\tau_i$, $\lambda_j = 1/\tau_j$, $k_{01} = 1/\tau_0$):

$$\lambda_i = \{(X + Y) + \sqrt{[X - Y]^2 + 4k_{21}k_{12}}\}/2 \tag{1}$$

$$\lambda_i = \{(X + Y) - \sqrt{[X - Y]^2 + 4k_{21}k_{12}}\}/2 \tag{2}$$

$$\frac{a_i}{a_j} = \frac{\lambda_i - Y}{Y - \lambda_j}; \quad X = k_{01} + k_{21}; \quad Y = k_{02} + k_{12} \tag{3}$$

For **N1P1** in *deoxygenated* diethyl ether, this yields the results shown in Table 2. The calculations have been done using a value of 2.1×10^9 s^{-1} for k_{01} corresponding to the inverse decay time of 4.7 ns obtained in deoxygenated diethyl ether for a similar dendritic structure as **N1P1**, but where the nitrogen core is replaced by a sp^3-carbon core.

As only an analysis yielding positive rate constants is physically meaningful, the combination τ_1 with τ_3 and hence also the associated combination τ_2 with τ_4 have to be rejected. The ratio f_1/f_2 with which both isomers are present can be given in this framework by

$$\frac{f_1}{f_2} = \frac{a_1 + a_4}{a_2 + a_3} \tag{4}$$

and amounts to 2.1 ± 0.5.

For **N1P1** in *aerated* diethyl ether, in principle, three series of solutions are possible as only one of the decay times is longer than that of peryleneimide: (1) the combination τ_1 with τ_2 and τ_3 with τ_4, (2) the combination τ_1 with τ_3 and τ_2 with τ_4, and (3) the combination τ_1 with τ_4 and τ_2 with τ_3.

While the combination τ_1 with τ_2 and τ_3 with τ_4 yields a result that is physically irrelevant, both the combination τ_1 with τ_3 and τ_2 with τ_4 and the combination τ_1 with τ_4 and τ_2 with τ_3 yield results that are physically relevant (see Table 3).

Here it was assumed that the most likely solution for the *aerated* **N1P1** in diethyl ether is the one (τ_1 with τ_3 and τ_2 with τ_4) which is , with respect to k_{21} and k_{12}, most similar to the physically meaningful solution for **N1P1** in *deoxygenated* diethyl ether. As expected, the changes of k_{21}, k_{12}, and K upon deoxygenating are then small, while k_{02} decreases dramatically. In *aerated* diethyl ether, the ratio of both isomers is given by

$$\frac{f_1}{f_2} = \frac{a_1 + a_3}{a_2 + a_4} \tag{5}$$

and amounts to 1.6 ± 0.4, which equals within experimental error the value found for the *deoxygenated* solution.

The different values found for the free energy change of charge separation (ΔG_{cs}) in both isomers could link the different decay components to the proper isomer. Using the equilibrium constant reported in Table 2, we obtained a value for the energy change of charge separation of −1.6 kcal/mol for one isomer and −0.8 kcal/mol for the other isomer for **N1P1** in *deoxygenated* diethyl ether at room temperature. The more negative free energy difference found for "isomer 1" can be related to a smaller distance between donor and acceptor and hence a larger

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Table 2. Calculated Rate Constants of the *Deoxygenated* Solution of **N1P1** in Diethyl Ether

	τ_1 & τ_3	τ_2 & τ_4	τ_1 & τ_4	τ_2 & τ_3
k_{01} (ns^{-1})	$2.13 \pm 0.10 \times 10^8$	$2.13 \pm 0.10 \times 10^8$	$2.13 \pm 0.10 \times 10^8$	$2.13 \pm 0.10 \times 10^8$
k_{21} (ns^{-1})	$1.36 \pm 0.01 \times 10^9$	$3.97 \pm 0.01 \times 10^9$	$4.06 \pm 0.01 \times 10^9$	$1.30 \pm 0.12 \times 10^9$
k_{12} (ns^{-1})	$2.73 \pm 0.16 \times 10^8$	$3.75 \pm 0.16 \times 10^8$	$2.90 \pm 0.01 \times 10^8$	$3.41 \pm 1.45 \times 10^8$
k_{02} (ns^{-1})	$-1.13 \pm 0.22 \times 10^7$	$2.99 \pm 0.07 \times 10^7$	$9.03 \pm 0.60 \times 10^6$	$6.2 \pm 1.98 \times 10^6$
K	5.01	10.59	13.98	3.82

