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Influence of Structural and Rotational Isomerism on the Triplet Blinking of Individual Dendrimer Molecules

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Sample preparation and measurement conditions.

For the single molecule experiments, samples were prepared by spincoating at 1000 RPM on a glass coverslip a toluene solution of 15 mg/ml Zeonex (polynorbornene) containing a 10^{-10} M of **1**. AFM measurements showed a film thickness between 500 to 1000 nm. As excitation light we used the 488 nm line of a continuous wave Argon-Ion-Laser (Stabilite, Spectra-Physics). A 488 nm notch plus filter of Kaiser Optics was put in the detection path to suppress remaining excitation light. The applied power was 400-600 W/cm^2 at the sample. The Confocal Fluorescence Microscope that works in the epiluminescence mode and the analysis methods are described elsewhere in more detail.[1]

Fluorescence decay measurements.

For the fluorescence decay measurements, the frequency doubled output of a TiSa laser (Spectra Physics) was used to excite individual molecules (repetition rate of 4MHz). Passing a beamsplitter a part of the light was focused onto a Photodiode (Newfocus) to obtain the trigger pulses. After a linear Glan-Thomson polarizer (Newfocus) a λ/2 waveplate was used to adjust the linear excitation polarization. The same setup as in [2] was used. The single photon counting signals of the APD were split: One part was collected in a frequency counter PC card (Keithley, CTM-05/A) to obtain the fluorescence intensity trajectory with a binning time of 10 ms (not shown). The other is acquired in a Time-Correlated Single Photon Counting (TCSPC) PC Card (SPC 630, Picoquant GmbH) together with the trigger signal to record the fluorescence decays of the single molecule in continuous steps of 10 seconds. Details on the analysis of the single molecule decays can be found in [3].

Triplet absorption measurements.

The recording of the triplet absorption spectrum was done using acetonitrile, benzene and toluene (Fluka, spectroscopic grade) as solvents without further purification. Benzophenone (Aldrich, gold label) and Fluoren-9-one (J.T. Baker Chemicals, Photosensitizers Kit) were used as triplet energy donors. The ns-transient absorption measurements were performed by the set up previously described in

[4]. The direct excitation of the samples at 460 nm was carried out using the output of an Optical Parametric Oscillator (OPO, l_{exc} = 460 nm, pulse width ca. 7 ns, energy ca. 1.0 mJ/pulse Continuum) which was pumped by the third harmonic of a Nd:Yag laser. In the sensitisation experiments the samples were excited at 355 nm using the output of the third harmonic of a Nd:Yag laser (l_{exc} = 355 nm, pulse width ca. 5 ns, energy ca. 1.5 mJ/pulse, Continuum). Transient absorption spectra were constructed based on measurements every 10 nm over the 300-800 nm spectral range, averaging at least 10 shots wavelength recorded. The triplet-triplet molar extinction coefficients (e_T) were determined by the energy transfer method using benzophenone and fluoren-9-one as energy donors.[5] The product $f_T \times e_T$ for each compound was obtained by the laser energy effect on the change of absorbance (DA) measured at the l_{max} for the samples under investigation and using an optically matched solution of benzophenone in acetonitrile ($f_T \times e_T$ = 6500 $M^{-1}cm^{-1}$)^2. The plots of DA vs. laser dose were linear and passed through zero indicating that only one-photon processes were occurring. The triplet quantum yields were calculated from the experimantal values of $f_T \times e_T$ and e_T.

Details on calculations.

