Site-selective measurement of coupled spin pairs in an organic semiconductor

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From organic electronics to biological systems, understanding the role of intermolecular interactions between spin pairs is a key challenge. Here we show how such pairs can be selectively addressed with combined spin and optical sensitivity. We demonstrate this for bound pairs of spin-triplet excitations formed by singlet fission, with direct applicability across a wide range of synthetic and biological systems. We show that the site-sensitivity of exchange coupling allows distinct triplet pairs to be resonantly addressed at different magnetic fields, tuning them between optically bright singlet (S = 0) and dark triplet, quintet (S = 1, 2) configurations: this induces narrow holes in a broad optical emission spectrum, uncovering exchange-specific luminescence. Using fields up to 60 T, we identify three distinct triplet-pair sites, with exchange couplings varying over an order of magnitude (0.3-5 meV), each with its own luminescence spectrum, coexisting in a single material. Our results reveal how site-selectivity can be achieved for organic spin pairs in a broad range of systems.

Results and Discussion

Method for selectively addressing exchange-coupled triplets.

Despite their key role in light-emitters and harvesters, triplet pairs have only recently been discovered to form exchange-coupled states (13–17) - we start by outlining how such states can be selectively addressed to provide a site-specific measurement of their exchange interactions and optical profiles. We extract multiple triplet-pair states with exchange couplings varying by an order of magnitude and decouple their distinct luminescence spectra from an otherwise inhomogeneously broadened background, reaching sub-nm spectral linewidths. Our results open up new means of determining structure-function relations of coupled spins, and identify unambiguous pair signatures. This approach is directly applicable to a range of organic systems: from electron-hole pairs in next-generation light-emitting diodes to coupled excitons in artificial and naturally occurring light harvesters.

Significance Statement

Pairs of spins in molecular materials have attracted significant interest as intermediates in photovoltaic devices and light-emitting diodes. However, isolating the local spin and electronic environments of such intermediates has proved challenging due to the complex structures in which they reside. Here we show how exchange coupling can be used to select and characterise multiple coexisting pairs, enabling joint measurement of their exchange interactions and optical profiles. We apply this to spin-1 pairs formed by photon absorption whose coupling gives rise to total-spin S = 0, 1 and 2 pair configurations with drastically different properties. This presents a way of identifying the molecular conformations involved in spin-pair processes, and generating design rules for more effective use of interacting spins.

All authors discussed the results. S.L.B. and L.R.W. analysed the data and wrote the manuscript with input from all authors. S.L.B., L.R.W., A.M. and K.Y. carried out the experiments at the HPMF. S.L.B., L.R.W., K.G., Z.Y., K.Y., A.S. and A.D.C. carried out the experiments at the LNCMI. K.J.T. and J.E.A. provided the materials. All authors discussed the results. The authors declare no conflict of interest. The data underlying this publication are available at [URL to be added in proof].

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Fig. 1. Selective addressing of exchange-coupled triplet-exciton pairs. (A) Schematic of spin-pair generation by singlet fission for an ensemble of pair sites with different exchange interactions. Photon absorption generates a spin-singlet exciton \( S_1 \), which can radiatively decay, producing photoluminescence (PL), or undergo fission into a pair of triplet excitons \( TT \). Fusion of this triplet pair reforms the singlet exciton, while dissociation destroys it. (B)/(C) Triplet-pair level anticrossings for a single exchange energy. A magnetic field tunes optically dark triplet or quintet spin sub-levels into near-degeneracy with the bright singlet state, resulting in selective reductions in the PL at fields proportional to the exchange interaction \( J \). \( \Delta PL/PL=\{PL(B)-PL(0)\}/PL(0) \). (D) The magnetic field induced anticrossings create spectral holes linked to specific triplet pair. This enables the narrow associated emission profiles of triplet pairs with different exchange interactions to be extracted.

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Fig. 1A outlines the process of triplet-pair generation by singlet fission, where both fission and the subsequent fusion process are spin-conserving. This makes the spectral regions associated with triplet pairs sensitive to their spin states, which can be resonantly tuned with an external magnetic field (Fig. 1B). For strongly exchange-coupled triplets, the eigenstates at zero magnetic field consist of the pure singlet \( S = 0 \), triplet \( S = 1 \) and quintet \( S = 2 \) pairings of the two particles. Due to its singlet precursor, fission selectively populates the \( S = 0 \) triplet-pair configuration, which is energetically separated from the optically inactive triplet or quintet states due to the exchange interaction. Application of a magnetic field enables these triplet or quintet states to be tuned into resonance with the optically active singlet pair state when the Zeeman energy matches the singlet-triplet or singlet-quintet exchange splitting. At these field positions, bright singlet pair states become hybridized with a dark triplet or quintet pair-state, manifesting as a resonant reduction in the relevant PL spectral window (Fig. 1C) (16–18).