Table 3. Calculated Rate Constants of the *Aerated* Solution of **N1P1** in Diethyl Ether

	τ_1 & τ_3	τ_2 & τ_4	τ_1 & τ_4	τ_2 & τ_3	τ_1 & τ_2	τ_3 & τ_4
k_{01} (ns^{-1})	$2.38 \pm 0.10 \times 10^8$	$2.38 \pm 0.10 \times 10^8$	$2.38 \pm 0.10 \times 10^8$	$2.38 \pm 0.10 \times 10^8$	$2.38 \pm 0.10 \times 10^8$	$2.38 \pm 0.10 \times 10^8$
k_{21} (ns^{-1})	$1.67 \pm 0.22 \times 10^9$	$4.38 \pm 0.07 \times 10^9$	$3.98 \pm 0.03 \times 10^9$	$2.02 \pm 0.02 \times 10^9$	$-5.90 \pm 0.50 \times 10^7$	$3.71 \pm 0.06 \times 10^9$
k_{12} (ns^{-1})	$5.13 \pm 0.25 \times 10^8$	$1.35 \pm 0.62 \times 10^8$	$5.70 \pm 0.27 \times 10^8$	$9.98 \pm 0.70 \times 10^7$	$-6.39 \pm 0.77 \times 10^8$	$3.44 \pm 0.18 \times 10^8$
k_{02} (ns^{-1})	$3.33 \pm 0.28 \times 10^7$	$5.62 \pm 0.01 \times 10^8$	$5.60 \pm 0.12 \times 10^7$	$5.71 \pm 0.01 \times 10^8$	$1.09 \pm 0.07 \times 10^9$	$2.85 \pm 0.04 \times 10^9$
K	3.26	32.4	6.98	20.2	0.083	10.78

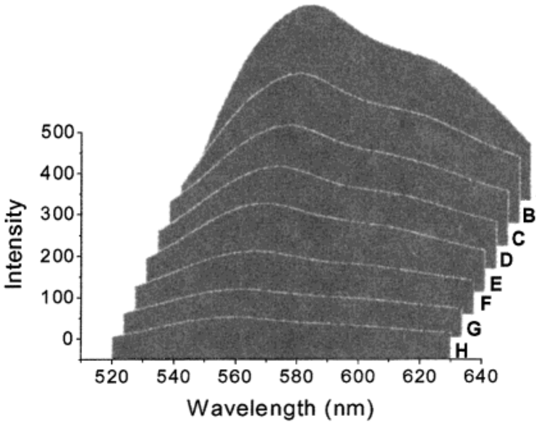

Figure 2. Time-resolved emission spectra of a *deoxygenated* solution of **N1P1** in diethyl ether A, 500−600 ps; B, 601−700 ps; C, 701−800 ps; D, 801−900 ps; E, 901−1000 ps; F, 1001−1500 ps; G, 1501−2000 ps; H, 2001−3500 ps.

Coulomb attraction as compared to “isomer 2”. As molecular models (vide supra) suggest a difference of 2 Å between both isomers, “isomer 1” could be identified as the para,meta,meta isomer (see Chart 2) with a delayed fluorescence decay time of 45 ns and a quenched fluorescence decay time of 220 ps in *deoxygenated* ether solution. Following this line of thought, “isomer 2” is the para,para,meta isomer with a delayed fluorescence decay time of 22 ns and a direct fluorescence decay time of 550 ps.

The electron-transfer process of **N1P1** in diethyl ether appears to be dominated by through-space electron transfer because of the faster charge separation (shorter direct fluorescence lifetime) in the isomer with the spatially closer donor and acceptor moieties. Because of the replacement of a para- by a meta-link in this isomer, one would, on the other hand, expect a smaller through-bond interaction.[84−87]

The time-resolved emission spectra of the *deoxygenated* **N1P1** diethyl ether solution were recorded. Within experimental error, no evolution of the emission spectra in function of the delay time after excitation (Figure 2) of the *deoxygenated* **N1P1** diethyl ether solution was observed.

