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Author(s):

Sam L. Bayliss, Felix Kraffert, Rui Wang, Chunfeng Zhang, Robert Bittl, and Jan Behrends

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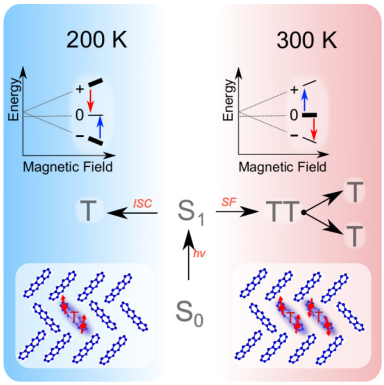
Tuning Spin Dynamics in Crystalline Tetracene

Sam L. Bayliss,[†,‡,‖] Felix Kraffert,[†,‖] Rui Wang,[¶] Chunfeng Zhang,[¶,§] Robert Bittl,[†] and Jan Behrends[*,†]

†*Berlin Joint EPR Lab, Fachbereich Physik, Freie Universität Berlin, D-14195 Berlin, Germany*
‡*Present address: Institute for Molecular Engineering, University of Chicago, Chicago, Illinois 60637, USA*
¶*National Laboratory of Solid State Microstructures, School of Physics, Nanjing University, Nanjing 210093, China*
§*Synergetic Innovation Center in Quantum Information and Quantum Physics, University of Science and Technology of China, Hefei, Anhui 230026, China*
‖*Contributed equally to this work*

Received March 26, 2019; E-mail: j.behrends@fu-berlin.de

Abstract: Tetracene is the archetypal material undergoing singlet fission - the generation of a pair of triplet excitons from one singlet exciton. Here, using time-resolved electron spin resonance, we show how the spin dynamics in tetracene crystals are influenced by temperature and morphology. On cooling from 300 to 200 K, we observe a switch between singlet fission and intersystem crossing generated triplets, manifesting as an inversion in transient spin polarization. We extract a spin dephasing time of approximately 40 ns for fission-generated triplets at room temperature, nearly 100 times shorter than the dephasing time we measure for triplets localized on isolated tetracene molecules. These results highlight the importance of morphology and thermal activation in singlet fission systems.



Singlet-exciton fission is a process in which two spin-1 triplet excitons are created from one photogenerated singlet exciton. First discovered approximately fifty years ago[1,2], singlet fission has recently seen a resurgence in interest for its potential to enhance photovoltaic device efficiencies beyond the Shockley-Queisser limit[3–6]. Singlet fission (SF) has now been demonstrated in a number of materials[3,4], and there have been impressive results integrating fission materials into devices and hybrid architectures[7–9]. Tetracene (Figure 1), was the first material to clearly show the signatures of fission[1,2], and has subsequently been the subject of detailed optical studies providing insights including the timescales of the fission process[10–12], the role of thermal activation and morphology[13,14], and the presence of entangled triplet-pair states[15,16]. Alongside fission, intersystem crossing (ISC) is an alternative pathway to generate triplet excitons in tetracene (and other polycyclic aromatic hydrocarbons[17–21]). Figure 1 shows these two possible outcomes from an initial singlet exciton: the spin-conserving process of SF, and the non-spin-conserving process of ISC. These two processes have very different requirements and properties: SF requires that the initial singlet state must be able to share its energy across (at least) two molecular units, and the energy of the triplet-pair state must be comparable to that of the singlet exciton within $\sim k_{\mathrm{B}}T$, the thermal energy. Under optimal conditions, this can lead to fission on ultrafast timescales (∼ fs-ps). On the other hand, ISC is an intramolecular process, which does not require coupling between neighboring molecules, but instead mandates a spin-orbit mediated spin flip to convert between singlet and triplet states. This latter requirement means that ISC is comparably slow (∼ ns-μs), although a separation in timescales is not sufficient for an unambiguous identification of these processes.

