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# TIPS-anthracene: a singlet fission or triplet fusion material?

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**Abstract.** Triisopropylsilylethynyl-substituted acenes (TIPS-acenes) have received prominent attention in the field of singlet fission, the pentacene derivative being an exothermic singlet fission material, and the tetracene being a prototypical endothermic material. Little attention has been given to TIPS-anthracene, which is expected to exhibit exothermic triplet–triplet annihilation, despite literature reports to the contrary. We show that there is some evidence for singlet fission in TIPS-anthracene solutions, and that it does exhibit triplet–triplet annihilation. We apply anti-Stokes action spectroscopy to determine the upconversion efficiency of a composition of TIPS-anthracene and platinum octaethylporphyrin. At a bias equivalent to 0.86 suns, the composition exhibited an annihilation efficiency of 3.2%, which may be compared to diphenylanthracene, which yielded 9.2% under the same conditions. We attribute the low efficiency to a combination of a shorter triplet lifetime and low lying $T_2$ and $T_3$ states. The results are supported by *ab initio* quantum chemical calculations. © *2018 Society of Photo-Optical Instrumentation Engineers (SPIE)* [DOI: 10.1117/1.JPE.8.022006]

**Keywords:** triplet states; upconversion; *ab initio* calculations.

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## 1 Introduction

The interconversion of two triplets and an excited singlet can be utilized to adapt the solar spectrum to the bandgap of a solar cell, either by splitting the energy of one photon in singlet fission (SF)[1–6] or merging the energy of two photons in triplet fusion.[7–13] An experimental manifestation of the latter is photochemical upconversion (PUC).[14]

PUC is a phenomenon that has been intensively explored over the past decade, with potential applications not limited to photovoltaics, solar fuels, water purification, drug delivery, and biological imaging. PUC proceeds by absorption of low energy photons by sensitizer molecules, which are chosen to have high intersystem crossing yields and a small $S_1 - T_1$ gap. Commonly, metallated porphyrins are chosen as sensitizers. The triplet energy is transferred to a second species either by collision or proximity. At sufficiently high concentrations of triplet excitons, they can "annihilate" to generate an excited singlet state higher in energy than the originally absorbed photons, resulting in upconverted delayed fluorescence.

The triplet–triplet annihilation (TTA) process can potentially result in the generation of higher energy triplet or even quintet states, which are usually undesirable. The efficiency with which triplet pairs annihilate to generate excited singlets, $\eta_c$, directly impacts the maximum efficiency of the upconversion process.[11,15,16]

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For the emitter species, the acenes (anthracene and tetracene) are the most commonly studied structural motif, with diphenylanthracene (DPA) by far the most intensively studied. Indeed, this species could be considered the *drosophila* of PUC. DPA cannot exceed about 0.25 PUC quantum yield, pointing to $\eta_c$ near 0.5.[17–20] Rubrene, a tetraphenyltetracene, is similarly limited to a quantum yield of about 0.3 (the maximum being 0.5), implying $\eta_c \simeq 0.6$.[15]

The conjugate process to TTA is SF.[1] Indeed, TTA is sometimes referred to as "triplet fusion." In many studies, acenes appended with triisopropylsilylenthynyl (TIPS) groups have been found to undergo SF both endothermically and exothermically.[2–4,6] TIPS-pentacene is an efficient SF material, with the energy of two $T_1$ triplets lower than that of the $S_1$ state.[2,4] TIPS-tetracene does undergo SF, but the energy of two triplets exceeds that of the $S_1$ state and thus the process is thermally activated.[3,6] Surprisingly, TIPS-anthracene (TIPS-An) is the subject of very few studies: a literature search for "TIPS-anthracene" only results in a few publications, two of which are density functional theoretical studies.[21–26] Despite claims to the contrary,[26] we expect it to be a poor SF material and, as such, lends itself to investigation as a TTA material for PUC.

In this work, we compare the upconversion efficiency of TIPS-An with DPA and find that it is a poor upconvertor. We attribute the poor upconversion to a shorter triplet lifetime than DPA and, on the basis of *ab initio* calculations, low-lying $T_2$ and $T_3$ states, which may serve as competing annihilation pathways.

