Spin fine-structure reveals bi-exciton geometry in an organic semiconductor

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In organic semiconductors, bi-exciton states are key intermediates in carrier-multiplication and exciton annihilation. Of particular recent interest is the spin-2 (quintet) bi-exciton. Comprised of two triplet excitons, the bi-exciton can be formed by singlet fission (the formation of two triplet excitons from one singlet state) or by triplet-triplet annihilation (the reverse process). Of interest for photovoltaics and photocatalysis, the wavefunction of these optically dark bi-excitons is difficult to probe and predict. However, the local geometry of the pair-state is imprinted in the fine structure of its spin Hamiltonian. To access the fine structure of the quintet-state we develop and deploy broadband optically detected magnetic resonance (0 – 9 GHz). Here we correlate the experimentally extracted spin structure with the molecular crystal structure to identify the specific molecular pairings on which the bi-exciton state resides.

I. INTRODUCTION

Bi-exciton states are key excited-state species in a range of nano-structured materials from quantum-confined inorganic systems [1][3] to synthetic molecular structures [4][6]. In organic semiconductors the exciton-pair is an intermediate in both the process of singlet fission [7][9] – the formation of a pair of spin-1 (triplet) excitons from an initial spin-0 (singlet) excitation – and its reverse process, triplet-triplet annihilation [10]. While singlet fission is of particular interest for photovoltaics [11][13] where it has been shown to increase efficiencies of solar energy harvesting beyond traditional limits [14][15], triplet-triplet annihilation enables the up-conversion of light via the conversion of two low-energy triplet excitons to one higher energy singlet excitation [10][15]. This process is of particular interest for catalysis [17][18], photovoltaics [16][19], and bio-imaging [20][21]. In both fission and annihilation the bi-exciton state mediates the transition between one excited-state and two dissociated excited-states [22][24].

The wavefunction of these transient, intermediate pairs remains challenging to probe. Purely optical characterization of bi-excitons can be ambiguous as their optical signatures typically overlap with those of singly-excited states. By contrast, light-induced spin resonance has played a key role in showing, unexpectedly, that in several molecular systems, singlet fission produces a long-lived, bound spin-2 bi-exciton, termed the quintet state [25][27]. The observation of the quintet state reflects a dominant exchange interaction between the triplets within a pair. This exchange interaction (parametrized by exchange energy J) separates the pure singlet (S = 0) from the triplet (S = 1), and quintet (S = 2) pairings by J and 3J respectively [28]. The spin signatures of this strongly coupled state provide an unambiguous marker of the bi-exciton state [25][28].

Where are such pairs located in a solid-state system with many possible pair configurations? Here the sensitivity to inter-spin distance and orientation of the spin dipole-dipole interaction provides a window into the geometry of the multi-exciton state. Indeed, spin-spin dipolar interactions are used as a ruler for nano-scale distances in widespread applications of spin-labels to biological and synthetic systems [29]. Typically non-native spin-probes are required to take advantage of the dipolar interaction between synthetic radical-bearing ligands attached to biologically relevant structures. Conveniently, the dipolar interactions between the two triplet states in the quintet Hamiltonian provides a native probe of its spatial confinement and orientation [20][31].

These dipolar interactions are reflected in the fine structure in the quintet (and triplet) spin manifold: the energetic splitting within the spin-manifold even in the absence of a magnetic field. The zero-field splitting (ZFS) Hamiltonian in its principal axes takes the form

$$\hat{H}_{zfs}/\hbar = S^T \cdot D \cdot S = D(S_S^2 - \frac{1}{3}S(S+1)) + E(S_z^2 - S_{\hat{z}}^2)$$

(1)

where D is the dipolar tensor (D-tensor) and S is the relevant vector of spin operators (with total spin S = 1, 2 for triplet, quintet states) defined along the principal axes (x, y, z) of the D-tensor. These directions are defined by the symmetry of the spin distribution with the z-axis defined by the axis of maximum absolute magnitude of dipolar coupling. The strength of the dipolar coupling
parameters \((D, E)\) reflect the degree of confinement and asymmetry of the spin-system as we describe in detail in the next section.

