

Tailoring ultrafast singlet fission by structural modification of phenazinothiadiazoles

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Abstract: Ultrafast transient absorption and quantum chemistry calculations are combined to demonstrate singlet fission in newly functionalized TIPS-Tetracenes. The coupling strength (but not the energy gap) between S_1 and $^1(TT)$ states gauges singlet fission efficiency and rate.

1 Introduction

The efficiency limit of organic photovoltaic devices can be overcome by Singlet Fission (SF), a photoinduced process where two triplet states result from the “fission” of one excited singlet state [1]. The process was observed in films and occurs on the fs timescale with high yields. Molecular structure, and packing arrangement, are critical for SF. For instance, the SF rate was found to be increased by a factor of two by double Nitrogen substitution in the aromatic skeleton of TIPS-Pentacene (TIPS-Pn) [2]. In turn, further Nitrogen substitution slows down the SF rate [3]. In an attempt to rationalise this effect, a series of phenazinothiadiazoles has been synthesized. The molecules, with four fused aromatic rings, bear some resemblance with TIPS-tetracene, where SF is endothermic [4]. The anthracenothiadiazaole core meets the key requirement for SF, namely, that the energy of the first excited singlet state exceeds twice the energy of the lowest triplet, $E(S_1) > 2E(T_1)$. This is shown by quantum chemical calculations, which suggest minor changes upon halogen substitution. Ultrafast broadband transient absorption provides experimental evidence and supports the correlation between key molecular properties and SF rates.

2 Experimental details

Broadband transient absorption (TA) is performed with fs pump pulses and supercontinuum probing at 1 kHz repetition rate. Pump pulses (<15 fs) spectrally centred at 620 nm are generated in a home-built non-collinear optical parametric amplifier. The supercontinuum white light ranges from 450 to 720 nm and is generated in a 1 mm sapphire plate. A time delayed white light laser (STM-2-UV) is used as probe

for sub- μ s measurements. The synthesis of molecules here studied (TDT, TDCl₄ and TDF₄, see Fig. 1a) was described elsewhere [5]. Thin films were prepared by spin coating. The layers are typically 40 nm thick. UV-Vis absorption spectra of the films are shown in Fig. 1b.

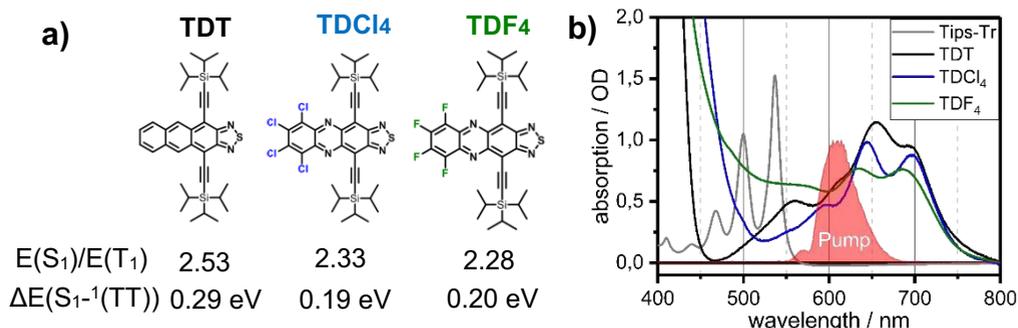


Fig. 1. a) Molecular structures of TIPS-anthracenothiadiazole (TDT) and its tetrachloro (TDCl₄) and tetrafluoro (TDF₄) derivatives; calculated $S_1^{-1}(TT)$ vertical energy gaps and energy ratios $E(S_1)/E(T_1)$ are indicated; b) Absorption spectra TDT (black), TDCl₄ (blue), TDF₄ (green) and TIPS-Tetracene (TIPS-Tn, grey) in thin film (left) and in toluene solution (right). Typical pump spectrum is shown as a red-filled curve.

3 Results and discussion

The transient absorption spectra of TDCl₄ in thin film evolves on the fs timescale. A broad excited state absorption (ESA) band with maximum at 560 nm is observed at earliest time. The band decays on the way towards longer delays while a second ESA band rises concomitantly at 620 nm (Fig 2a). Sharply defined isosbestic points are observed at 480, 570 and 640 nm. Single exponential fits yield characteristic times of (370 ± 10) fs for the decay of ESA at 560 nm and (360 ± 12) fs for the rise of the new ESA band at 620 nm (Fig 2b). No further spectral evolution is observed. The resulting band-shape stays constant and decays with a much longer time constant of (180 ± 30) ns, which is typical for triplet decay (Fig. 3a). Thus, the slowly decaying spectrum is assigned to the triplet state, which is formed by SF with a characteristic time constant of $\tau_{SF}(TDCl_4) = 360$ fs. The spectral assignment was confirmed by quantum chemical calculations (see below). TDT and TDF₄ show very similar spectral evolution. The corresponding SF time constants are $\tau_{SF}(TDT) = 90$ and $\tau_{SF}(TDF_4) = 300$ fs.

