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Single perylene diimide dendrimers as single-photon sources

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Abstract

Single-molecule fluorescence spectroscopy was performed on a number of perylene diimide multichromophores with different dendritic geometries, with the particular goal of characterizing their performance as single-photon sources at room temperature. The quality of the different perylene diimide-containing dendrimers as single-photon sources was evaluated by determining the Mandel parameter. Values similar to ones reported previously for perylene monoimide dendrimers were found. The different arrangements of the chromophores in the different dendrimers do not noticeably affect their efficiency as single-photon emitters. Due to the formation of oxygen-enhanced long dark states, anaerobic conditions are found to be the best for optimizing their performance, which is in contrast with the case for perylene monoimide containing dendrimers.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Nowadays, the desire to realize controllable single-photon (SP) sources is driven mainly by applications in quantum cryptography and certain quantum computational problems since SP sources can deliver photons one at a time [1]. The majority of quantum optical experiments are conducted by using macroscopic parametric sources that generally deliver a Poissonian distribution of photons, which need to be attenuated to reduce the probability of obtaining two or more photons at the same time. This attenuation thus leads to a limitation in the efficiency of this method. Therefore, most current efforts on developing SP sources rely on single-emitting

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nanometric objects. In most cases, the mechanism of such SP sources involves a spontaneous emission process after excitation of the emitter. The first examples of SP emitters were obtained at cryogenic temperatures by using atoms and ions in the gas phase or by using semiconductor nanoparticles [2], although with low detection efficiency (10^{-3} – 10^{-4}) due to the characteristics of the equipment. Another approach has therefore been the generation of SP sources at room temperature (detection efficiency 10^{-1}) and different systems have been explored such as nitrogen–vacancy colour centres in diamond crystals [3], CdSe quantum dots [4] and single organic molecules excited by pulsed laser sources [5–8]. In the latter case, the pulse repetition period must be longer than the fluorescence lifetime and the pulse duration much shorter than the fluorescence lifetime to guarantee the emission of only one photon per excitation pulse. The efficiency of organic molecules as SP sources is limited by the absorption probability, fluorescence quantum yield and, most importantly, photostability. Thus, our approach is based on the use of rylene-based chromophores because of their strong absorption ($\epsilon_{\lambda \text{ max}} \approx 5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), their excellent photostability [9] and their fluorescence quantum yield near to 1 [10]. We have incorporated multiple rylene dyes into dendrimers in order to increase the absorption cross section, count rates (and hence the number of single emitted photons) and survival times as compared to single chromophores. As demonstrated recently for perylene monoimide (PMI)-containing dendrimers [6, 7, 11], controlling the efficiency of energy transfer processes such as energy hopping, singlet–singlet (SS) and singlet–triplet annihilation (ST) is important for obtaining an efficient dendrimer-based SP source. Control over the distances and orientations between the chromophores is thus necessary in order to influence the efficiencies of these processes, and the synthetic versatility and well defined spatial relationships between the chromophores provided by the dendrimers [12] do indeed allow tuning the efficiency of the different processes. SS annihilation ($S_1 + S_1 \rightarrow S_0 + S_n$, followed by $S_n \rightarrow S_1$), which is the main mechanism responsible for SP emission even when more than one excitation per dendrimer is present, should compete efficiently with the fluorescence decay ($S_1 \rightarrow S_0$). On the other hand, ST annihilation ($S_1 + T_1 \rightarrow S_0 + T_n$) should be suppressed as much as possible in order to avoid the appearance of additional triplet dark states that would affect the efficiency of the SP source. An experimental demonstration of the principles explained above has recently been published for polyphenylene dendrimers decorated with four PMI chromophores [7, 11]. It was shown that the parameters influencing the efficiency of that multichromophoric system as the SP source are the interchromophoric distance, the surrounding polymer matrix, the number of chromophores and the presence or absence of oxygen. Herein, we report a study on multichromophoric compounds containing perylene diimide (PDI) units, which have been shown to be brighter and more photostable than PMI [9]. The chromophoric units are arranged in a different geometry via ethynylene bridges (figure 1), which is an advantage because their synthesis results in a single isomeric form, in contrast to the mixture of isomers that the synthesis of polyphenylene dendrimers yields [13]. We have included in our study also polyphenylene dendrimer with four PDI units for comparison with the PMI-based dendrimer previously investigated. A study on a polyphenylene dendrimer decorated with eight PDI units already indicated that this chromophore performs better as a single-photon emitter compared to PMI in terms of the influence of triplet formation [14].

Besides studying their SP emitting properties, we have fully characterized the single-molecule photophysical behaviour of these PDI-based compounds. To interpret the single-molecule data correctly, it is crucial to understand the ensemble photophysical behaviour of the different systems. We will thus provide a brief description on the bulk properties of the dendrimers studied, in addition to the single-molecule data recorded by means of confocal microscopy.

