

# Acceleration of Ultrafast Singlet Fission in Aza-derivative of TIPS-Pentacene

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**Abstract:** We unveil a new general channel for formation of triplet states via singlet fission in TIPS-pentacene derivatives by probing sub 100 fs dynamics in the near infrared spectral region with transient absorption.

**OCIS codes:** (160.4890) Organic Materials; (300.6500) Spectroscopy, time-resolved.

## 1. Introduction

The efficiency of organic materials acting as single junction solar cells depends on the formation of two triplet states via the fission of a singlet state [1]. In this regard, a singlet fission (SF) occurring on an ultrashort time scale is an advantage since competing channels will be not populated, potentially leading to very high quantum yields. Pentacene (Pn) and its derivatives are very attractive compounds in organic electronics, especially because of their high efficient formation of triplets via SF [2]. TIPS-pentacene (TIPS-Pn) is one important derivative since it enhances orbital overlap due to its side groups, leading to quantum yields of 144% through the formation of triplet states [3]. The SF dynamics has been suggested to take place on a time scale of 1 ps. This contrasts to SF in unsubstituted pentacene, which reaches a quantum yield of 160-180%, but takes place on a much shorter time scale of just about 80 fs [2]. Here we apply transient absorption with high time resolution to TIPS-Pn and a new derivative in a spin-coated thin-film. It is shown that the formation of triplet states via SF in these compounds is much faster than observed previously. In order to avoid overlapping contributions in the visible spectral region, we additionally probe the formation of triplet states in the near infrared (NIR) region. Moreover, we show that the carbon to nitrogen substitution can accelerate SF in Diaza-TIPS-Pn by almost a factor of two.

## 2. Experimental Details

Transient absorption measurements were performed at 1kHz repetition rate using a short pulse generated in non-collinear optical parametric amplifier (at about 600 nm) as pump pulse and a white light supercontinuum as probe pulse. Pump duration was about 20 fs. Probe light was generated via tight focusing of few microjoules at 800 nm in a 2mm sapphire crystal. TIPS-Pn was obtained from Sigma-Aldrich and used without further purification. Diaza-TIPS-Pn has been synthesized according to [4]. Thin films were prepared via spin coating, leading to a thickness of ca. 100 nm. The thin films were provided by U. Bunz group at the Organisch Chemisches Institut, Heidelberg Universität.

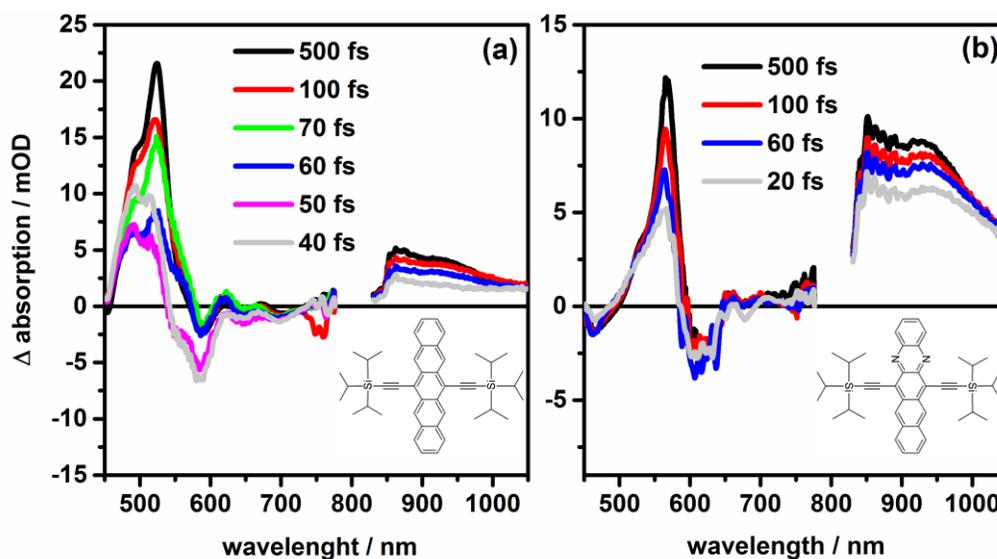


Fig.1 Transient absorption spectra at several probe delay times for (a) TIPS-Pn and (b) Diaza-TIPS-Pn.