## 2 Methods

### 2.1 *Spectroscopy*

Platinum octaethylporphyrin (PtOEP, Porphychem), DPA (Aldrich), and TIPS-An (Aldrich) were obtained commercially and used as received. All solutions were made in toluene (spectroscopic grade). Absorption and emission spectra are displayed in Fig. 1. Excitation spectra were recorded with concentrations [DPA], [TIPS-An] $=2\times10^{-2}$ M and [PtOEP] $=2\times10^{-3}$ M. Fluorescence lifetimes were measured by time-correlated singlet photon counting (TCSCP) using a Horiba Fluoromax with 373 nm excitation.

Anti-Stokes excitation spectra were obtained using a home-built setup.[27] The samples were excited by two beams, both originating in a laser-driven light source (Energetiq EQ-1500).

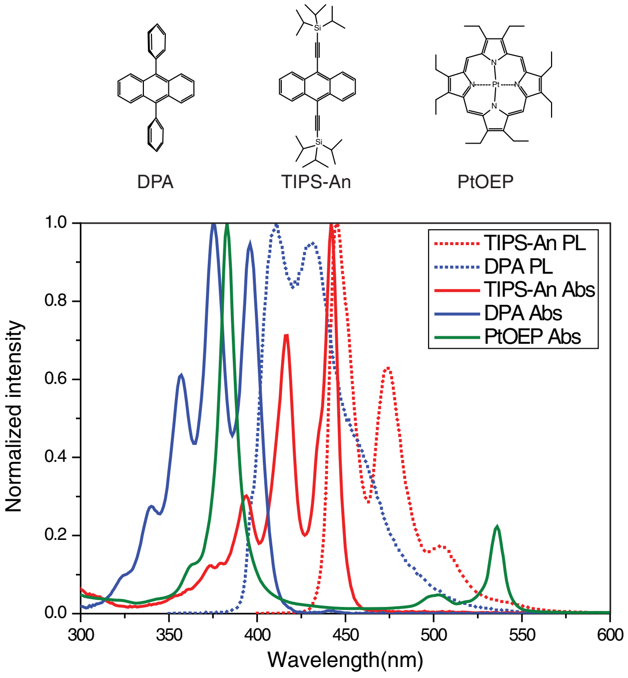

**Fig. 1** Normalized absorption and emission spectra of TIPS-An and DPA, and absorption spectrum of PtOEP.

The output of the EQ-1500 was split, with one part monochromated (CM110) and chopped, forming the probe, and the other part long-pass-filtered, forming the bias. The bias generated a background triplet concentration, which was then perturbed by the probe. The upconverted, anti-Stokes emission was detected and fed into a digital lock-in amplifier to determine the response to the probe light. Scanning the wavelength of the probe revealed the excitation spectrum for a given bias excitation, $f(\lambda)$, which we relate to an equivalent solar concentration. The relative strength of the excitation peaks corresponding to the sensitizer and the emitter are an indication of upconversion efficiency.

To extract the efficiency of the TTA process, the recorded traces, $f(\lambda)$, were modeled by the following equation, as previously described.[27]

$$f(\lambda) = A\left[\frac{\alpha_p^e(\lambda)}{\alpha_p(\lambda) + \alpha_{PL}} + \Phi_{\text{TTA}} \frac{\alpha_p^s(\lambda)}{\alpha_p(\lambda) + \alpha_b + \alpha_{PL}}\right], \tag{1}$$

where $A$ is an experimental scale parameter and $\alpha$ are extinction coefficients, with dimension length$^{-1}$, of the composition at: $p$ = probe wavelength; $PL$ = detection wavelength; $b$ = bias wavelength; of $e =$ emitter; and $s =$ sensitizer. $\Phi_{\text{TTA}}$ is the TTA efficiency.

Time-resolved photoluminescence was recorded using an intensified CCD camera (Princeton Instruments PI-MAX4) mounted to a small spectrograph (Acton sp-2-150i). The luminescence spectra of various samples were recorded as a function of time delay after (sub-ps) laser excitation (Clark-MXR 2210/Light Conversion Topas).