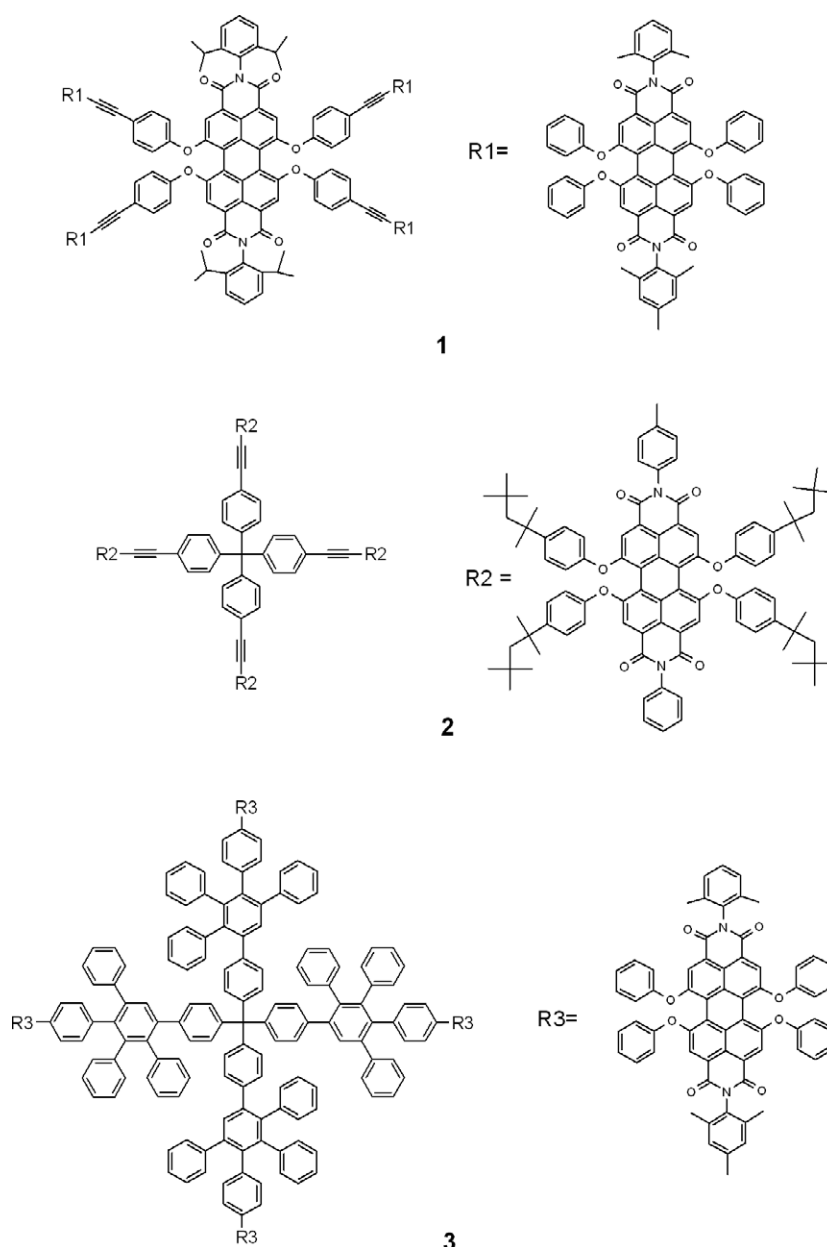


Figure 1. Molecular structure of the dendrimers studied.

2. Experimental details

Ensemble steady-state spectra were collected with a Lambda 40 spectrophotometer (Perkin-Elmer) and a Fluorolog 1500 fluorimeter (Spex). Fluorescence quantum yields (Φ_F) were measured using cresyl violet in methanol as the reference ($\Phi_F = 0.55$) [15], with $\lambda_{ex} = 543$ nm. Time-resolved measurements were performed using the time-correlated single-photon counting (TCSPC) technique [16], with excitation at 543 nm (8 MHz, 1.2 ps FWHM) from the

frequency-doubled output of an optical parametric oscillator (GWU) pumped by a Ti:sapphire laser (Tsunami, Spectra Physics).

For continuous wave (CW) experiments, a 543 nm Melles Griot laser was used. For pulsed experiments, the same excitation source and wavelength were used for both single-molecule experiments and ensemble measurements. The excitation light was rendered circularly polarized by a Berek compensator, directed into an inverted microscope (Olympus IX 70) and focused onto the sample through an oil immersion objective (1.3 NA, $\times 100$, Olympus). Fluorescence was collected through the same objective and focused onto an avalanche photodiode (SPCM 15, EG&G). In some cases, the fluorescence was again split with a polarizing beam splitter (50:50) and sent to two different avalanche photodiodes detecting polarization directions perpendicular to each other. Time-resolved data were collected with TCSPC card (SPC 630, Becker & Hickl) operated in first-in–first-out mode. A detailed description of the set-up and the data acquisition process has been published previously [6].