### 3. Results and Discussion

The transient absorption signal of TIPS-Pn and Diaza derivative shows similar features (Fig. 1). The visible region is dominated by a strong and broad excited state absorption (ESA). In TIPS-Pn, the ESA band has a shoulder at about 460–490 nm, which decays fast while the maximum at about 530 nm rises. Such a transient evolution of the shoulder and the maximum of the ESA cannot be clearly observed for Diaza, due to the faster and overlapping dynamics. For TIPS-Pn, the band with a maximum at 530 nm is usually identified as the triplet band, while the shoulder at 490 nm is originated from a singlet absorption [3].

A careful analysis and fitting of selected transients at the maximum of the ESA and its shoulder unveils an ultrafast rise and decay time, respectively (Fig. 2(a) and (b)). For TIPS-Pn, the transient at 490 nm decays with just 120 fs while at 530 nm it rises with a time constant of just 200 fs, instead of 1 ps as observed previous. For the Diaza derivative, the rise time of the triplet band is much faster with a time constant of about 100 fs. In order to avoid the overlap between the singlet and triplet absorption bands in the visible, the dynamics in the NIR was probed. For pentacene, bands in the NIR at about 900 nm were assigned exclusively to triplet ESA [5]. The rise of NIR bands (Fig. 2(c)) shows a rise time of 200 fs for TIPS-Pn and 100 fs for diaza, agreeing with the results observed in the visible spectral region. The relative amplitude of the NIR to visible absorption bands further indicates a high efficient formation of triplets for diaza when compared TIPS-Pn.

Moreover, a global target analysis (not shown) was performed, taking into account several models. A sequential model with an ultrafast triplet formation fitted well the data for both TIPS-Pn and diaza. In this regard, no additional loss channels from the initially populated singlet state were required to fit the data.

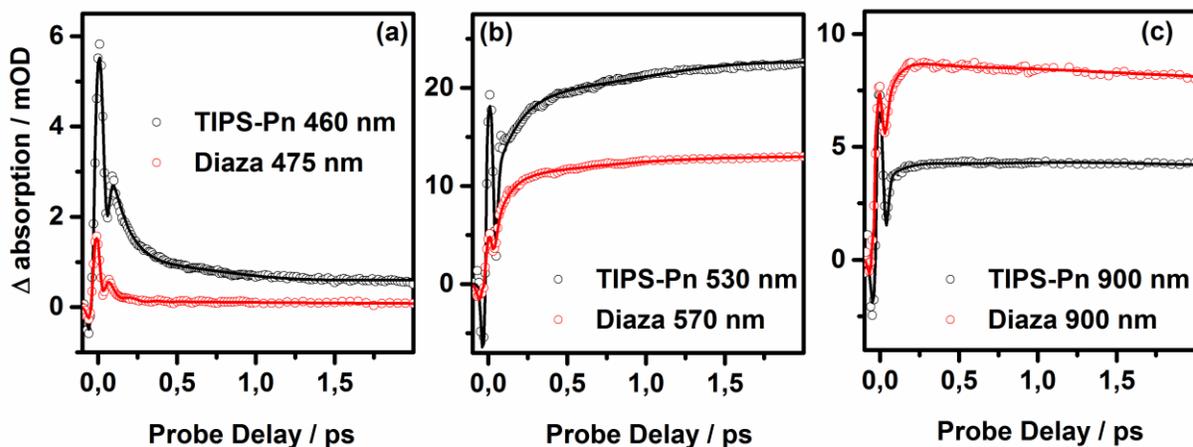


Fig.2 Transients at selected detection wavelengths with corresponding fits. (a) TIPS-Pn at 460 nm and Diaza-TIPS-Pn at 475 nm. (b) TIPS-Pn at 530 nm and Diaza-TIPS-Pn at 570 nm. (c) TIPS-Pn and Diaza-TIPS-Pn at 900 nm.

Summing up, transient absorption of TIPS-pentacene derivatives shows that the formation of triplets is much faster than observed before. In this process, loss channels are not required to explain the dynamics. Such an ultrafast singlet fission can now explain the high quantum yield of TIPS-pentacene. Moreover, substitution of carbon by nitrogen atoms in Diaza-TIPS-pentacene, the SF process is accelerated by a factor of two, making it a promising new compound for organic electronics applications.

### 4. References

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