### 2.2 *Calculations*

Following previous studies,[26] we calculated a truncated TIPS-An structure, which was expected to be spectroscopically equivalent to the full structure. This structure, which has the isopropyl groups replaced by hydrogens, was calculated by Bhattacharyya and coworkers to exhibit $S_1$ and $T_1$ states within a few tens of meV of the species where the isopropyl groups were replaced by methyl groups.[26] As such, it is assumed that the complete molecule would yield very similar results but at considerably greater computational cost.

Ground state singlet and triplet geometries of truncated TIPS-An were calculated using the Gaussian09 program with the 6-311G(d) basis set and the B3LYP functional.[28] At the B3LYP/6-311G(d) geometry, the excited states were calculated by CAS-CI involving up to 10 electrons in 10 tzv(d,p) RHF orbitals, using the Firefly program,[29] which is based in part on the GAMESS program.[30] The energies were further refined using the MC-XQDPT2 method, which we have previously shown to give reliable excitation energies.[31]

## 3 Results

### 3.1 *Spectroscopy*

The recorded anti-Stokes excitation spectra are plotted in Fig. 2. The general shape of the excitation spectra are well reproduced by Eq. (1), which takes account of the reabsorption of emitted light by both the sensitizer and the emitter. The peaks corresponding to absorption by the sensitizer leading to upconversion are at 500 and 530 nm.

At first glance, DPA would seem, by far, to be the more efficient emitter species. The TTA efficiency, $\Phi_{\text{TTA}}$, approaches 0.10 at one sun, as others have reported.[18,20] The results for TIPS-An are underwhelming. While the excitation spectra are well described by Eq. (1), the upconversion is rather feeble and does not even reach half that obtainable by DPA.

The fluorescence lifetime of TIPS-An as a function of concentration and emission wavelength is given in Table 1. The lifetimes were obtained from a single exponential fit at the given emission wavelength. At low concentration (0.1 mM), the lifetime is not a strong function of wavelength, being about 6.6 ns. On substantially increasing the concentration to 48 mM (the practical limit that we could achieve), a measurable lifetime shortening is observed at the shortest

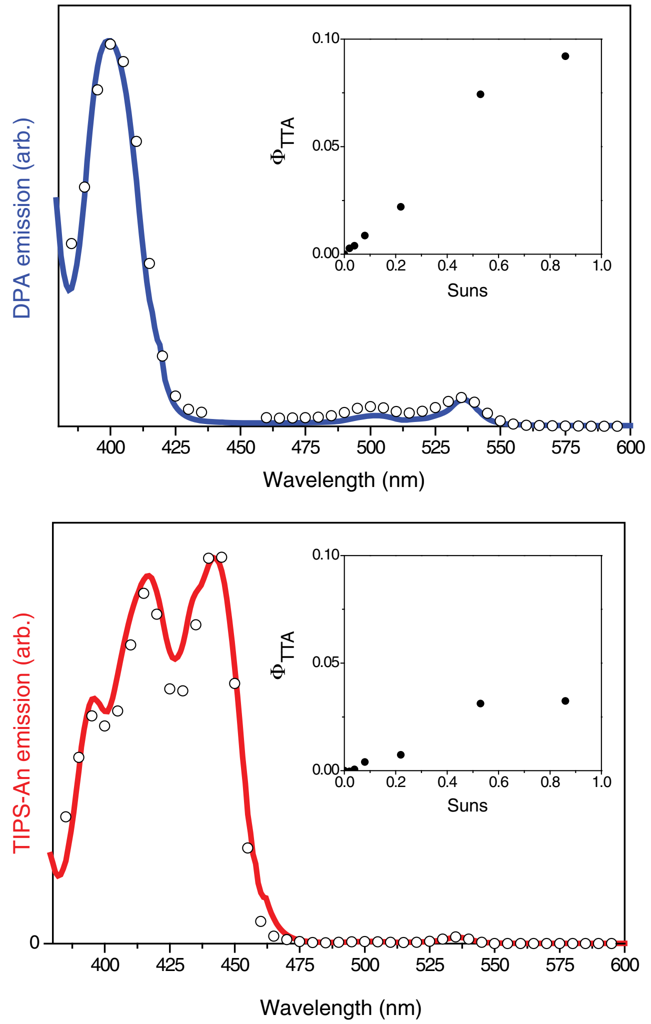

**Fig. 2** Action spectra for PtOEP/DPA and PtOEP/TIPS-An compositions as a function of the bias conditions. The solid lines are fits using Eq. (1). The bias was long-pass-filtered broadband light. DPA is the more efficient emitter, by a factor of about 2.