For coincidence measurements, a classical Hanbury-Brown and Twiss antibunching set-up is used [17]. In the confocal microscope described above, the fluorescence from a single molecule was split by a 50:50 nonpolarizing beam splitter and detected by two APDs. The signal from both APDs was fed into the router coupled to the TCSPC acquisition card. Because the TCSPC card has a dead time of 125 ns, an electronic delay is applied to the signal of one of the two APDs, so that multiple fluorescence photons eventually generated by the same laser pulse can be detected. The TCSPC card registers for both APDs the arrival time after the beginning of the acquisition with a resolution of 50 ns (a, macrotime) and the time delay between the start pulse (fluorescence) and stop pulse (laser) with a time resolution of 6 ps (b, microtime). The electronic delay was set to 1.44 μs . Histograms of interphoton arrival times were obtained by combining microtimes and macrotimes using timing of the laser pulse with a home-made program in visual C⁺⁺.

Samples for single-molecule experiments were prepared by spin-casting $\sim 10^{-10}$ M solutions of the compounds in chloroform containing ~ 6 mg ml⁻¹ polymer onto thoroughly cleaned glass cover-slips. Single-molecule measurements were performed with typical excitation power of ~ 2 kW cm⁻². Polystyrene (PS, Acros, $M_w \approx 250\,000$), polymethylmethacrylate (PMMA, Aldrich, $M_w \approx 93\,000$) were used without further purification. The synthesis of the dendrimers **1** and **2** has been described previously [13].

3. Results and discussion

3.1. General photophysical features: energy hopping and electron transfer

The absorption and emission spectra of compounds **1–3** are shown in figure 2, and their main photophysical parameters are summarized in table 1. As shown before for compounds **1** and **2** [13], the fluorescence quantum yield Φ_F is equal to 1 and the fluorescence lifetime τ_F is equal to 5–6 ns in toluene, which are typical values for unquenched PDI. A similar behaviour is found for compounds **2** and **3** in THF. However, in this more polar environment, the fluorescence from the central PDI unit in **1** can be quenched by the adjacent ethynylene bridges via an electron transfer process, from the ethynylene to PDI, giving rise to a low Φ_F and different fluorescence decays for the central and the peripheral chromophores [13]. This quenching does not occur in **2** or **3**, since both compounds lack the central chromophore (and the ethynylene bridge in the case of **3**).

Time-resolved anisotropy decays of **1** and **2** showed that the main excited state pathway in both compounds is energy hopping between chromophores [13]. At the single-molecule level, energy hopping is visualized by using two channels that detect the fluorescence light emitted

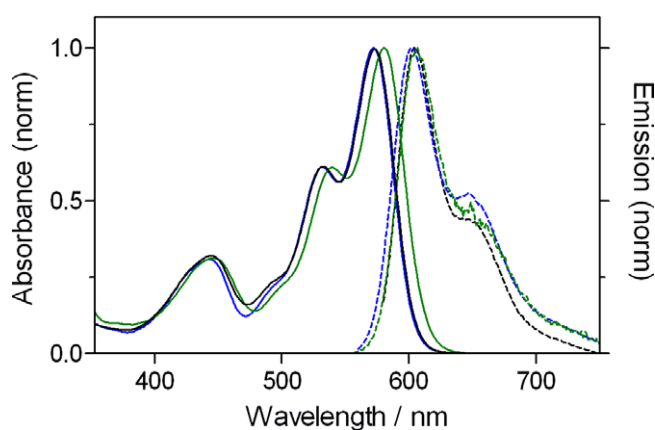


Figure 2. Normalized absorption and emission spectra of compounds **1** (black/solid), **2** (green/dashed) and **3** (blue/solid grey) in toluene.

Table 1. Photophysical parameters of compounds **1–3**.

Compound	Toluene			THF		
	1 ^a	2 ^a	3	1 ^a	2 ^a	3
$\lambda_{\max}^{\text{abs}}$ (nm)	573	579	573	569	573	568
$\lambda_{\max}^{\text{emi}}$ (nm)	604	606	602	601	603	600
Φ_{F}	0.99	1.00	0.94	0.42 1.0 (14%)	1.00	n.m.
τ_{F} (ns)	5.1	5.3	5.2	2.8 (86%)	5.6	n.m.