Experimentally these parameters \((D, E\text{ and }\hat{x}, \hat{y}, \hat{z})\) can be extracted from magnetic resonance spectra, which can be detected via microwave absorption in a cavity or via spin-dependent electrical or optical transitions. In this work we use optically detected magnetic resonance (ODMR) as shown in Fig. 1a, which combines three key advantages for probing the geometry of the transient bi-exciton state: (1) sensitivity of photoluminescence-detection to the recombination of intermediate states, (2) detection sensitivity from optical (versus microwave) read-out, and (3) the sensitivity to dipolar interactions (on the MHz-GHz scale) of magnetic resonance.

II. THEORY

In this section we establish the relationship between the triplet pair geometry and the resulting measurable \(S = 2\ bi\text{-exciton fine structure} (D_Q, E_Q \text{ and the principal axes } \hat{x}_q, \hat{y}_q, \hat{z}_q)\), which we then go on to determine experimentally. Previous measurements of quintet states in various materials have found that \(D_Q \sim D_T/3\) [25, 26], yet this relation holds only in the case of co-linear triplet \(D\text{-tensors}\) and in the absence of dipolar coupling between the excitons, and so acts as an approximate guide to identifying quintet spectra [31].

For triplet excitons in organic semiconductors \(D_T\) and \(E_T\) are set by the spatially averaged spin-spin interaction of electron and hole, reflecting triplet states localized on a single molecule in the material used here, TIPS-tetracene [32, 33]. As shown in Fig. 1b, the \(\hat{z}\)-axis of maximal spin-spin coupling is out of the plane of the TIPS-tetracene molecule and the \(\hat{x}\) and \(\hat{y}\)-axes are in the plane of the molecule along the long and short axes.

The \(S = 2\) triplet-pair fine-structure depends on the underlying orientation of two such triplets localized on two molecules (labeled here \(A\) and \(B\)). We assume that each triplet has the same zero-field parameters \((D_T, E_T)\) and differ only in orientation and position. We define the principal axes of the triplet state on molecule \(A\) as \((\hat{x}_a, \hat{y}_a, \hat{z}_a)\) and on molecule \(B\) as \((\hat{x}_b, \hat{y}_b, \hat{z}_b)\) with the unit vector between them given by \(\hat{u}_{ab} = \hat{r}_{ab}/|\hat{r}_{ab}|\). The zero-field Hamiltonian of the pair in the uncoupled basis is then given by

\[
\hat{H}_{zfs}^{(1\oplus 1)}/\hbar = \sum_{i=a,b} S_i^T \cdot D_i^T \cdot S_i - \Gamma(\hat{u}_{ab} \cdot S_a)(\hat{u}_{ab} \cdot S_b) + JS_a \cdot S_b
\]  

(2)

where \(\Gamma = \frac{3\mu_0\hbar^2\sigma^2}{4\pi|\hat{r}_{ab}|^3}\) gives the strength of the dipolar interaction with \(\mu_0\) the magnetic permeability of free-space, \(\mu_B\) the Bohr magneton, \(g\) the \(g\)-factor, and \(|\hat{r}_{ab}|\) the inter-triplet distance. In the limit of strong exchange coupling \((J \gg D_T)\) the Hamiltonian is approximately diagonal in the coupled spin-basis defined by the states of pure total spin \([28, 31, 34]\). Projecting the above Hamiltonian into the \(S = 2\) subspace and converting to the coupled basis gives the quintet zero-field Hamiltonian as

\[
\hat{H}_{zfs}^{(2)}/\hbar = S^T \cdot D_Q \cdot S
\]  