The two minimized structures were obtained using a molecular mechanics optimization method (Merck Molecular force field) present in SPARTAN®. The ZINDO code was first applied to generate the INDO/S

Hamiltonian using geometry's obtained from molecular mechanics calculations (Merck Molecular Force Field). In a next step, the Hartree-Fock ground-state density matrix is calculated which is used as input to the following CEO calculations. In detail, this means that we compute the reduced single-electron density matrix $\bar{ñ}_{mn} \equiv \left\langle g \middle| c_m^+ c_n \middle| g \right\rangle$, where $c_m^+ (c_n)$ are creation (annihilation) operators of an electron at the *m*th atomic orbital and $\left| g \right\rangle$ is the ground-state many-electron wave function. The diagonal elements $\bar{ñ}_{nn}$ represent the electronic charge density at the *n*th orbital, whereas the off-diagonal elements, $m \neq n$, reveal the bonding structure (i.e., bond order) associated with each pair of atomic orbitals. When the molecule interacts with an external driving field, its electronic density matrix acquires a time-dependent component $äñ(t)$, which can be explained as $äñ(t) = \sum_n a_v(t) x_n + a_n^*(t) x_n^+$. $a_n(t)$ are time-dependent expansion coefficients and the electronic normal mode x_n is a matrix representing the optical transitions between the ground-state $\left| g \right\rangle$ and an electronic excited state $\left| í \right\rangle$. Its matrix elements are given by $(î_í)_{mn} \equiv \left\langle í \middle| c_m^+ c_n \middle| g \right\rangle$. The electronic normal modes allow us to interpret and visualize the changes induced in the electronic structure upon excitations in terms of collective motions of the electronic density matrix. The diagonal elements $(î_í)_{nn}$ represent the net charge induced on the *n*th atomic orbital by an external field, whereas $(î_í)_{mn}$ $m \neq n$ are the dynamical bond orders (or electronic coherence) representing the joint amplitude of finding an electron on orbital m and a hole on orbital n. The CEO approach provides a simple computational algorithm for optical excitations of large and complex molecules with hundreds of heavy atoms. Furthermore, the resulting modes allow a direct real-space interpretation of these absorption spectra. Besides absorption spectra one can also calculate the coupling values among the chromophores using the CEO approach. Further information on the calculations can be found in [6]. All calculated values reported below apply to a molecule in vacuum at zero Kelvin. Only the absorbing parts are considered in the calculation. The hydrogen atoms are not shown in the density matrices. The density matrix is numbered from chromophore 1 to 3, meaning that the first 37 atoms correspond to the atoms of chromophore 1. These 37 atoms can be divided in subgroups. Atoms 1-20 build up the perylene unit, atoms 21-25 represent the imide region, atoms 26-31 represent the phenyl and atoms 32-37 represent the two isopropyl groups. From the transition density matrices shown in figure 2, one can see that there are different interactions among the chromophores. Transition frequencies, oscillator strengths of the transitions in isomer A and B are given in Table 1.

Isomer A	First	Second	Third
Energy	19032.83 cm^{-1}	19033.21 cm^{-1}	19068.59 cm^{-1}
Oscillator strength	25.16 $eVe^2Å^2$	24.89 $eVe^2Å^2$	1.64 $eVe^2Å^2$
Isomer B	First	Second	Third
Energy	18959.83 cm^{-1}	19044.19 cm^{-1}	19150.42 cm^{-1}
Oscillator strength	1.43 $eVe^2Å^2$	21.19 $eVe^2Å^2$	28.25 $eVe^2Å^2$

Table 1:Transition frequencies, oscillator strength of isomer A and B

The transitions of isomer A are delocalized over the three chromophores. The first and second transition are degenerated transitions and we see in the first transition mainly contributions on chromophore one and two, and in the second transition mainly contributions on chromophore one and three. The third transition is equally delocalized over chromophore one, two and three. Isomer B shows a completely different behavior. The first transition is delocalized only on chromophore two and three. These are two chromophores that are closer together. The second transition is localized on chromophore one, and the third transition is again situated on chromophore two and chromophore three. This demonstrates that if two chromophores are closer together, their photophysical behavior can be different. From purely delocalized transitions over the three chromophores in isomer A, we go to localized transitions on pair two and three and a localized transition on chromophore one.

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