While ISC is ultimately exothermic due to the large exchange splitting in organic materials, SF can be endothermic, making its triplet yield sensitive to temperature. Furthermore, the spin properties of photoexcited triplets are strongly dependent on their interaction with multiple crystal sites, which can be tuned between a bulk crystal and well-isolated molecules. Here we tune these two influences (thermal energy and intermolecular coupling) in order to explore their role on ISC and SF and triplet spin dynamics.

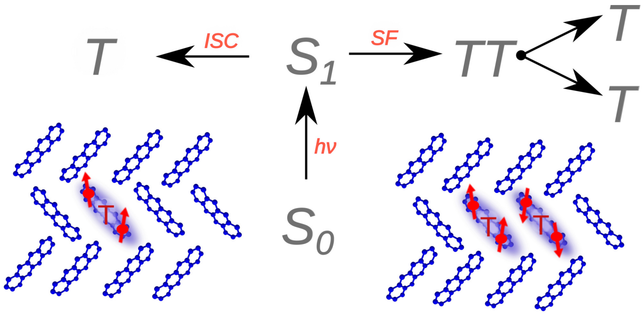


Figure 1. Tuning spin dynamics in tetracene. In single crystal tetracene at room temperature, singlet fission can generate pairs of spin-polarized triplets (TT) from an initial singlet exciton (S_1), photogenerated from the singlet ground state (S_0) by a photon of energy $h\nu$. By lowering the temperature, or preventing intermolecular coupling, intersystem crossing can instead become the dominant triplet-generation mechanism, generating a single triplet (T) from the initial singlet state.

While all-optical studies provide crucial insight into the electronic structure and dynamics involved in triplet-pair generation, fission generates spin-carrying states, which can be directly probed by spin-sensitive techniques, such as electron spin resonance (ESR). Since ESR probes the populations of individual spin sublevels, rather than the populations of electronic states, it enables access to triplet–exciton generation mechanisms (ISC or SF), which can otherwise be challenging to distinguish. In particular, SF selectively populates the T_0 triplet sublevel (with the quantization axis defined by the magnetic field)[22,23], while ISC selectively populates the zero-field triplet eigenstates T_X, T_Y, T_Z (quantization axis defined by the molecule/crystal structure). These two processes therefore lead to different polarization patterns and hence can be distinguished. Using continuous-wave (cw) ESR, Yarmus et al.[22,23] identified non-equilibrium spin sublevel populations from SF in a tetracene crystal at room temperature, and subsequent studies showed the utility of cw optically detected magnetic resonance for probing fission in tetracene[24,25]. While cwESR techniques can provide valuable insights, time-resolved methods allow direct access to spin dynamics such as dephasing and polarization evolution. Despite detailed optical studies, to our knowledge there have been no time-resolved (tr) or temperature dependent ESR studies of tetracene. Here, using trESR, we study the spin dynamics in crystalline tetracene. We first show how in reducing the thermal energy from 300 to 200 K, the initial transient spin polarization in a tetracene crystal inverts from singlet-fission generated to ISC generated. We then demonstrate the role of morphology on triplet spin properties: we observe a spin dephasing time at room temperature of approximately 40 ns for fission-generated triplets, while for isolated tetracene triplets in a host crystal we observe a spin dephasing time of approximately 2.5 μs. These results demonstrate the utility of directly probing fission-generated spin states and the influence of temperature and exciton mobility on their spin dynamics.