(3)
**III. FINE STRUCTURE TENSOR PARAMETERS OF THE QUINTET STATE**

TIPS-tetracene is a solution-processable singlet fission material of interest for its high singlet fission efficiency [36, 37]. Structured with side-chain modification of the canonical fission molecule, tetracene, as shown in Fig. 1i, TIPS-tetracene crystallizes with a distinct molecular packing shown in Fig. 1g. The unit cell contains four orientationally inequivalent molecules yielding six possible nearest-neighbor pair sites within a unit cell in addition to non-crystalline defect sites. Both biexcitons and free triplet excitons have been identified in this material with transient electron spin resonance, but the nature of the local site housing the bound pair remains a key question. The theoretical framework above demonstrates how the parameters of the quintet fine structure (its principal values $D_Q, E_Q$ and the orientation of the principal axes $\hat{x}_q, \hat{y}_q, \hat{z}_q$) are specific to the crystal structure for each of the six possible pair states and reported in Section [V].

With this motivation we use a macroscopic crystal (∼mm-scale single-crystalline domain) and measure the principal values of the $D$-tensors of the triplet and quintet states using broadband zero-field ODMR and then apply a magnetic field to find the orientation of their principal axes in the laboratory frame in Section [IV]. The experimental setup is shown in Fig. 1f and includes 532 nm continuous-wave (CW) light excitation, microwave radiation ($B_1$) with variable frequency delivered by a broadband copper strip-line and a static magnetic field ($B_0$). The ODMR signal is measured by lock-in detection of microwave-induced changes in photoluminescence (see the Methods section for further details).

We first perform standard fixed-frequency (9 GHz) field-swept ODMR to confirm that, in agreement with previous measurements using transient electron spin resonance, we observe two pairs of spin-transitions consistent with the $\Delta m = \pm 1$ transitions of the $S = 1$ triplet exciton ($T^\pm$) and the $\Delta m = \pm 1$ transitions of the $S = 2$ quintet state ($Q^\pm$), as shown in Fig. 2b [26, 27]. The corresponding energy-level diagrams and transitions fields are shown in Fig. 2a.

These observed high-field transitions are correlated with zero-field transitions (magnetic field strength $B_0 = 0$, Fig. 2c–d), measured for the first time here. These zero-field spectra allow us to extract the zero-field splitting parameters for the triplet and quintet states directly.
In the absence of a magnetic field, the energy eigenstates of triplets and quintets are determined by their spin-spin dipolar interactions. The energy eigenstates are given by the $B_0 = 0$ spin-eigenstates. Microwave transitions at zero-field are determined by the energy-splitting between these zero-field states. As shown in the theoretical sketch in Fig. 2c, the triplet energy levels are separated in energy by $|D_T|$ and further split by $|2E_T|$ between the two upper eigenstates, where $D_T$ and $E_T$ are the zero-field splitting parameters for the triplet. Zero-field ODMR resonances therefore occur at microwave frequencies $\nu = D_T \pm E_T$.

The quintet eigenstates in zero-field are likewise defined by the eigenstates of the quintet fine-structure tensor. As shown in Fig. 2c, the three lowest quintet levels are split by $|D_Q|$ from the ground state to the first two states with a further splitting of $|6E_Q|$ between those two upper levels. This leads to ODMR transition frequencies at $\nu = D_Q \pm 3E_Q$. Note that the previously reported $D$-parameters for TIPS-tetracene are $D_T \sim 1.4$ GHz and $D_Q \sim D_T/3$ [26, 33]. However previous experiments did not determine $E$-parameters and molecular frame orientations which, as we will show, are needed to identify the contribution of triplet dipole-dipole interaction to the quintet fine structure tensor.