To investigate more closely the decay pathway of the long-lived ion-pair state for **N1P1** in *deoxygenated* ether solution and the dramatic shortening effect of oxygen on its lifetime, nanosecond transient absorption measurements were performed on *deoxygenated* and *aerated* solutions of **N1P1** in diethyl ether (Figure 3). In general, three distinct bands are observed in the transient absorption traces. In the *aerated* solution, Figure 3B, bands with maxima at 390, 550, and 585 nm are observed between 10 ns and 1 μs after excitation. On the basis of literature data,[68] these bands are attributed to the triplet−triplet absorption spectra of peryleneimide (**PI**). The decay time of this triplet in *aerated* diethyl ether is approximately 400 ns. Furthermore, a negative band with maxima at 460 and 485 nm is observed together with an isosbestic point at 440 nm over this time range. Because of its correspondence with the inverted ground-state absorption spectrum (Figure 1), this band is attributed to ground-state depletion.[68] The amount of triplet formed increases strongly from toluene to diethyl ether. In *deoxygenated* solutions of **N1P1** in toluene, no transients could be detected on a ≥10 ns time scale. However, in *deoxygenated* diethyl ether bands (Figure 3A) with maxima at 402 and 620 nm, shoulders at 555 and 730 nm and a long wavelength tail are observed between 10 and 70 ns after excitation. Between 100 and 1000 ns, these are transformed in bands with maxima at 395, 555, and 580 nm. Furthermore, between 10 ns and 1 μs, a negative band with a maximum around 485 together with an isosbestic point at 445 nm is observed. The negative band and the bands observed between 100 ns and 1μs can again be attributed to the ground-state depletion and the triplet−triplet absorption, respectively. The decay time of this triplet in *deoxygenated* diethyl ether is approximately 160 μs. The absorption band observed between 10 and 70 ns at 620 nm is attributed to the radical anion of peryleneimide which is characterized by an absorption maximum at 600 nm.[60] The maximum of the observed radical ion absorption band is shifted to the red because of the overlap with the absorption band of the radical cation of the donor moiety (triphenylamine radicalcation) which has its absorption maxima at 400, 700, and 770 nm.[88,89] Hence, the absorption band at 402 nm can also be attributed to the radical cation of the donor.

Clearly, a remarkable difference is observed when comparing the transient absorption traces of the *aerated* and *deoxygenated* dendrimer solutions. **N1P1** in diethyl ether is displayed in Figure 3A and B as a representative example. The formation of a locally excited triplet is strongly enhanced in the presence of oxygen.

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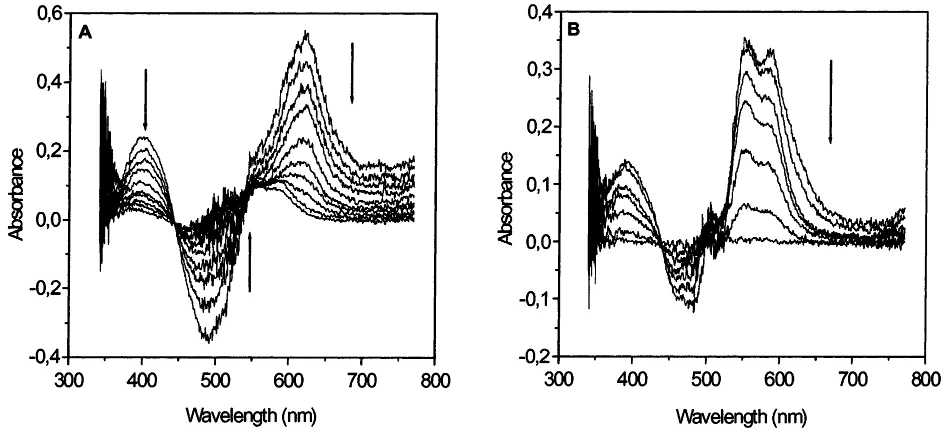

Figure 3. Nanosecond transient absorption traces of *deoxygenated* (A) and *aerated* (B) solutions of **N1P1** in diethyl ether as a function of different delay times after excitation: (A) 0, 10, 20, 30, 50, 70, 90, 120, 200, and 1000 ns; (B) 0, 10, 50, 100, 200, 400, and 1000 ns.