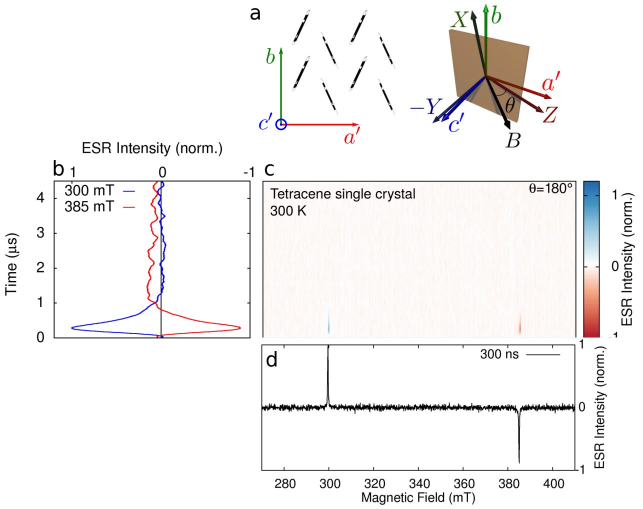


Figure 2. Transient spin-polarization in single-crystal tetracene at room temperature. **a** Tetracene unit cell with orthogonal axes (a', b, c'), and magnetic axes (X, Y, Z). The angle θ of the external magnetic field B is indicated. (The main extention of the tetracene molecule is along c'). **b-d** Transient electron spin resonance. A 532 nm laser pulse (400 μJ) excites the sample in the presence of a cw microwave field ($\omega_1 = 0.27$ MHz). Sweeping an external magnetic field reveals the time-resolved ESR spectra. (The selected orientation represents the maximum splitting between the emissive and absorptive transition, $\theta = 180°$.)

To study both bulk and isolated molecule properties, we investigate two tetracene samples using time-resolved ESR: a tetracene single crystal and a para-terphenyl crystal weakly doped with tetracene. Samples are excited by a 5 ns, 532 nm laser pulse, and the transient ESR signal recorded as a function of time following the laser pulse, giving direct access to the dynamics and polarization pattern of the resulting photoexcited triplets. (Further experimental details are given in the Supporting Information.) We first describe temperature-dependent measurements on the single crystal sample, before turning to the isolated-molecule system.

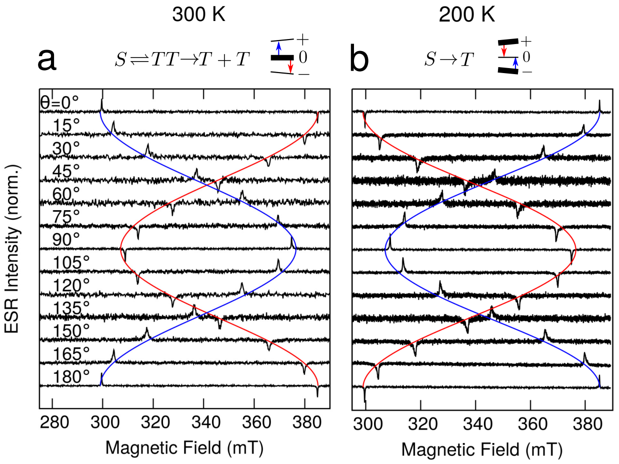


Figure 3. Tuning spin dynamics with temperature. **a** Room-temperature rotation pattern - ESR spectra taken at early times ($\simeq$ 300 ns) after the laser pulse, for different angles θ. **b** Rotation pattern at 200 K. The locations of the absorptive and emissive peaks invert from 300 to 200 K demonstrating a temperature-induced switch between fission-generated and intersystem-crossing generated triplets. Solid lines are simulations using the tetracene zero-field splitting parameters ($D = 1205$ MHz, $E = 277$ MHz). Further details on the simulations are given in the Supporting Information.

The tetracene crystal structure and crystal axes are outlined in Figure 2a. Also shown are the magnetic axes, which define the orientation of the zero-field splitting tensor, characterizing the spin-spin interaction within the triplet state[22]. This interaction gives rise to ESR transition frequencies which depend on the relative orientation of the magnetic field and the crystal axes. The orientation of the tetracene crystal was determined optically by using its polarization-dependent absorption[26], and the angle $\theta = 0°$ determined by maximizing the separation between the ESR transitions. In this orientation, the field is approximately in the ZY plane, and the zero-field splitting interaction gives rise to ESR transitions which depend on the angle θ given by $g\mu_B B_\pm \simeq \hbar\omega_{mw} \pm \frac{3}{2}[(D+E)\cos^2\theta - (D/3+E)]$, where g is the triplet $g-$factor, $B_\pm$ are the resonant fields, μ_B is the Bohr magneton, ω_{mw} the microwave frequency, and D and E the zero-field splitting parameters. The transition separations are therefore maximal for $\theta = 0^\circ, 180^\circ$.