**Table 1** Fluorescence lifetimes of TIPS-An. Lifetimes are from a single exponential fit to each wavelength.

| Conc. (mM) | $\lambda_{\mathrm{em}}$ (nm) | $\tau$ (ns) |
|---|---|---|
| 48 | 445 | 6.29(5) |
| 0.1 | 445 | 6.59(3) |
| 48 | 475 | 8.27(5) |
| 0.1 | 475 | 6.62(3) |
| 48 | 505 | 9.25(10) |
| 0.1 | 505 | 6.66(4) |

wavelength, which would be characteristic of SF in solution.[2,3,6] But a lengthening of the lifetime is observed at longer emission wavelengths, which is consistent with reabsorption effects.[32]

The concentrated sample (48 mM) has a peak decadic extinction of 170 $\mathrm{mm}^{-1}$ ($\epsilon = 35500\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$). As such, a large proportion of the emitted photons are reabsorbed, especially at low Stokes shift. In an optically dense sample excited on its front face, it has been shown that the observed fluorescence lifetime is increased: $\tau = \tau_0/(1 - a\Phi_F)$, where $\Phi_F$ is the fluorescence quantum yield and $a$ is the proportion of emission that is reabsorbed.[32,33] The lifetime will increase with a higher fraction of reabsorbed emission ($a$). Emission is stokes shifted so any reabsorbed photon will be emitted at lower energy. At lower emission energies there are more emitted photons that could be reabsorbed. Hence longer wavelengths will have higher values for $a$, and thus longer observed lifetimes. Monte-Carlo ray-tracing should also show this, and give you a predicted value of $a$ at each emission wavelength. The lifetime lengthening at longer wavelengths is because fluorescence re-emitted after reabsorption deep in the cuvette can only be detected at longer wavelengths, the short wavelength part being yet again reabsorbed. Such effects can be modeled by Monte–Carlo ray-tracing.

## 3.2 *Calculations*

Table 2 reports the calculated excited state energies of TIPS-An at the [10,10] MC-XQDPT2/tzv (d,p) level. The calculated $S_1 \leftarrow S_0$ excitation at 2.87 eV (432 nm) is in excellent agreement with the experimentally observed absorption spectrum in Fig. 1. With a Huang–Rhys parameter of $S = 0.712$, the vertical transition is expected to be about $S\hbar\omega = 0.12$ eV above the experimental

**Table 2** Calculated [10,10] MC-XQDPT2/tzv(d,p) vertical energies (eV) of states relative to the $S_0$ state and transition moments (au) from lowest state of same spin for TIPS-An. $S_0$ and $T_0$ geometries are calculated at the B3LYP/6-311G(d) level of theory.

| State | $E$ (MC-XQDPT2) | $\mu$ |
|---|---|---|
| $S_0$ | 0 | — |
| $S_1$ | 2.87 | 2.29 |
| $S_2$ | 3.03 | 0.31 |
| $S_3$ | 3.89 | 0.04 |
| $T_1$ | 1.37 | — |
| $T_2$ | 2.77 | 0.02 |
| $T_3$ | 2.79 | 0.34 |
| $T_4$ | 3.08 | 0.01 |

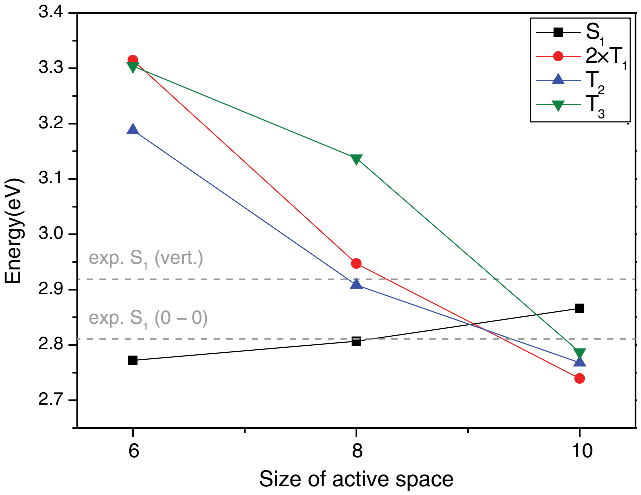

**Fig. 3** Calculated $[n, n]$ MC-XQDPT2/tzv(d,p) vertical energies for TIPS-An at the B3LYP/6-311G (d) geometries of the lowest state of a each multiplicity.