This locally excited triplet can be formed, either directly from the charge-transfer singlet by Dexter type energy transfer to the oxygen,[90] or by intersystem crossing,[91−94] yielding eventually a locally excited triplet. In the former case, the locally excited triplet must be situated at least 7000 cm^{-1} (energy difference between the $^3\Sigma$ and $^1\Delta$ state of oxygen) below the CT-singlet. In the latter case, oxygen will, in a contact complex, enhance the spin−orbit coupling by mixing with a charge-transfer state or by exchange interactions and, in this way, enhance the intersystem crossing from the singlet to the triplet charge-transfer state or to the locally excited triplet state.[91−97] This mechanism is also assumed to be involved in the enhancement of $S_0 \rightarrow T_1$ absorption by oxygen.[97−99] It is rather unlikely that the inhomogeneous magnetic field of oxygen plays an important role here.[100] As to the role of a charge-transfer complex with O_2, this should have its CT-state at about $E_{CT} = IP_D - 3.57$ eV.[98] With 6.84 eV[101] for the ionization potential of triphenylamine (IP_D), this corresponds to 3.27 eV for E_{CT} which is about 1 eV above the charge-transfer state of **N1P1**.

From Figure 3B, it can also be seen that in diethyl ether the decay of the ion-pair absorption band is accompanied by a growing in of the triplet−triplet absorption band indicating the link between the formation of the triplet and the electron-transfer process. After the decay of the ion-pair state, triplet−triplet absorption is observed.

The transient spectra obtained between 100 ns and 1 μs for the *deoxygenated* solution indicate furthermore that (although to a much smaller extent) a LE triplet of the peryleneimide is formed from the CT-state in the absence of oxygen. The mechanism for this process is either spin−orbit coupling yielding directly the LE triplet or singlet triplet interconversion in the radical ion pair followed by a rapid recombination in the triplet manifold. The latter mechanism is governed either by hyperfine interactions or by the different *g*-factor for the radical anion and cation. The latter effects can lead to singlet triplet interconversion on a time scale of 10^{-8} s.[102−107]

Also, nanosecond (delayed) fluorescence measurements were performed on the *aerated* and *deoxygenated* solutions of **N1P1** in toluene and diethyl ether at 293 and 77 K. As expected on the basis of the SPC measurements at 293 K (vide supra), in toluene no delayed fluorescence was observed in contrast to diethyl ether where delayed fluorescence was present. The intensity is higher in the *deoxygenated* solutions as compared to the *aerated* ones. The decay of the delayed fluorescence is a first-order process. A plot of the decay of the emission as a function of the time is depicted in Figure 4A and B for the *aerated* and *deoxygenated* **N1P1** solutions in diethyl ether, respectively. The resulting rate constants yield decay times of 16.7 and 38.5 ns for the *aerated* and *deoxygenated* dendrimer solutions, respectively. These decay times correspond well with the long decay time recovered from the analysis of the fluorescence decays obtained by the single photon counting. The decay of the ion-pair (CT-state) absorption band is also a first-order process and yields a decay time of the same order of magnitude as the long decay times of the fluorescence decays obtained by SPC.

When performing the experiments at 77 K, one can observe two distinct emitting species. The time-resolved emission spectra at 77 K of **N1P1** in diethyl ether are depicted in Figure 5. At delay times below 100 ns, one observes a fluorescence with the spectral characteristics of the peryleneimide, while at longer times (microsecond) the luminescence spectrum is converted to a structureless band with a maximum at around 600 nm. Because of the extremely small energy difference (4.14 kcal/