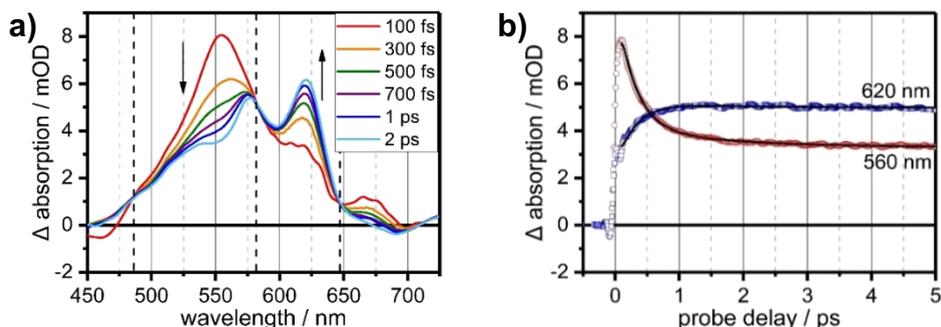


Fig. 2. a) Transient absorption spectra of TDCl₄ at the indicated pump-probe delays and b) Kinetic traces obtained at 560 nm (red circles) and 620 nm (blue squares). Monoexponential fits are shown in black.

The behaviour just described can be rationalized with the help of quantum chemical calculations at the B3LYP/6-31G(d) level of theory. Vertical excitation energies and transient spectra of the S₁ state, the ¹(TT) intermediate and the final T₁ state were obtained (Figs. 1a and 3b). All molecules fulfil the condition for SF ($E(S_1) > 2E(T_1)$). In comparison, $E(S_1)$ is calculated to be 1.99 times $E(T_1)$ in TIPS-Tetracene. Moreover, calculated triplet-triplet absorption spectra show qualitative agreement with the non-decaying component of the fs transient absorption experiment at 5 ps delay (Fig. 3b), which further confirms ultrafast triplet formation by SF.

The calculated singlet-triplet energy gap of TDF₄ and TDT differs by 5% only, while the experimental SF rate changes by a factor of 4 in these compounds. These changes in the experimental SF rates cannot either be explained by the calculated energy gaps between the S₁ state and the ¹(TT), since smaller energy gaps are expected to lead to faster SF rates. The contrary is observed, e.g. TDT shows the larger energy gap, but the faster SF among all compounds. This suggests that it is the coupling strength between the S₁ and the ¹(TT) states (and not the vertical energy gap) that plays a major role in determining the singlet fission rate for these new compounds.

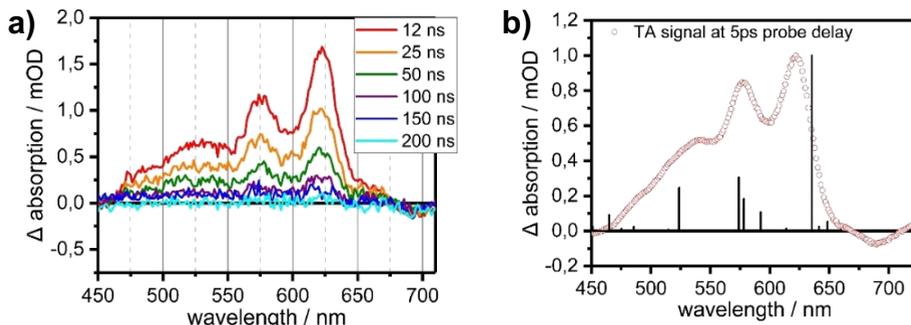


Fig. 3 a) Time evolution of the TDCl₄ transient absorption spectrum in the ns range. b) Transient absorption spectrum of TDCl₄ at 5 ps delay (red circles). Triplet-triplet optical transitions calculated with TD-DFT/B3LYP/6-31G(d) are shown as black vertical bars. Amplitudes are proportional to the corresponding oscillator strengths.

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