The magnetic resonance spectra of triplets and bi-excitons can be distinguished in ODMR due to the difference in lifetime of the two species [26, 33]. The microwave amplitude modulation frequency (137 Hz) is chosen to correspond with the inverse lifetime of the longer-lived species (triplets), which then appear with equal amplitude on the in-phase (X-channel) and out-of-phase (Y-channel) lock-in channels. The signal from shorter lived bi-excitons appears only on the X-channel and can be isolated by subtracting X and Y channels. The zero-field X- and Y-channel ODMR spectra are plotted in Fig. 2d in black (X-channel) and blue (Y-channel). The transitions on the Y-channel are consistent with triplets with $|D_T| = 1.4$ GHz and $|E_T| = 14$ MHz (Fig. 2d). Transitions in the frequency region expected for the quintet only appear on the X-channel and give $|D_Q| = 477$ MHz and $|E_Q| = 22$ (Fig. 2d inset). The sign of $D_T$ was determined in Ref. [26] to be positive, which in turn determines $E_T$ to be negative. The resolution of the splitting afforded by this technique allows extraction of $E_Q$ and $E_T$, highlighting the sensitivity of the zero-field approach. The measurement of the $E$-parameters here is made possible by the reduced linewidths observed at zero-field relative to previous measurements under non-zero magnetic field.

**IV. EXTRACTION OF BI-EXCITON FINE STRUCTURE ORIENTATION**

Having extracted the principal components of the triplet and quintet fine-structure tensors at zero-field, we now map the resonant frequencies as a function of magnetic field to determine the corresponding orientations of the principal axes. The experimental ODMR maps for quintet and triplet states are shown in Fig. 3a-f (separated by lock-in detection phase as described in the previous section).

The orientation of the quintet fine-structure axes in the lab frame is obtained by fitting these maps with the
spin transitions predicted by the fine structure parameters determined at zero-field (see Sec. II) with the orienta-
tion as input. The polar angle $\theta$ and azimuthal angle $\phi$ parametrize the orientation of the principal axes relative
to the magnetic field in the laboratory frame as shown in
Fig. 3. (c). There are 10 possible transitions between the
five quintet spin sub-levels (Fig. 2b), which are overlaid
on the quintet ODMR map (Fig. 3a). It should be noted
that the visibility of transitions depends on populations
and selection rules, and transitions 3,4,9, and 6 are not
observed experimentally. The observed resonances can-
not be fit by a spin-1 state, which further confirms the
assignment (see SI). The quintet state is oriented with
fixed $\theta_q = 90 \pm 5^\circ$ between $\hat{z}_q$ and $\mathbf{B}_0$ and $\phi_q = 30 \pm 5^\circ$
between $\hat{x}_q$ and $\mathbf{B}_0$.

The evolution of the $\sim 1.4$ GHz zero-field transitions
with field, shown in Fig. 3 are consistent with $\theta_1 = 0^\circ$
and $\theta_2 = 90^\circ$ with the latter perpendicular component
more prominent (calculated transitions for $\theta_1 = 90^\circ$
are plotted in black) and the $\theta_1 = 0^\circ$ consistent with
the presence of a weak powder background. The domi-
nant $\theta_1 = 90^\circ$ triplet orientation correlates with the
high-field spectrum (Fig. 2b): triplet peaks are separ-
ated by $\Delta B_0 \sim D/g\mu_B$, which occurs when $\theta_1 \sim 90^\circ$,
whereas no peaks are observed for $\theta_1 = 0^\circ$ (separation
$\Delta B_0 \sim 2D/g\mu_B$). [Note that $\phi_1$ could not be extracted
reliably as $E_T \ll D_T$, and this parameter was not
required for subsequent analysis because the triplet states
are nearly axially symmetric (i.e., as $E_T \approx 0$, $E_Q$ and $D_Q$
do not depend significantly on the relative orientation of
$\hat{x}_l$ and $\hat{y}_l$).] As the $D$-tensor values and orientations
in the laboratory frame are obtained from a bulk crystalline
sample, we can now compare them with the theoretically
predicted $D$-tensors in the TIPS-tetracene crystal
structure.