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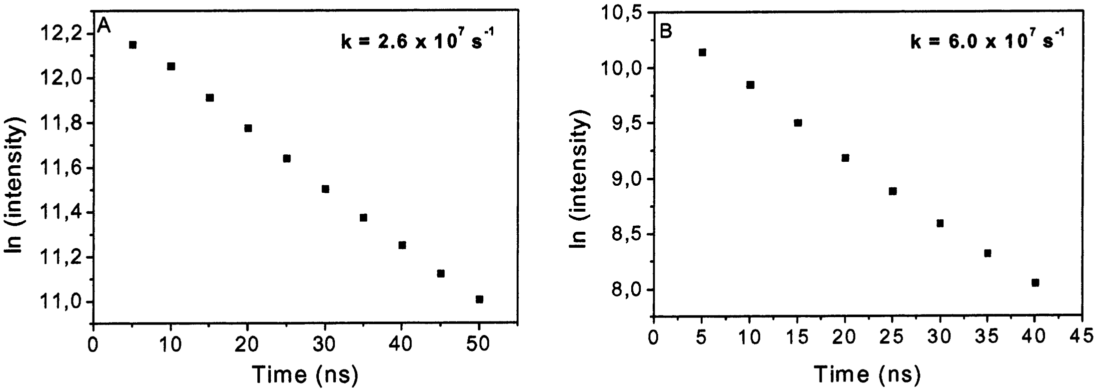

Figure 4. Plot of the decay of the emission as a function of the delay time for the *deoxygenated* (A) and *aerated* (B) solutions of **N1P1** in diethyl ether.

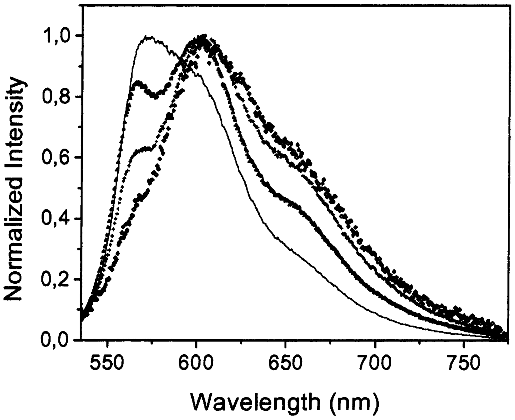

Figure 5. Emission spectra of **N1P1** in diethyl ether at 77 K for different delay times after excitation: (−) delay = 0 ns, gate = 10 ns; (▲) delay = 100 ns, gate = 100 ns; (+) delay = 1 μs, gate = 1 μs; (◊) delay = 10 μs, gate = 10 μs.

mol) between the two emission bands, it is highly unlikely that this luminescence is phosphorescence originating from the T_1-state of the peryleneimide chromophore. Instead, the observed emission at microsecond delay times is attributed to charge recombination luminescence emerging from the long-lived CT-state. Cooling to 77 K apparently slows down the (uphill) recombination to the S_1-state of **PI**, which is responsible for the delayed fluorescence at 290 K, to such an extent that direct radiative decay to S_0 becomes detectable. In this connection, it is important to point out that even if the recombination to the local S_1-state of **PI** (k_{12}) would have an activation energy not larger than $-\Delta G_{CS}$, cooling to 77 K would reduce k_{12} by 2 to 3 orders of magnitude, increasing, in this way, the decay time of the charge-transfer state to the microsecond region.

Conclusions

By means of steady-state and time-resolved spectroscopy, photoinduced long-range intramolecular electron transfer has been demonstrated in the amine core dendrimer **N1P1** in a moderately polar solvent, leading to a long-lived ion-pair state. Although formally **N1P1** can be considered as a donor-bridge-acceptor (DBA) compound with an unsaturated bridge,[19−31,36−37] the electron transfer occurs, in contrast to most DBA compounds, by a through-space mechanism.

Despite the large donor acceptor separation and the restricted rotational mobility of the polyphenylene bridge, time-resolved fluorescence experiments indicate two distinct sets of forward and back electron-transfer rates which could be linked to two constitutional isomers of **N1P1**. Oxygen influences the photophysical kinetics in this system very strongly, probably because of its interaction with the nearly degenerated triplet and singlet ion-pair state. Picosecond and nanosecond fluorescence experiments have revealed a fast charge separation and a thermally activated back reaction from the charge-separated state to the locally excited state leading to a prompt and a delayed fluorescence component at room temperature. While a thermally activated back electron transfer has been observed for exciplexes[1−4,9−12,108,109] where a direct contact between donor and acceptor is obtained, as well for DBA compounds with a short and rigid linear saturated[14,36,110] bridge, this process is uncommon for a polyaryl bridge or long-distance through-space electron transfer. The unique properties of this amine core dendrimer are even more obvious from the substitution of the delayed local fluorescence at room temperature by charge-recombination luminescence at 77 K.

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