To explore the transition from SF to ISC triplet polarization with temperature we measure orientation-dependent trESR spectra (rotation patterns). We confine ourselves to temperatures $\geq$ 200 K, to avoid any lower-temperature phase transitions[27,28], and the influence of structural reconfiguration on spin-polarization creation. Figure 2c shows the trESR 2D spectra of the tetracene single crystal at room temperature together with a spectrum 300 ns after laser excitation (Figure 2d), showing a low-field absorptive transition and a high-field emissive transition, as well as the time traces for the two resonant transitions (Figure 2b). (The signal rise time is limited by our instrument response function $\tau_{\mathrm{IRF}} \simeq 300$ ns). We note that while the tetracene crystal unit cell contains two rotationally inequivalent molecules (Figure 2a), only a single pair of ESR transitions is observed due to hopping between the two inequivalent sites[29], leading to a single, site-averaged zero-field splitting interaction. The signs of the early-time transitions are consistent with a singlet-fission mechanism which selectively populates the $m = 0$ triplet sublevel T_0, since this mandates a low-field absorptive transition along with a high-field emissive transition in the case of maximum splitting ($\theta = 0, 180^\circ$) between the two lines[22,23]. However, compared to a powder sample, for which a selective population of the $m = 0$ triplet sublevel T_0 can be unambiguously assigned from a single spectrum[30], assignment is more involved for a single crystal since not all orientations are sampled. To enable a reliable assignment, we therefore perform sample rotation in our trESR experiment: for population by SF, a given transition should not change sign with angle, whereas this is possible with ISC (see Supporting Information for futher details).

Figure 3a shows the early-time ($\simeq$ 300 ns) ESR spectra at 300 K as a function of the angle θ. The rotation pattern leads to an unambiguous determination of the dipolar coupling parameters D, E agreeing well with the zero-field splitting tensor previously determined for tetracene (simulation: solid lines, Figure 3)[22]. The 300 K data show no sign inversion for a given transition as a function of angle, consistent with a SF population, but also consistent with certain special cases of ISC (Supporting Information). The measurements at 200 K (Figure 3b) allow us to separate SF and ISC populating mechanisms. Strikingly, from 300 to 200 K the polarization properties are inverted: the emissive ESR transitions become absorptive and vice versa. This demonstrates a change in the mechanism of spin sublevel population and cannot be explained if the dominant process at both temperatures would be SF. Since the 200 K rotation pattern is not possible with T_0 populations, we assign that filling pattern to ISC. Furthermore, since we do not expect a strong temperature dependence in ISC populations between 200-300 K, this requires another mechanism at 300 K, which we therefore assign to SF. Further details of the polarization patterns of crystals with different generation mechanisms are given in the Supporting Information. Since we do not observe the signature of strongly interacting triplet-pair states[30,31], we conclude that we probe either weakly interacting triplet pairs (interaction strength<ESR linewidth), or dissociated triplets.

These observations indicate the inhibition of SF at lower temperatures, enabling ISC to become more competitive with the remaining singlet decay channels. This is consistent with early magnetic field studies[32], and recent time-resolved photoluminescence experiments which demonstrate that fission is thermally activated in single-crystal tetracene[14]. A different situation appears to hold in evaporated films however, where fission appears to be temperature insensitive[13,14]. We note that we were not able to measure any triplet ESR signals in evaporated tetracene films, in contrast to the strong signals we observe in single-crystal samples. This may be due to reduced triplet-exciton lifetimes in thin films as compared to single crystals[33,34], or the broader triplet powder spectra, which leads to lower peak signal intensities.

