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Supporting Information

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Single Molecule Spectroscopy Probes the Influence of Molecular Oxygen on Photo-induced Reversible Electron Transfer in Perylenediimide-Triphenylamine-Based Dendrimers

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SUPPORTING INFORMATION

A. Ensemble spectroscopy.

Shown in Figure S1a are the absorption and fluorescence spectra of PN8 in toluene (TOL). Data were collected on a Perkin-Elmer Lambda 40 spectrophotometer (absorption spectrum) and a Spex Fluorolog 1500 fluorimeter (Spex Industries, Metuchen, NJ, fluorescence spectrum on 543-nm excitation). Fluorescence quantum yields reported in the main text were estimated by the reference method [1] by using cresyl violet in ethanol (0.51).

Fluorescence decays were recorded at 600-nm upon 543-nm excitation by using the time-correlated single photon counting (TCSPC) technique on a setup described previously [2]. The decays were analyzed by a weighted iterative reconvolution method based on the Marquardt algorithm [2]. The contribution of the decay times were estimated as relative amplitudes according to $a_j^{rel}=a_j/\Sigma a_j$. Figure S1b displays fluorescence decays and fits of PN8 in methylcyclohexane (1), deaerated toluene (2) and aerated toluene (3).

Shown in Figures S.1c and d are ns-transient absorption spectra of deaerated and aerated TOL solutions of PN8, respectively. Data were measured on a setup that has been described previously in detail [3]. In both cases, together with the GS-depletion (band at 590-nm), we detect

new bands around 500 and 800-nm. For the unsubstituted PDI, radical anion and triplet-triplet absorption were found to peak around 800 and 500-nm, respectively.[4] Therefore, for PN8, the strong band at 800-nm (Fig.S1c, deaerated TOL) must relate to the CSS formation and is a clear indication for the occurrence of ET in TOL. Within the first 10 ns after excitation, the radical anion absorption (800-nm) is higher in deaerated TOL (Fig.S1d) compared to aerated TOL (Fig.S1c), while for triplet-triplet absorption (500-nm peak) the situation is reversed. When O_2 is present, we detect at least a two-fold increase in triplet formation.