Crucially, the crossings directly address pairs with a specific exchange coupling. For an exchange interaction \( J_{S_1 \cdot S_2} \), where \( S_{1,2} \) are the spin operators for the two triplets, the resonances occur at \( |J| \) (singlet-triplet crossing), and \( 3|J|/2 \), \( 3|J| \) (singlet-quintet crossings), giving a direct measurement of the exchange. (Here we take \( J > 0 \) - see SI Appendix.) Furthermore, only the emission linked to the resonant triplet pair will be diminished at each level crossing. The magnetic field resonances will therefore selectively burn spectral holes linked to pairs with a given exchange coupling (Fig. 1D). From these resonant spectral changes, both the spin and optical properties of pair sites are therefore reconstructed. Importantly, since triplet pairs with different exchange interactions will have separated resonant fields, their associated spectra can be individually measured. Specific spin-pairs with distinct spectral and spin properties can therefore be disentangled in an ensemble measurement and their local environment and microscopic properties probed. This is the key principle of our approach to provide a spin- and site-selective measurement of organic spin pairs.

**TIPS-tetracene.** Of the expanding class of singlet fission materials for photovoltaic application, solution-processable systems with a triplet energy close to the bandgap of silicon are particularly important since they could be integrated directly with established high-efficiency silicon technologies. One such material is TIPS-tetracene (Fig. 2A/B), a solution-processable derivative of the archetypal fission material tetracene (19, 20), which has been shown to undergo effective fission and generate exchange-coupled triplet pairs (13, 21, 22). Furthermore, singlet and triplet-pair states are nearly iso-energetic in TIPS-tetracene, and so photoluminescence can be used to interrogate the fission products (21–23). Here we use TIPS-tetracene to study the spin and electronic structure of coupled triplet excitons. To achieve both high spectral and field resolution, we perform measurements using both pulsed (< 60 T) and cw (< 33 T) magnetic fields on three identically prepared samples (Materials and Methods). Sample 1 under pulsed field at 1.4 K, and samples 2 and 3 under cw fields at 2 and 1.1 K respectively. Samples are crystallites of \( ~\text{nm} \) linear dimensions, containing multiple domains, prepared by evaporation from saturated solution and were not specifically oriented with respect to the magnetic field. We first identify triplet-pair level crossings in TIPS-tetracene and then use these to spectrally characterise multiple distinct triplet pairs.

**Triplet-pair level crossings.** Fig. 2C shows the changes in integrated PL up to 60 T for a TIPS-tetracene crystallite at 1.4 K (Sample 1, pulsed fields - see Materials and Methods), where \( \Delta PL/PL=\{PL(B)-PL(0)\}/PL(0) \). Below 1 T, the conventional singlet fission magnetic-field effect is observed, indicative of weakly coupled triplet pairs (19), while at \( \geq 1 \text{T} \) a very different behavior arises. On top of the monotonic PL reduction with field, which we discuss later, multiple PL resonances are apparent: a series below 15 T, and additional resonances above 30 T, indicating triplet-pair level anticrossings. As shown in Fig. 1C, for a given triplet pair there are three possible resonances with the fission-generated singlet state, occurring with...
Vibrational structure in \(TT\) spectra. In keeping with previous assignments, the first spectral peaks at \(\gtrsim 560\,\text{nm}\) are attributed to 0-0, i.e., zero-phonon, transitions (22). This is also consistent with the greater overlap of low-energy modes on the higher-order vibrational transitions described in detail below (Fig. 4B). Sample 3 (measured at the lowest temperature) exhibited pronounced \(TT_a\) signatures (Fig. 4A), with linewidths of the extracted spectra reaching as low as 0.5 nm (15 cm\(^{-1}\)), significantly narrower than the \(\sim 10\,\text{nm}\) linewidth of the 0-0 peak in the steady-state PL spectrum. This allows us to identify the vibrionic transitions shown in Fig. 3 with greater accuracy (Fig. 4B). (Note that Sample 2 spectra - Fig. 3F-H - were measured using a spectrometer with lower spectral resolution, limiting the minimum linewidths). We use this spectrum to extract four ground-state vibrational modes involved in the emission process. Fig. 4B shows a stick spectrum of the progression of one lower energy mode with wavenumber \(\nu_4 = 310\,\text{cm}^{-1}\), and three higher energy modes \((\nu_2,\nu_3,\nu_4 = 1160, 1270, \text{and } 1370\,\text{cm}^{-1})\), showing good agreement with the measured spectra. These frequencies are in agreement with modes found in the ground state Raman of TIPS-Tetracene films (22) with \(\nu_4\) similar to typical C-C-C out-of-plane bending modes and \(\nu_2,\nu_3\) similar to typical C-C stretching/C-C-H bending modes (25).