^a From reference [13]; n.m. = not measured.

by an individual molecule with polarization directions perpendicular to each other [18]. The change in relative intensity of the two channels is more clearly illustrated by the change in steady-state polarization (p), defined as

$$p = \text{polarization} = \frac{A - GB}{A + GB}$$

in which A and B are the intensities of the two different channels, and G is a correction factor that accounts for the difference in detection sensitivity in the two channels. Figure 3(A) shows a typical intensity trace of **1** in PMMA, in which the polarization level changes stepwise concomitantly with the stepwise photobleaching in the fluorescence traces. The emission is supposed to occur at all times from the chromophore that is lowest in energy. This implies that one chromophore acts as a fluorescent trap and receives the excitons of the other chromophores via energy transfer. The different polarization levels correspond to differently oriented chromophores. The fact that different chromophores serve as fluorescent trapping sites as a function of time may be attributed to sequential photobleaching of the chromophores or to temporal stabilization of a certain chromophore by the local environment due to polymer motions [18]. Figure 3(B), which represents data measured for compound **3**, depicts a particular case in which the polarization level is rather constant throughout the trace. This means that the emissive trapping site is the chromophore that bleaches only in the end. Indeed, while the polarization stays constant, the intensity still shows stepwise changes.

Another type of information that can be retrieved from such single-molecule experiments is the evolution of the fluorescence lifetime, which is shown in the bottom panels of figure 3.

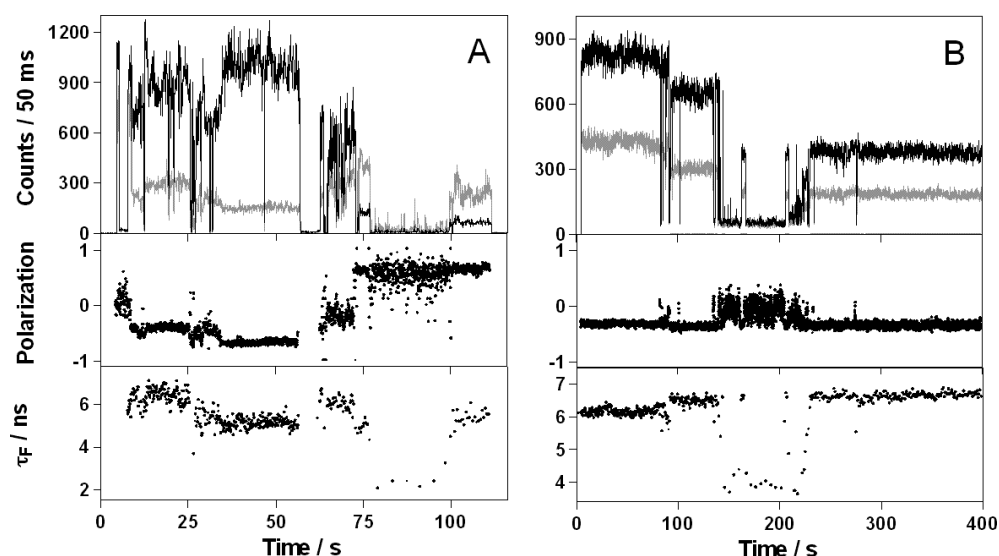


Figure 3. Two examples of single-molecule intensity traces of **1** (left) and **3** (right) in PMMA (air environment). Channel (A) (grey) and (B) (black) correspond to polarization directions perpendicular to each other. The lower panels show changes in polarization and fluorescence lifetime (τ_F).

The stepwise variations in lifetime that correspond to stepwise variations in polarization show once again the change in the emitting chromophore in the case of compound **1** [19]. Some parts of the traces show a lifetime of about 5–6 ns, characteristic for unquenched PDI. In other cases, the lifetime is lower than 5 ns, indicating some kind of intramolecular quenching. In the case of trace A (compound **1**), it is likely that the chromophores that emit at 5–6 ns are the peripheral ones, while the one characterized by a 2 ns decay is the central unit, quenched by electron transfer by the ethynylene bridges (*vide supra*). PMMA can provide a sufficiently polar environment to allow the latter process to take place [13].

Another characteristic of the traces shown in figure 3 is the occurrence of periods of no emission or dark states. The nature of these dark states will be discussed in section 3.3.

3.2. Single-photon emission

As discussed above, SS annihilation is the key process leading to SP emission in multichromophoric systems. To characterize this process at the ensemble level, femtosecond transient absorption spectroscopy is an essential tool. Preliminary results using this technique on compound **3** in toluene clearly show that SS annihilation occurs at high excitation power with a time constant of around 100 ps [20]. This value is 10 times slower than for PMI [21] which might influence the efficiency of PDI as a SP source, but still fast enough compared to the fluorescence decay (5.2 ns). For comparison, the overlap between the $S_1 \rightarrow S_n$ absorption spectrum and the fluorescence spectrum, which is an indication of the efficiency of SS annihilation, is around $10^{-14} \text{ cm}^6 \text{ mmol}^{-1}$ for PDI in toluene [14], and around $10^{-13} \text{ cm}^6 \text{ mmol}^{-1}$ for PMI [22].