Upon rotating the sample, we note that we did not observe a sign inversion of the early-time signal, as was seen in earlier cwESR experiments[22]. Yarmus et al. attributed this sign inversion to effects caused by spin-relaxation times that depend on the rotation angle. However, the two-component nature of the transient ESR signal at 300 K provides an alternative explanation for a sign inversion in cw ESR: Figure 2 (and Supporting Information) shows that in addition to the main fast component at the high-field transition at 300 K, a second slower component arises giving a change of sign at $\simeq 1\,\mu s$ (Figure 2b), observable in the time-resolved measurement. This suggests that two different processes, i.e. SF and ISC, are active at generating triplet polarization at 300 K. Since a steady-state method like cwESR measures the time integral of the ESR signal and therefore cannot distinguish between these two transient processes in series, such a behavior could give rise to the sign inversions observed by Yarmus et al.. Further comparison of transient and cw measurements are discussed in the Supporting Information. We also note that the two-component transient behavior is also supported by the laser energy dependence shown in the Supporting Information revealing different laser energy dependences for the early and late component, the late component at 300 K having the same laser energy dependence as the signal at 200 K.

Having discussed how tetracene spin dynamics are influenced by temperature, we now turn to their dependence on exciton mobility. To do so, we compare the behavior of single crystal tetracene to tetracene doped in a para-terphenyl host crystal (Figure 4). Doping tetracene in para-terphenyl at low concentrations (4.6×10^{-5} mol/mol) results in isolated tetracene molecules, enabling us to compare intramolecular spin properties to those observed in a bulk crystal. For this sample we can exclude SF because of the separation between neighboring tetracene molecules due to dilution in the host. ISC is therefore the dominant process (confirmed by measurement of a powdered sample shown together with a simulation in the Supporting Information).

We first compare triplet spin dephasing times $T_2^\star$ in the two systems. We find that the short $T_2^\star$ in the tetracene single crystal precludes the use of pulsed ESR techniques, and so we extract $T_2^\star$ through modeling microwave-power dependent transient ESR dynamics (Figure 4a and Supporting Information). We find $T_2^\star \simeq 40$ ns for the single crystal sample, while $T_2^\star \simeq 2.5\,\mu$s for tetracene in para-terphenyl[35], nearly two orders of magnitude longer, giving rise to coherent Rabi oscillations in the dynamics. Further simulation details are contained in the Supporting Information. (We note that the longer dephasing time for tetracene in para-terphenyl enabled us to use pulsed ESR to measure its

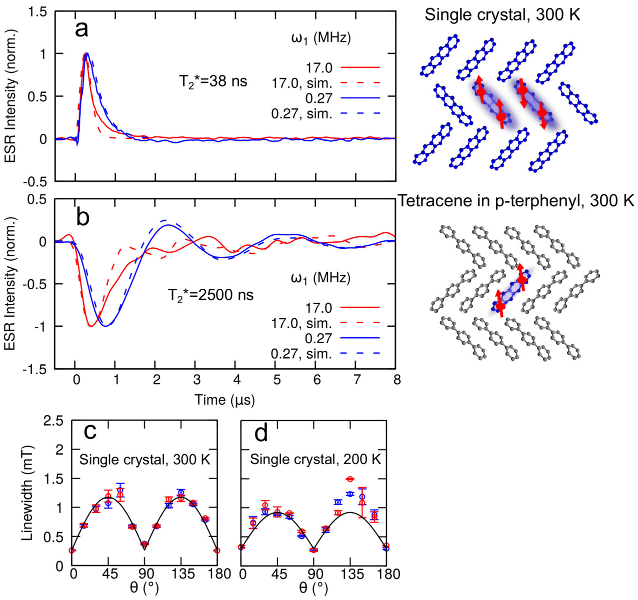


Figure 4. Tuning spin dynamics with morphology. **a**/**b** Extracting the triplet dephasing time from microwave-power dependent kinetics. In single crystal tetracene (**a**), we find a dephasing time $T_2^\star \simeq 40\,\mathrm{ns}$, while for isolated tetracene molecules (**b**) $T_2^\star \simeq 2.5\,\mu\mathrm{s}$, nearly two orders of magnitude longer. **c**/**d** Role of anisotropy in spin resonance linewidths. For the single crystal, the linewidth anisotropy is consistent with a rotational disorder model (solid lines). Blue and red colors correspond to absorptive and emissive transitions respectively.