To our knowledge these are the first measurements of narrow optical spectra which can be associated with triplet pairs. The sub-nm optical linewidths obtained here are comparable to those obtained in fluorescence line narrowing experiments of tetracene (26), highlighting the sensitivity of this approach.
of the resonances in the integrated PL and the corresponding evolution of the emission spectrum. By 10 K, the resonances below 15 T are lost, concurrent with the loss of the $\lambda_a$ and $\lambda_b$ spectral features (Fig. 5B). The fact that the resonances at $\sim 33$ and 42 T have distinct temperature dependences supports their assignment to the first crossing of different triplet pairs (rather than a single species with a more structured exchange interaction (27)). By 30 K, no PL resonances are observed, with no magnetic-field effect beyond $\sim 1$ T. Measurement of PL spectra between 4.2-1.4 K (Fig. 5C) shows that the $\lambda_a, b$ spectral features evolve significantly over this temperature range, indicating that escape from the associated emission sites has an activation temperature on the order of a few Kelvin ($\sim 0.1$ meV). Interestingly, this is approximately the exchange coupling for $TT_a, b$. However, we note that this energy scale may alternatively be: (i) a reorganisation energy due to molecular reconfiguration or (ii) an electronic barrier between different excited states.

**High-field spin mixing.** While resonant spectral analysis provides a window into the electronic structure associated with triplet pairs, the magnetic lineshapes provide insight into spin-mixing mechanisms and the emissive species. The magneto-PL shows a monotonic decrease with field, up to nearly 50% at 60 T (Fig. 2C), a drastically higher field than the $0.5$ T scale usually seen in organic systems. This 'anticipated high-field effect can be explained due to $g$-factor anisotropy which can non-resonantly mix the singlet $|S\rangle$ and $m = 0$ triplet state $|T_b\rangle$, when triplets are orientationally inequivalent, analogous to $\Delta g$ effects observed in spin-1/2 pairs due to differences in isotropic $g$-values (4, 28, 29). The competition between spin-mixing $\Delta g$ Hamiltonian terms and total-spin-conserving exchange terms sets a characteristic saturation field for the effect $\propto J/\Delta \Delta g_{eff}$, where $\Delta \Delta g_{eff}$ is the relevant effective $g$-factor difference (SI Appendix). Triplet pairs with a larger exchange interaction should therefore have a larger characteristic field scale for this effect and hence also be distinguishable through their non-resonant spin-mixing. Fig. 6C shows $\Delta$PL/PL for...
We obtained similar linewidths in a single crystal sample (SI Appendix). Clear singlet-triplet crossings seen for the crossings, which would give linewidths of ∼50 mT. This maximum is based on the distribution of S = 0 character across one state at zero-field, vs. two states at resonant positions/high field (18). The fact that the PL can be reduced by nearly 50% by a magnetic field (Fig. 2C, Fig. 4A) therefore indicates that strongly coupled triplet pairs can dominate the steady-state emission properties of singlet-fission systems. For identifying singlet fission, the observation that exchange-coupled triplets can dominate steady-state magnetic field effects is highly significant. Often, a low-field effect (∼100 mT) characteristic of weakly coupled triplets (19) is taken to be a signature of the fission process (6). In contrast, our results show that singlet fission magnetic field effects can be drastically different between strongly and weakly coupled triplets, and that high-field effects (∼1 T) can instead dominate.

We note that for fission generated triplet pairs the emissive species may either be a distinct singlet exciton or, as proposed recently (22, 34), the triplet pairs themselves. While typically challenging to distinguish these scenarios, the combination of a low-field effect (18), the PL can be reduced by nearly 50% by a magnetic field (Fig. 2C, Fig. 4A) therefore indicates that strongly coupled triplet pairs can dominate the steady-state emission properties of singlet-fission systems. For identifying singlet fission, the observation that exchange-coupled triplets can dominate steady-state magnetic field effects is highly significant. Often, a low-field effect (∼100 mT) characteristic of weakly coupled triplets (19) is taken to be a signature of the fission process (6). In contrast, our results show that singlet fission magnetic field effects can be drastically different between strongly and weakly coupled triplets, and that high-field effects (∼1 T) can instead dominate.

**Fig. 6.** Triplet-pair spin-mixing. (A) Spectrally resolved high-field effect (Sample 1) showing ∆PL/PL at spectral positions $\lambda_{a-c}$. (B) Simulation of the role of $g$-anisotropy. Inclusion of an anisotropic $g$-factor enhances the singlet-triplet level crossing at field $J/g\mu_B = 3.8$ T and produces a monotonic reduction in PL with field.