Figure 4 shows the comparison of the interphoton arrival time for a single molecule of compound **2** and a bulk sample of monomeric PDI in PMMA under nitrogen calculated every 50 000 photons. Each peak is spaced by 122 ns, equivalent to the frequency of the laser pulse

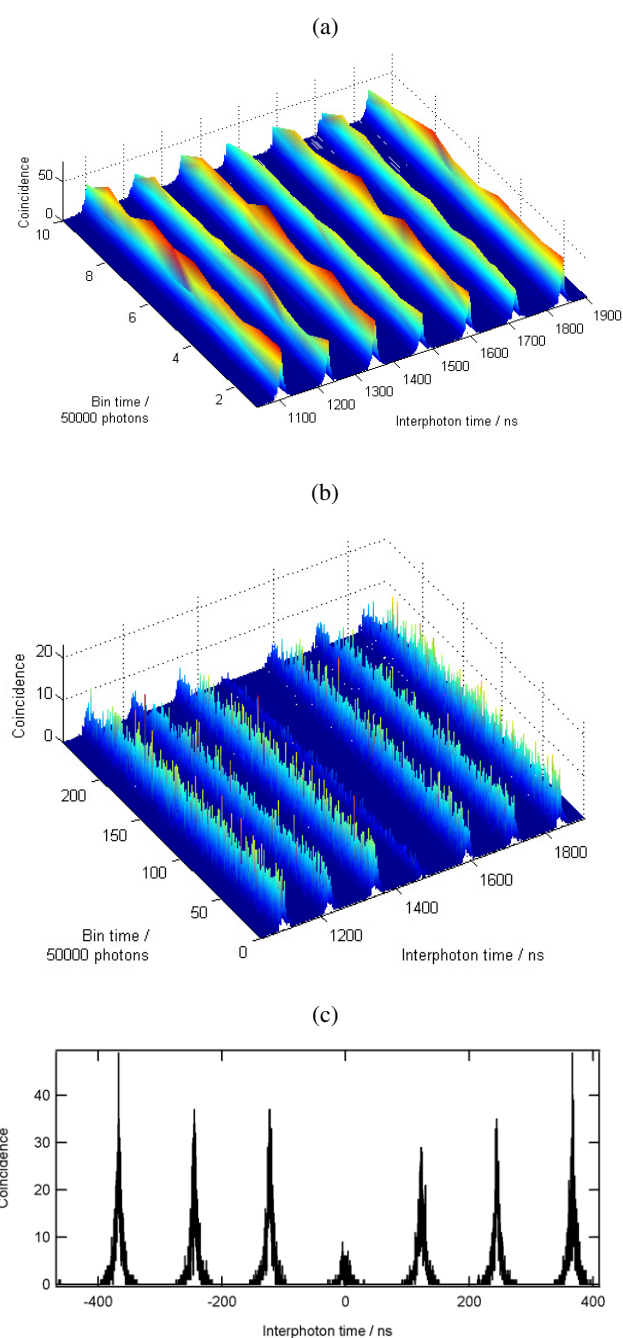


Figure 4. 3D interphoton time histogram (50 000 photons bin) for a bulk sample of a monomeric PDI film (a) and a single molecule of compound **2** in PMMA (b). (c) 2D interphoton time for the first level of the trace in figure 5(b).

(8.18 MHz). For the bulk sample (figure 4(a)), the intensities of all peaks in the interphoton arrival times will be similar. However, for a SP emitter, the peak intensity at time zero, which represents photon pairs induced by the same laser pulse, should be close to zero (figures 4(b)

