

Unveiling the concentration dependent direct triplet formation via singlet fission in a tetracene derivative

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Abstract: Singlet fission is slowed down on diffusional timescales in highly concentrated solutions compared to thin films for a tetracene-like molecule. The underlying mechanism suggests competing intersystem crossing and singlet fission, where in the latter singlets are converted directly to triplets without an intermediate excimer state.

1 Introduction

Singlet fission (SF) is the process by which one excited singlet state yields two triplet states upon close interaction of two chromophores. This ultrafast photoreaction was first observed in solid state and has strong implications in organic photovoltaics [1]. SF was also reported in concentrated solutions, where the diffusion of the reaction partners extends the dynamics to longer timescales [2]. Thus, the rate of the SF process can be on the same order of magnitude as other triplet forming processes such as intersystem crossing (ISC). In this work, ultrafast transient absorption spectroscopy as well as time-correlated single photon counting (TCSPC) is used to investigate concentrated solutions of a tetrachlorinated phenazinothiadiazole (TDCI₄) in toluene. Measurements at different concentrations shows a correlation between singlet decay and triplet formation and an acceleration of the reaction dynamics with increasing concentration. Both observations together speak for a diffusion mediated SF which occurs on the order of several nanoseconds. Within this process, no intermediate state can be identified, which points towards very efficient, almost instantaneous SF.

2 Experimental

Broadband transient absorption measurements are carried out using fs pump pulses and continuum probing with 4 kHz repetition rate. Pump pulses (<100 fs) at 620 nm are generated in a two stage femtosecond optical parametric amplifier of white-light continuum (TOPAS

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Prime). The mechanically delayed white light continuum for sub-ns measurements ranges from 440-740 nm and is generated within a sapphire crystal inside a HELIOS transient absorption spectrometer (Ultrafast Systems). For sub- μ s measurements, an electronically delayed white light laser acts as the source for the probe pulse within an EOS transient absorption spectrometer (Ultrafast Systems). The synthesis of TDCl_4 is described elsewhere [3]. TDCl_4 was dissolved in toluene and the concentration determined by the extinction coefficient at 670 nm.

3 Results and Discussion

3.1 Spectral Evolution

Analysing the change of TA spectra over time shows a blueshift of the excited state absorption (ESA) within the first 20 ps, centred around 545 nm for all concentrations. This behaviour is typical for a vibrational relaxation process. Afterwards, an initial, uniform decay of the ESA is followed by a spectral change on the order of ns (Fig. 1a, b). Spectral similarity with solid state measurements as well as the lifetime of the emerging ESA (≈ 600 ns) allows for the assignment of this process to a triplet formation.

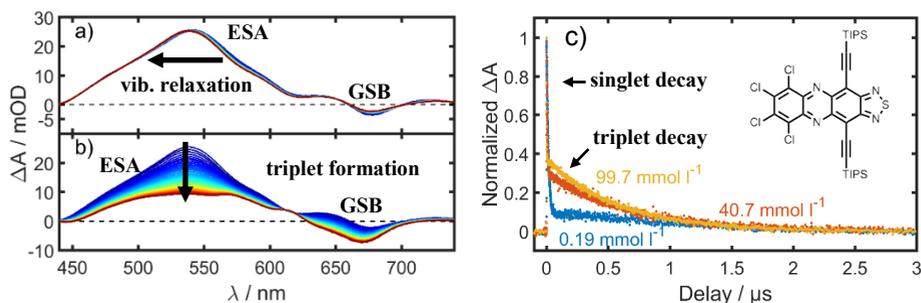


Fig. 1: a) Spectral evolution of the TA spectrum of 48.4 mmol l^{-1} TDCl_4 in toluene on a timescale of 2 – 20 ps. A blueshift of the ESA is observed which can be attributed to a vibrational relaxation process. b) Spectral evolution of the TA on a timescale of 20 – 7000 ps. A clear change of the spectral form is observed, which represents the formation of a triplet species. c) Triplet decay at 545 nm for selected concentrations, normalized at maximum singlet intensity. The increased yield of the long-living triplet at higher concentrations shows the occurrence of a second triplet forming process besides ISC, namely SF.

3.2 Concentration Dependence

Long-time dynamics show an increased triplet yield for highly concentrated solutions (Fig. 1c). This is in accordance with the concept of SF, which inherently implies a higher quantum yield for triplet formation than pure ISC. Additionally, TCSPC experiments display a monoexponential decay of the singlet state in good agreement with results obtained by TA. A comparison with a diffusion model for bimolecular reactions [4] shows, that the triplet yield at low concentrations is higher than expected. This leads to the conclusion that two competing reaction pathways are taking place on a similar timescale: The direct formation of the triplet species via concentration independent ISC and SF. Thus, the triplet formation rate k_T can be formulated as $k_T = k_{\text{ISC}} + c \times k_{\text{SF}}$. A linear fit of the experimental data leads to a SF

rate of $k_{SF} = 7.43 \pm 0.43 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$, which lies within 40 % of the calculated diffusion limited association rate of $1.17 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$.

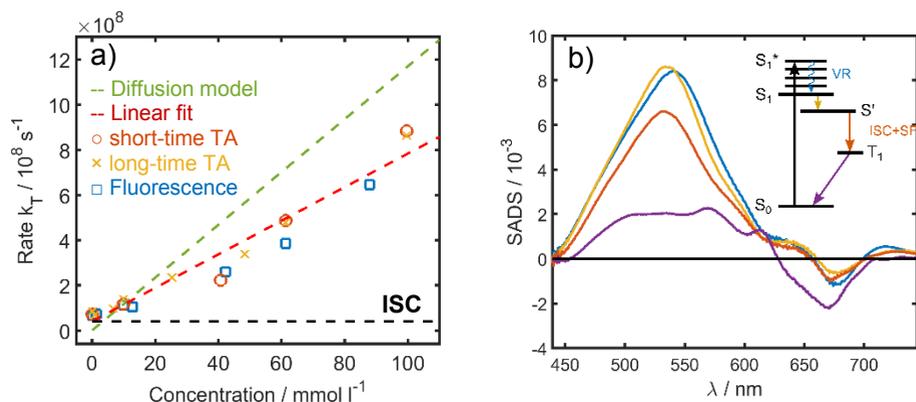


Fig. 2: a) Triplet formation rates obtained with TA and TCSPC with corresponding linear fit (red) and the diffusion-limited association rate (green). The value for k_{SF} ($7.43 \pm 0.43 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$) is within 40 % of the calculated diffusion limited association rate of $1.17 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$. b) Normalized species associated decay spectra (SADS), obtained for a three-step sequential model. The first three SADS only slight deviations, suggesting that they belong to the same electronic state.

3.3 Global Target Analysis

Applying a global target analysis with a three-step sequential model allows for the identification of the species associated spectrum of the species involved in the process within the first 8 ns (Fig. 2b). It can be seen that the hot S_1^* state has the same lineshape as the one assigned to the vibrationally relaxed S_1 state. The slight blue shift of 7nm is assigned to the increase in energy needed to excite the S_1 state due to the loss of vibrational energy. The third SADS is almost identical and merely has a lower amplitude compared to the one assigned to the S_1 state, suggesting an intramolecular rearrangement process within the singlet manifold (S'). The offset of the GTA represents the final and thus triplet state. This model explains the dynamics over a broad concentration range (10^{-1} - 10^2 mmol l^{-1}) whereas no excimer state can be identified. This points towards a singlet fission process, where the initial singlet states are converted very fast and efficient to triplet states.

References

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