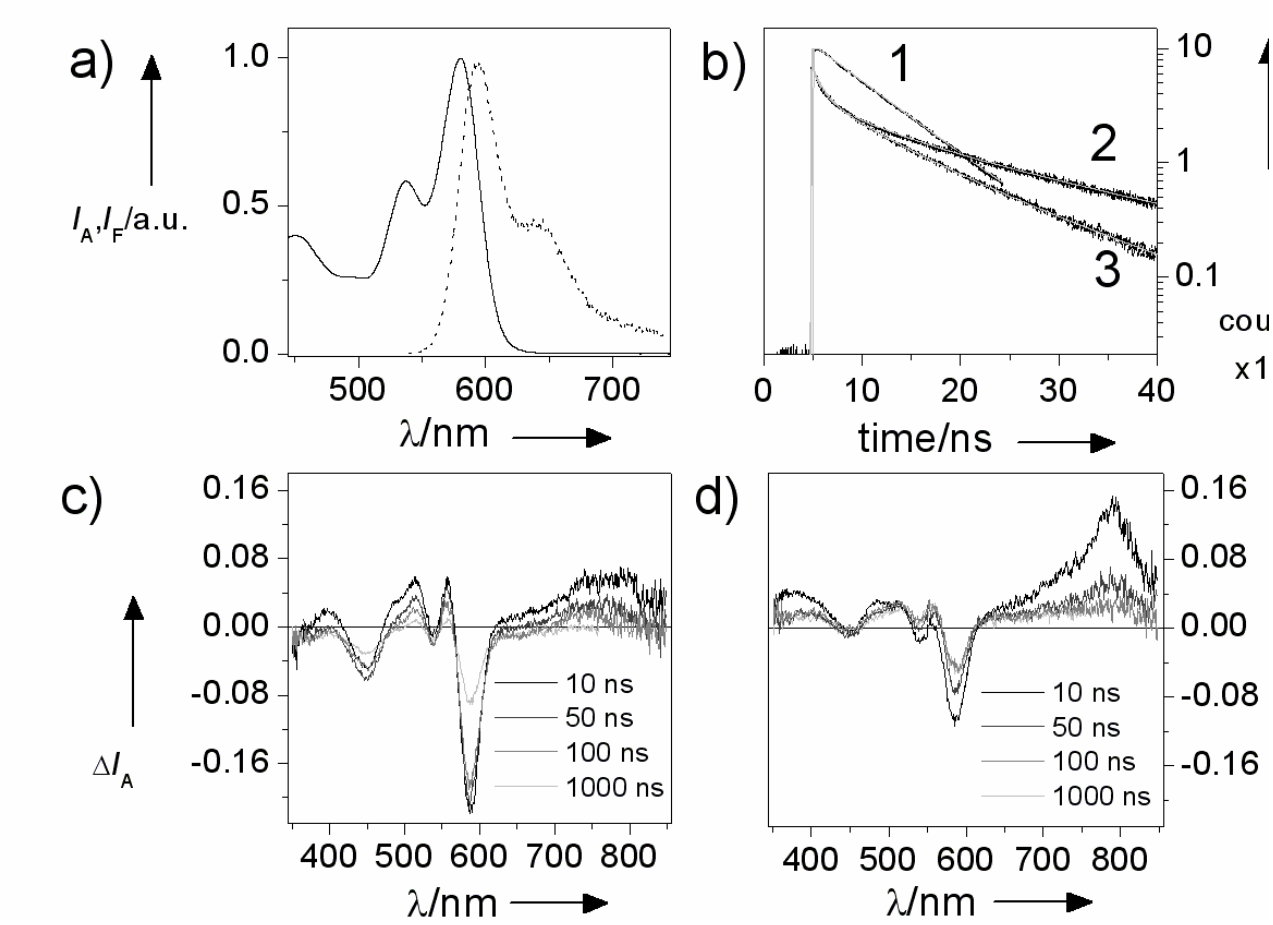

Figure S1. a) Absorption (I_A, line) and fluorescence (I_F, dash, 543-nm excitation) spectra of PN8 in toluene (TOL). b) fluorescence decays (black color) and fits (gray color) of PN8 in methylcyclohexane (curve 1), deaerated

(curve 2) and aerated TOL (curve 3). c) and d) are ns-transient absorption spectra of PN8 in aerated and deaerated TOL, respectively.

B. Single molecule spectroscopy.

Single molecule spectroscopy of individual PN8 and PN0 molecules embedded in polystyrene (PS) was performed on a scanning stage confocal microscope coupled to a picosecond laser system. Samples for single molecule spectroscopy were mounted on an Olympus IX 70 inverted fluorescence microscope equipped with a feedback controlled scanning stage (Physics Instruments) [5]. Optical excitation with 543 nm laser light occurred through an oil immersion objective lens (Olympus 1.4 NA, 60x). Fluorescence was collected by the same lens, passed through a dichroic mirror (DRLP590 Chroma Technologies), filtered through a notch filter (Kaiser Optics) and confocally imaged on a single photon counting avalanche photodiode (SPAD-SPCM 15 EG&G). After parking an individual molecule in the laser focus, the single molecule fluorescence trajectory was registered by a TCSPC card (SPC 630 Becker-Hickl, GmbH) operated in FIFO (first-in, first-out) mode. By doing so, we can register for each detected photon the time lag with respect to the excitation pulse (microtime) and with respect to the previously detected photon (chronological time). From such a single molecule trajectory (FIFO data set), it is possible to construct the fluorescence intensity trajectory with a specific bin time and fluorescence decays of certain amount of photons, here 1000 [5].

Fluorescence decay times were estimated by using MLE (maximum likelihood estimator) fitting and reiterative convolution of the instrumental response function (*IRF*) of the microscope setup (width of 0.38 ns) with a single exponential model function (M) according to [5,6]

$IRF_j \otimes M_j = a_j \exp(-jT/k\tau) + NBG_j + \gamma BG_j$. Here $j=1,k$ with k=64 the number of channels over which the photons of a decay are spread, T is the time window of the experiment (here 45 ns), a and τ are amplitude and decay time, NBG is a constant accounting for non-correlated background and γ is a scaling factor correcting for the presence of correlated background BG, that is, scattered Raleigh and/or Raman photons.

For fluorescence lifetime imaging microscopy (FLIM, 543-nm pulsed excitation), the TCSPC card was synchronized with the controller of the scanning stage and time-resolved photons were recorded in the FIFO mode [7]. For a FLIM image, a single molecule sample area of 20x20 μm was scanned with a resolution of 100x100 pixels at a speed of 10 ms/pixel. A FLIM image was generated pixel by pixel by binning the time-resolved photons from each pixel into a fluorescence decay that was further analyzed by MLE fitting with a single exponential model [6,7].

The autocorrelations of the fluorescence intensity (AC) were constructed from the FIFO data by using a quasi-logarithmic time scale where each channel has an individual time length and delay time [8]

$$AC = \left(\frac{1}{M-m} \sum_{k=1}^{M-m} n(k\Delta t_i) n(k\Delta t_i + m\Delta t_i) \right) / \left[\left(\frac{1}{M-m} \sum_{k=m}^{M} n(k\Delta t_i) \right) \left(\frac{1}{M-m} \sum_{k=1}^{M-m} n(k\Delta t_i) n(k\Delta t_i \right) \right]$$

Here m is an integer, Δt_i is the time length of the channel i, $M=T/\Delta t_i$ with T the time length of the fluorescence intensity trajectory, $n(k\Delta t_i)$ is the number of photons (intensity) at time $k\Delta t_i$ and $n(k\Delta t_i+m\Delta t_i)$ is the number of photons at a later time $m\Delta t_i$. Here, each AC was constructed in 256 channels with a starting channel of a time length of 1μs. By doing so, we can retrieve on/off dynamics in the fluorescence intensity from μs to tens of seconds.

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