0-0 band, in this case at 2.92 eV (425 nm). It is calculated to be a strong transition, with an oscillator strength of $f = 0.37$, which compares favorably to the integrated absorption spectrum, $f = 0.28$. The $S_1 \leftarrow S_0$ excitation dwarfs the nearby $S_2 \leftarrow S_0$ (410 nm) and $S_3 \leftarrow S_0$ (319 nm) excitations, which cannot be unambiguously observed due to the Franck–Condon envelope of the $S_1 \leftarrow S_0$ excitation. The calculated appearance of the singlet excitation spectrum is in generally good agreement with that previously calculated with the TD-PBE0 method.[25]

The B3LYP/6-311G(d) energies of the optimized $S_0$ and $T_1$ states differ by 1.36 eV, which is in close agreement with the B3LYP/6-31G(d,p) results of Bhattacharyya and coworkers.[26] This does not differ substantially from the MC-XQDPT2 calculation, which puts $T_1$ at 1.37 eV above $S_0$. The important value is the energy of $2 \times T_1$, which is calculated to be 2.74 eV. A summary of the calculated energies as a function of the size of the active space is given in Fig. 3.

## 4 Discussion

According to the B3LYP calculations,[26] TIPS-An should be a candidate for SF, rather than triplet fusion, with $E(2T_1) \sim 2.7$ eV. Here $E(2T_1)$ is calculated at 2.74 eV, which is just lower than the calculated $S_1$ zero-point energy (2.75 eV accounting for the Huang–Rhys parameter).

However, there is not strong *a priori* evidence for SF occurring in concentrated solutions. The apparent lifetime shortening in Table 2 allows an estimate of the SF rate constant. The observed lifetime of emission at 445 nm is 0.30(6) ns shorter than the dilute solution. This implies a new nonradiative process with rate $7.2 \pm 1.4 \times 10^6\ \mathrm{s^{-1}}$. If due to endothermic SF, this places $k_{\mathrm{SF}} \sim 1.5(3) \times 10^8\ \mathrm{M^{-1}\,s^{-1}}$, which is two orders of magnitude below the diffusion limit in toluene. The bimolecular SF rate constant determined for TIPS-pentacene in solution is $2.2 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$,[2] but for TIPS-tetracene, which exhibits endothermic fission, it is $3.2 \times 10^8\ \mathrm{M^{-1}\,s^{-1}}$.[6] As such, if indeed the lifetime shortening is due to SF, the observed rate constant is consistent with endothermic SF and the observation of TTA.

The lifetime lengthening at longer wavelengths in the concentrated sample, due to re-emission of absorbed fluorescence deep in the cuvette, may also be occurring at shorter wavelengths, masking a possible higher rate of SF. Indeed, ray-tracing simulations of the TCSCP experimental geometry suggest that the true lifetime could be shorter than 5 ns, and therefore that the bimolecular SF rate constant could be as high as $4.3 \times 10^8\ \mathrm{M^{-1}\,s^{-1}}$.

The observed $E(S_1)$ is 2.81 eV, implying $E(T_1) \gtrsim 1.41$ eV, at least 40 meV higher than the present "best" calculated value. This is a similar discrepancy to the difference between the calculated (2.87 eV) and derived (2.92 eV) vertical $S_1 \leftarrow S_0$ transition energies.

The upconversion efficiency, at a given triplet concentration, is related to the proportion of second-order decay (TTA), $f_2$, and the conversion efficiency with which triplet pairs are converted to excited singlets, $\eta_c$. The proportion of second-order decay is given by

$$f_2 = \frac{k_2[T]}{k_2[T] + k_1}, \tag{2}$$

where $k_1$ and $k_2$ are the first- and second-order decay constants of the emitter triplet state, respectively. The annihilation efficiency is given by $\Phi_{\mathrm{TTA}} = f_2 \eta_c$.