Hahn-echo coherence time T_2, an upper bound for $T_2^\star$. We found $T_2 \simeq 6.7\,\mu\mathrm{s}$, consistent with the $T_2^\star \simeq 2.5\,\mu\mathrm{s}$ found by simulating the transient ESR dynamics.) The difference in dephasing times ($T_2^\star$) between the crystal and the para-terphenyl sample indicates that site-to-site hopping between magnetically inequivalent sites is the predominant decoherence mechanism in crystalline tetracene. (We note that para-terphenyl and tetracene have a similar number of nuclear spins, and hence a difference in the nuclear spin bath is unlikely to account for this large difference.) A further contribution to dephasing for triplet-pairs can arise from fluctuations in the triplet-triplet coupling: the lack of an observable triplet-triplet interaction in the ESR spectra indicates that this interaction must be much weaker than the zero-field splitting interaction, and so we expect a smaller contribution to dephasing from this mechanism. The role of triplet-pair interactions on spin coherence warrants future investigation however. As outlined above, site-to-site hopping appears also in the static spin properties: the zero-field splitting tensor of triplets in a tetracene crystal is the average of the molecule zero-field splitting tensor over the two crystal sites[22]. This is further observed in the reduced ESR linewidths in single crystal tetracene compared to tetracene in para-terphenyl (Supporting Information): the hyperfine fields responsible for the several mT linewidths (∼1-3 mT) in the para-terphenyl sample[35] are motionally averaged in the single crystal (Supporting Information), giving much smaller linewidths (∼0.2-1 mT). The single crystal linewidths are also highly anisotropic, which has previously been ascribed to a site-to-site hopping mechanism[36,37]. Alternatively, we find that this linewidth anisotropy is consistent with a rotational disorder mechanism (solid lines in Figure 4c,d), where a small quasistatic rotation in angle of the zero-field splitting tensor will perturb the resonant fields $B_{\mathrm{res}}(\theta)$ by $\delta B_{\mathrm{res}}(\theta) \simeq (\partial B_{\mathrm{res}}(\theta)/\partial\theta)\delta\theta$, where $\delta\theta$ is the amplitude of the angular disorder, hence giving a linewidth which follows $|\partial B_{\mathrm{res}}(\theta)/\partial\theta|\delta\theta$, i.e. the derivative of the resonant fields (Figure 3) as a function of angle. Using this functional form we extract $\delta\theta \simeq 0.33^\circ$ at 300 K, providing an estimate of the small rotational variation within the crystal. We note that triplet state electron nuclear double resonance measurements can deliver further information on the line broadening caused by hyperfine couplings if T_2 is- sufficiently long[38].

Our study demonstrates the utility of spin resonance to probe SF systems. Futhermore our results support a thermally activated SF mechanism in crystalline tetracene. We found that triplet spin coherence is hampered by hopping while an additional influence on the spin coherence by fluctions in the triplet-triplet coupling requires further investigations, something that may be particularly important in isolated fission units such as dimers[31,39–41]. Furthermore, a departure from the thermodynamic crystal structure may provide more optimal spin-polarization generation through SF in more optimized geometries. Interestingly, we did not observe the signatures of spin-2 (quintet) triplet-pair states[30,31] at room temperature in single crystal tetracene. Recent results in pentacene[42] suggest that such states may be observed in a semi-dilute regime, where triplet-pairs may form, but diffusion is inhibited. Our results show that SF is the dominant triplet spin-polarization mechanism for single-crystal tetracene at room temperature and highlights how ISC can be an important generation pathway in singlet-fission materials. Future studies combining time-resolved optical and spin resonance techniques could provide a powerful tool to probe the dynamics of spin diffusion and transfer in hybrid organic-inorganic device architectures, and ultimately lead to control of such properties.

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Supporting Information Available

Supporting Information containing: Methods, Assignment of Spin Polarization, Fluence Dependence, Kinetics Comparison at 200 and 300 K, trESR Kinetic Simulations, Comparison with Cw Experiments, Additional Tetracene in Para-Terphenyl Data, Orientation-Dependent Linewidths

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