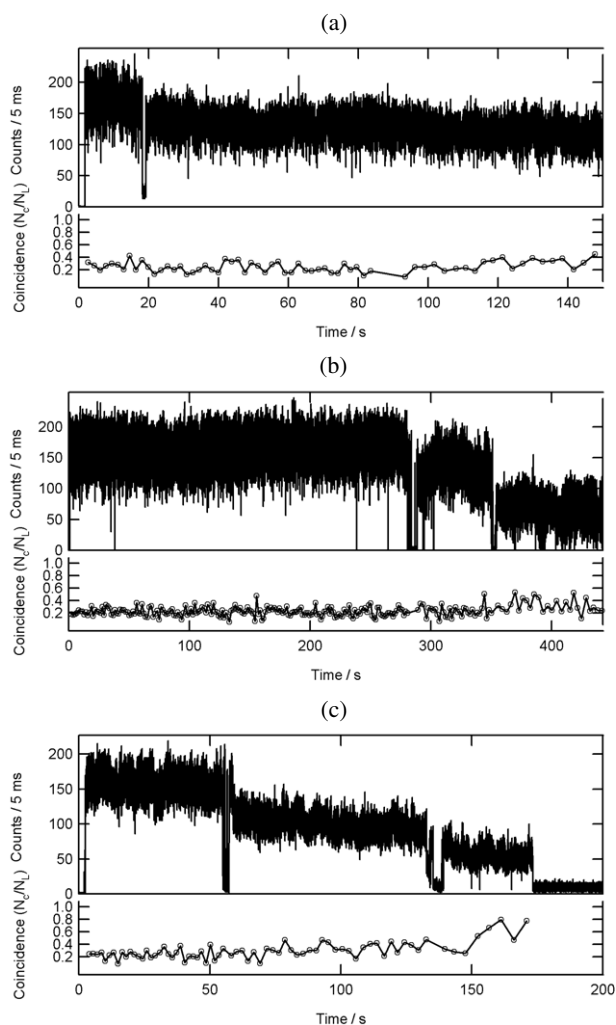


Figure 5. Fluorescence trajectories of single molecules of compounds (a) **1**, (b) **2** and (c) **3** plotted in 5 ms bins under N_2 atmosphere. For each trajectory, the lower panels show the N_C/N_L value calculated every 50 000 photons.

and (c)). A SP source is thus characterized by the ratio between the number of interphoton events in the central peak (N_C) and the number of noncoincident events (i.e. the average of the six lateral peaks N_L , three from each side of the central peak; figure 4(c)). It has been shown that the value N_C/N_L can be used to estimate the number of independently emitting chromophores [8, 23]. Neglecting the background, the N_C/N_L ratios of 0.0, 0.5, 0.67, and 0.75 are expected for 1, 2, 3 and 4 emitters, respectively. For a bulk sample, the ratio should be 1. It has been shown that some events do occur at time zero due to photon–background or background–background coincidence.

Figures 5(a)–(c) show the time evolution of the coincidence events for the individual dendrimers **1**–**3** (50 000 photons bin) under nitrogen. Anaerobic conditions proved to be better for these compounds (see the next section). The ratio N_C/N_L for the three compounds fluctuates around 0.2, low enough for considering these compounds as SP emitters. Note that the increase

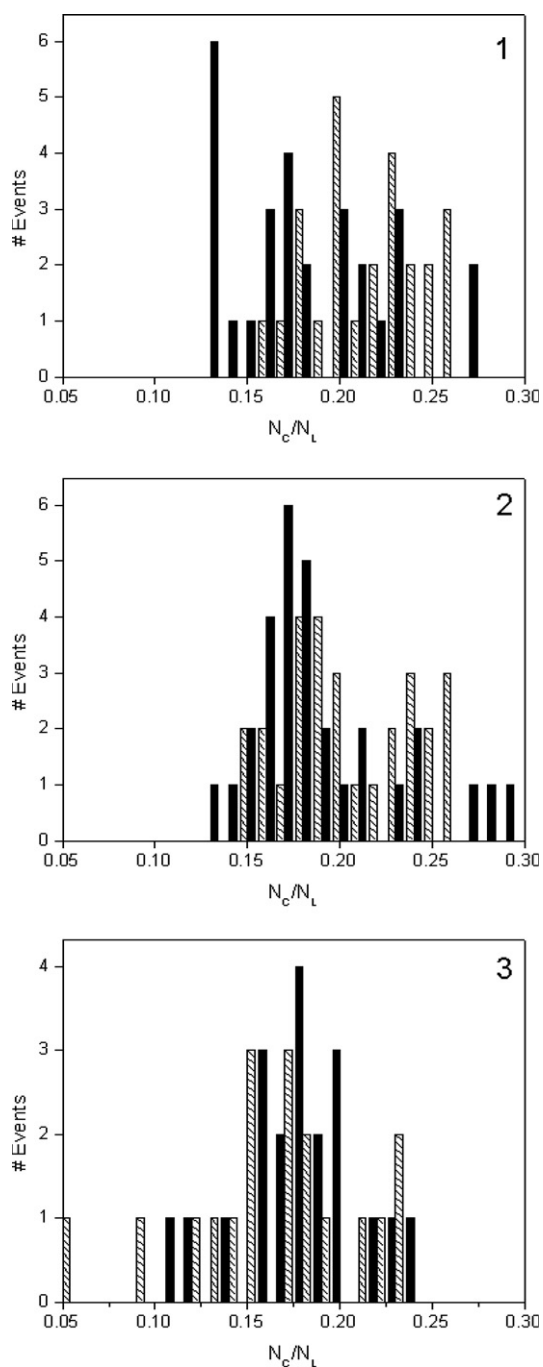


Figure 6. Histogram of N_C/N_L for compounds 1–3 under ambient atmosphere (black bars) and under nitrogen (striped bars).