Under identical pumping conditions, with an identical sensitizer, triplets are created at an identical rate, $k_\phi[S]$, where $[S]$ is the sensitizer concentration. At an emitter concentration of $2 \times 10^{-2}$ M, sensitizer triplet quenching is quantitative: we determined the PtOEP/TIPS-An triplet energy transfer rate constant to be $k_{\mathrm{TET}} = 1.5 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$. Where low annihilation efficiencies are observed, the emitter triplet concentration may be approximated as

$$[T] = \frac{k_\phi[S]}{k_1}. \tag{3}$$

An expression for $\Phi_{\mathrm{TTA}}$ may thus be written

$$\Phi_{\mathrm{TTA}} = \eta_c \frac{k_2 k_\phi[S]}{k_2 k_\phi[S] + k_1^2}. \tag{4}$$

Differences in the observed $\Phi_{\mathrm{TTA}}$ are thus ascribed to differences in $\eta_c$, $k_1$, and $k_2$.

A decrease of $k_2$ compared to DPA, or an increase in $k_1$ will reduce the observed TTA efficiency. Since the energy of the TIPS-An triplet is lower than that of DPA, the energy gap law would imply a shorter lifetime (higher $k_1$), and this on its own could explain the observed results. This effect has been observed in the comparison of DPA and 9-(4-phenylethynyl)-10-phenylanthracene (PEAP).[34] Here, PEAP [$E(T_1) \sim 1.5$ eV] was observed to exhibit a triplet decay 3.6 times faster than DPA [$E(T_1) \sim 1.75$ eV].

Fits to the first-order tail of the sensitized TTA kinetics revealed an extrapolated lifetime of 897 $\mu$s at $[S] = 0$. Under similar conditions, we determined the lifetime of DPA triplets to be 2.2 ms ($k_1 = 4.5 \times 10^2\ \mathrm{s}^{-1}$),[35] which is shorter than the value reported elsewhere[34] but longer than that determined presently for TIPS-An. As such $k_1$ is higher for TIPS-An than for DPA. The rate constant $k_2$ was not independently determined.

The inconclusive observation of SF is consistent with poor coupling between the $\mathrm{S}_1/\mathrm{S}_0$ and $\mathrm{T}_1/\mathrm{T}_1$ bimolecular states, and such a poor coupling could also reduce $k_2$, leading to lower efficiency. However, the exothermic SF rate of TIPS-pentacene in solution is $2.2 \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$,[2] and given its similar electronic structure it would seem implausible that TIPS-An could be significantly hindered in comparison. Indeed, the ethynyl-substituted PEAP and diphenylethynylanthracene exhibit $k_2$ values exceeding that of DPA.[34]

At the highest level of theory, both the $\mathrm{T}_2$ and $\mathrm{T}_3$ states of TIPS-An are calculated to be in the vicinity of $2 \times \mathrm{T}_1$, and thus pose possible competing annihilation pathways. Two annihilating triplets statistically form a triplet encounter complex three times more often than the singlet state desired in PUC. If monomer states of the same multiplicity exist at an energy accessible to the encounter complex, annihilation may occur. Annihilation into the $\mathrm{T}_2$ and $\mathrm{T}_3$ states will result in rapid deactivation to $\mathrm{T}_1$ and thus the loss of TTA efficiency (though the quintet and singlet may interconvert[5]). DPA is also afflicted with a low $\eta_c$ of about 0.45, probably due to accessible triplet states. From the calculated triplet energies, it would seem that this is probable and that the low TTA efficiency of TIPS-An can be attributed to these low-lying states, in addition to a shorter triplet lifetime than DPA.

## 5 Conclusions

TIPS-An was investigated as an SF and triplet fusion material. Some evidence of SF was observed, and TTA was observed to proceed, albeit inefficiently. From this, we conclude that the triplet energy exceeds half that of the lowest excited singlet, $E(\mathrm{T}_1) \gtrsim 1.41$ eV. *Ab initio* calculations of the excited states of TIPS-An point to low lying $\mathrm{T}_2$ and $\mathrm{T}_3$ states, which could be accessible to annihilating triplets. The poor performance of TIPS-An as a PUC emitter is attributed to a combination of these low-lying states and a shorter triplet lifetime than DPA.

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