**Singlet-triplet level-crossings.** A difference in $g$-matrices also provides a mixing mechanism for the singlet-triplet crossings. Since the pure $S = 1$ triplet-pair states are antisymmetric with respect to particle-exchange, while the $S = 0, 2$ states are symmetric (19), different mixing mechanisms are required for singlet-triplet vs. singlet-quintet hybridization. Singlet-quintet mixing can be mediated by the intratriplet zero-field splitting interaction (18) which characterises the dipolar interaction between electron and hole and has strength $D/g\mu_B = 50$ mT in TIPS-tetracene (13, 23, 24, 30). However, to first order this coupling, leaves the singlet-triplet crossing forbidden (SI Appendix). Clear singlet-triplet crossings seen for $TT_{a,b}$ therefore indicate an additional mixing mechanism. As with the high-field effect, this can be provided by a $\Delta g$ Hamiltonian term which mixes singlet and triplets to first order (Fig. 6B and SI Appendix) with strength $\sim \Delta g_{dip} B \sim 10^{-3} B$ for an expected $\Delta g_{dip} \sim 10^{-3}$ (31). Additionally, this crossing can be mediated by hyperfine interactions, with typical strengths of ∼mT in organic semiconductors (32, 33).

**The role of kinetics in magnetic field effect.** Interestingly, the magnetic linewidths of the PL resonances (Fig. 4A) are larger than expected based purely on the mixing matrix elements for the crossings, which would give linewidths of ∼50 mT. We obtained similar linewidths in a single crystal sample (SI Appendix), and therefore a distribution in $J$ can be ruled out as the dominant line broadening mechanism. Instead, as detailed in the SI Appendix, this indicates the broadening is predominantly due to the kinetics of the fission/fusion process.

For both resonant and non-resonant PL reductions, mixing is predominantly between the singlet, and one other (triplet or quintet) pair state, and this sets a maximum ∆PL/PL of ∼50% (neglecting annihilation to a single triplet). This maximum is predominantly due to the kinetics of the fission/fusion process. Often, a low-field effect (∼100 mT) characteristic of weakly coupled triplets (19) is taken to be a signature of the fission process (6). In contrast, our results show that singlet fission magnetic field effects can be drastically different between strongly and weakly coupled triplets, and that high-field effects (∼1 T) can instead dominate.

**Outlook.** The magneto-optic resolution of organic triplet pairs opens up the possibility to correlate their exchange and electronic structure with their chemical environment and physical conformation. Since the mixing matrix elements relevant for the PL resonances depend on the relative orientation between the external field and the triplet pair (18), measuring orientationally dependent PL resonances should allow triplet pairs to be assigned to specific molecular configurations. Identification of unambiguous spectral signatures of triplet pairs further means that these states can now be studied through purely optical means. For example, triplet-pair microscopy could be used to obtain information on the spatial distribution of pair sites across microcrystalline domains and map their...
diffusion (35–37), and resonant excitation could be used to address specific triplet pairs through site-specific fluorescence (38, 39).

While here we spectrally resolve triplet pairs in a singlet fission material, these results are applicable to a range of other organic spin-pair systems. For example, triplet-triplet encounters are pivotal in photovoltaic upconversion systems (40) and organic light-emitting diodes (9, 41), and triplet-pair level anticrossings should also be observable in photovoltaic device architectures, where resonances could be measured through solar-cell photocurrent or quantum-dot emission (11). In spin-1/2 pairs, analogous spectrally resolved level crossings should help to clarify the spin and electronic structure of the emissive species central to thermally activated delayed fluorescence in next-generation organic light-emitting diode materials, and extracting optical signatures from level-crossings observed in synthetic and biological radical pairs should provide further insights into these key intermediates (4, 33, 42, 43). Finally, the nanoscale sensitivity of exchange-coupled spins opens up the possibility to deliberately engineer them as joint spin-optical probes of complex molecular systems.

Materials and Methods

Samples were excited by 532, 514 or 485 nm laser illumination (similar results were obtained across this wavelength range). A long-pass filter was used to remove the laser line, and the collected PL was either sent to an avalanche photodiode for the integrated measurement or through a monochromator to a nitrogen-cooled CCD for the spectrally resolved measurements. Three different TIPS-tetracene crystallites prepared by vaporization from saturated solution were used which we refer to as samples 1-3. X-Ray diffraction confirmed that all samples indexed to the same unit cell previously determined.

Spectrally resolved experiments to 68 T were performed using Sample 1 under pulsed magnetic field at LNCMI Toulouse. Spectrally resolved measurements up to 33 T were performed using samples 2 and 3 under steady-state fields at the HFML, Nijmegen. For low-temperature measurements samples were either immersed in liquid helium (Samples 1 and 3) or cooled via exchange gas with a surrounding helium bath (Sample 2), giving base temperatures of ≃1.4, 2 and 1.1 K for samples 1-3 respectively. PL spectra in Fig. 5c were taken with Sample 1 in helium under continuous pumping. Further details and comparison of the samples are contained in the SI Appendix.

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