of the N_C/N_L ratio in the lower fluorescence intensity levels is expected as the S/N ratio decreases. For similar excitation powers, the histograms of the N_C/N_L values obtained from the first intensity level of compounds 1–3 are shown in figure 6. The comparison between

ambient atmosphere and nitrogen will be discussed in the next section. For comparison, a multichromophoric compound with four PMI units has an average value for the first intensity level of 0.1 [11]. It is worth noting that in our analysis we did not subtract the background, which may result in slightly poorer N_C/N_L values. To further evaluate our compounds as SP sources, the Mandel parameter Q [24] was calculated for the first intensity level. This parameter evaluates quantitatively the degree of deviation from a Poissonian distribution of photons and the efficiency of a SP source. For a Poissonian distribution, Q is equal to zero, whereas for a perfect SP source a value of -1 is expected. For the three compounds an average value of -0.3 with a maximum value of -0.6 is calculated under a nitrogen atmosphere. This value is similar to the one calculated for a multichromophoric compound with four PMI units in similar conditions [11]. Even though the rate constant for SS annihilation is roughly ten times higher for PMI than for PDI (see above), they perform similarly as SP sources. Comparing the three compounds studied, it seems that the different geometry imposed by the ethynylene bridges in compounds **1** and **2** as compared to that of the polyphenylene dendrimer **3** does not impair the performance of the dendrimers as SP sources. Another comparison may be done between **3** and the equivalent dendrimer with eight PDI units [14]. It was previously shown that increasing the number of chromophores in a PMI-based dendrimer did not lead to a more efficient SP source, due to stronger interchromophoric coupling, which in turn increases the efficiency of intersystem crossing [11]. This seems not to be the case for PDI, since the values of N_C/N_L are lower for the polyphenylene dendrimer containing eight PDI ($N_C/N_L < 0.1$) units than for that containing four. This observation emphasizes the difference in photophysical behaviour of PDI and PMI.

3.3. Blinking and its effect on SP source performance

In order to have efficient single-photon emitters, long periods of no emission should be avoided. PDI dyes often show long off times (longer than few ms) [14, 25, 26], which cannot be attributed to intersystem crossing to the triplet state. These long offs have been linked to electron transfer processes. In the particular case of these PDI dendrimers, a preliminary single-molecule study revealed frequent blinking in the fluorescence intensity traces with both pulsed and CW excitation [13]. Herein, we present a more thorough investigation of this phenomenon. Figures 3 and 7 show examples of the formation of long dark states in ambient atmosphere. This behaviour was present in 40–50% of the traces of the three compounds at a typical (pulsed) excitation power of $\sim 2 \text{ kW cm}^{-2}$, but its frequency of occurrence increased at higher power. On the other hand, the frequency of occurrence did not seem to be influenced to a great extent by the nature of the matrices studied (PS, PMMA). As previously discussed [13], the on–off behaviour was strongly oxygen dependent, since less than 5% of the molecules showed some blinking in a nitrogen atmosphere. Figure 7 shows a clear example of the effect that removing oxygen has on the long dark state formation. By comparison with several model compounds, we found that the blinking process is also related to the possibility for intramolecular electron transfer, i.e. between two PDI units or between one PDI and its bay area substituents [13]. The complex dependence of this blinking on oxygen and on the feasibility for intramolecular electron transfer was attributed to an enhancement of intersystem crossing by oxygen [27], leading to a long-lived triplet charge-separated dark state [13]. The power dependence of the frequency of the blinking, as well as its presence both under CW and under pulsed excitation, is consistent with the hypothesis suggested above. It is worth noting that even though the polarity of the matrix should have an effect on the driving force for electron transfer, i.e. more blinking in PMMA than in PS, it is probably compensated by the faster oxygen diffusion in PS [28], which might be why a net effect is not observed. From the autocorrelation curves from the

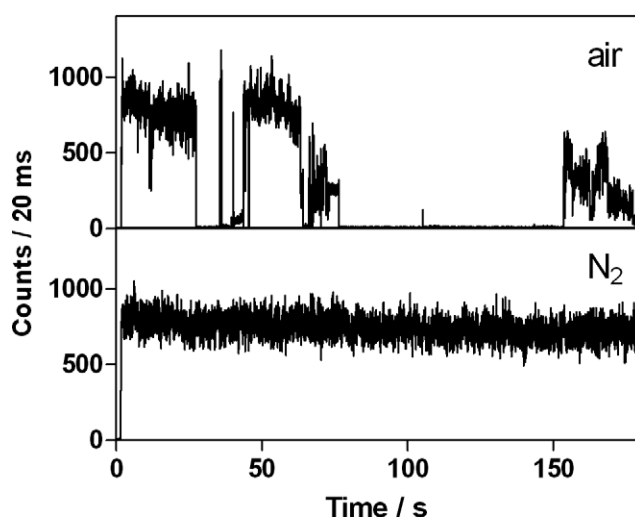


Figure 7. Influence of oxygen on the formation of long off-times in **1** (PMMA, CW excitation).

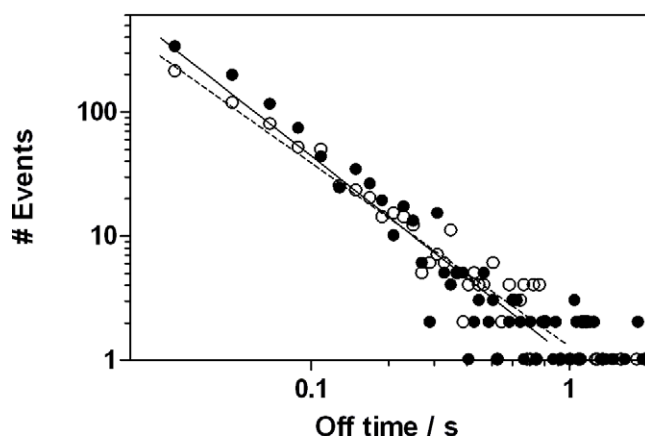


Figure 8. Histogram of off-time duration and best fits to power-law distribution of **1** in PMMA (hollow circles, $m = 1.4$) and PS (full circles, $m = 1.7$). Off events from 40 molecules in each matrix were used to build this histogram.

single-molecule traces [29], we have roughly estimated the quantum yield for the formation of the long-lived dark state as $\sim 10^{-7}$ for compound **1**. The analysis of the duration of the off-times in the latter compound, averaged over 40 molecules, yields a power-law distribution, $P(\tau_{\text{off}}) = P_0 \tau_{\text{off}}^{-m}$ (figure 8). Power-law distributed long off-times have been linked to spurious electron transfer to/from exponential distribution of sites in the matrix [26, 30, 31]. Unlike the frequency of the blinking, the exponent of the power law (m) did change with the polarity as expected, from 1.4 in PMMA to 1.7 in PS, similarly to other reports [26, 31] and consistent with the charge-stabilization properties of each matrix. This suggests that the initial, intramolecular formed charged species in the multichromophoric dendrimer interacts with the matrix in the same way as single, excited chromophores do, resulting in a similar power-law distribution of long off-times. To establish the exact mode of interaction of the intramolecular formed species in the dendrimer with the matrix, more research is needed.

From the practical point of view, the long off-times described above can be easily avoided by removing oxygen in order to increase the efficiency of these compounds as single-photon emitters. This is in contrast with the case for PMI-based compounds, which perform better as single-photon emitters in the presence of oxygen. The reason is that oxygen acts as a triplet state quencher in PMI-labelled compounds [11]. The efficiency as SP sources under nitrogen and under ambient atmosphere for the first intensity level of PDI containing compounds does not change significantly as judged by the similar value obtained for the Mandel parameter (-0.3) and the histograms of the N_C/N_L ratios (figure 6). Even though the quantum yield of intersystem crossing from S_1 to T_1 has been shown to be similar for PMI and PDI ($Y_T \approx 10^{-4}$ [11, 14, 32]), in the case of PMI there are additional pathways that enhance triplet formation [11, 33]. One of these pathways involves intersystem crossing from a higher excited singlet state S_n , itself formed by SS annihilation, to a higher triplet excited state T_n . Intersystem crossing from S_n to T_n in PMI might be favoured by a good energetic matching between the two states or by a favourable change in orbital symmetry ($n\pi^*$, $\pi\pi^*$) [33]. Another pathway feeding triplet formation in PMI was shown to be ST annihilation. These processes were evidenced by means of single-molecule spectroscopy with the observation that Y_T increased when changing from CW to pulsed excitation and by increasing the number of chromophore units in the dendrimer [11, 33]. In the case of PDI, Y_T is not affected by the above factors [14], suggesting that triplet state formation by higher excited state pathways is negligible. The reason for this observation might be related to a different relative energy difference or different orbital symmetry of the higher excited states in PDI. The consequence of this difference is that the formation of triplet states in PDI is not a limiting factor in the performance of these compounds as SP sources. Moreover, triplet lifetimes of PDI derivatives are slightly shorter than for PMI [14]. For compounds 1–3, the triplet lifetime in PMMA under a nitrogen atmosphere and pulsed excitation is around $280 \mu\text{s}$ and Y_T is between 2×10^{-4} and 4×10^{-4} . For the dendrimer with four PMI units, the triplet lifetime is around $400 \mu\text{s}$ and Y_T is 7×10^{-4} in similar conditions [11].

4. Conclusions

We have shown that multichromophoric PDI-based dendrimers behave as SP emitters. The main difference from PMI multichromophoric dendrimers, in which triplet formation is a critical limiting factor, is that PDI compounds will perform better in an oxygen-free environment. Working in oxygen-free conditions will avoid the formation of long off-times related to the formation of radical ions. This is an advantage if the compounds are to be incorporated into device-type samples, for example the configuration used in OLEDs, since these devices provide nearly oxygen-free environments.

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