V. PAIR SITES IN THE TIPS-TETRACENE
CRYSTAL STRUCTURE

We now compare the experimental observations to the
quintet fine-structure theoretically predicted in the
TIPS-tetracene crystal structure. As shown in Fig. 1,
in the TIPS-tetracene unit-cell molecules are packed with
two approximately parallel dimers each rotated with re-
spect to the other by $\sim 90^\circ$ about the $\hat{c}$ axis. There are
six potential nearest-neighbor dimer configurations and
for each we can calculate the expected $D_Q, E_Q$ param-
eters using Eq. 4. the molecular triplet axes shown in
Fig. 1b and the intermolecular distances extracted from
the crystal structure determined by X-ray diffraction. 
These values are summarized in Table I where we have
taken nearest-neighbor dimer configurations. (We note
that we have taken a point-dipole approximation for each
triplet localized at the center of each molecule in the pair
which is likely the main source of error in the predicted
fine structure parameters.)

The observed quintet and triplet signatures and ex-
tracted angles of $\theta_q \sim 90^\circ$ and $\phi_q \sim 30^\circ$ are consistent
with exchange-coupled triplets localized on dimers 1,2
and 3,4 (highlighted in blue in Table I) where molecules
in the unit cell are labeled $1-4$ in Fig. 1 and the cal-
culated angles are for $\mathbf{B}_0 \parallel \hat{c}$ as this orientation is con-
sistent with known crystal facets, both the quintet and
triplet transition maps, and the 9 GHz field-swept spec-
trum presented in Fig. 1 (see SI). Interestingly, these
dimer configurations correspond to the most closely
$\pi$-stacked dimers in the crystal suggesting that this geo-
metry is favorable for binding of the multi-exciton state.
The extracted local quintet fine structure is visualized
in Fig. 4 where the full quintet and triplet dipolar in-
teractions are shown with respect to the magnetic field
in the lab frame and crystallographic axes, summarizing

| $|D_Q|$ (MHz) | $|E_Q|$ (MHz) | $\theta_q$ (deg.) | $\phi_q$ (deg.) | $r_{ab}$ (Å) |
|------------|------------|----------------|----------------|----------|
| $TT_{1,2}$ | 474.0      | 22.5           | 91.6°          | 30.6°    | 10.0     |
| $TT_{1,4}$ | 227.5      | 72.4           | 13.5°          | 77.8°    | 10.5     |
| $TT_{1,5}$ | 250.4      | 42.7           | 15.5°          | 84.7°    | 9.7      |
| $TT_{2,3}$ | 234.8      | 62.0           | 13.8°          | 90.8°    | 15.7     |
| $TT_{2,4}$ | 245.5      | 69.7           | 11.0°          | 78.9°    | 17.7     |
| $TT_{3,4}$ | 474.0      | 22.5           | 88.4°          | 30.6°    | 10.0     |
| **Obs.**   | 477 ± 1    | 22 ± 1         | 90.0 ± 5°      | 30 ± 5°  |         |

Table I. Predicted fine structure parameters from distances in TIPS-tetracene crystal structure with $|D_Q| = 1414$ MHz and $|E_Q| = 14$ MHz from the measured zero-field values with angles given between $\mathbf{B}_0$ and $\hat{x}_q, \hat{y}_q, \hat{r}_{ab}$ for $\mathbf{B}_0 \parallel \hat{c}$. The final row shows the corresponding experimental observations, consistent with the predicted values of $TT_{1,2}$ and $TT_{3,4}$, highlighted in blue.
VI. CONCLUSIONS

We have developed the theoretical and experimental approaches to connect inter- and intra-triplet dipolar interactions, is highly sensitive to the underlying molecular structure. This sensitivity of the effective spin Hamiltonian to intermolecular geometry further opens up opportunities to tune spin parameters via crystal structure engineering of spin-based organic devices. Tuning spin energy levels and zero-field interactions is critical in spin-based applications, for example in tuning the amplification frequency in the newly emerging class of organic molecular spinors \[1\] or in minimizing spin relaxation and dephasing \[2\]. Dipolar spin interactions thereby provide a route toward engineering the spin level structure in organic materials in future spin-based quantum technologies.

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Acknowledgments We are thankful for insightful discussions with H. Bouchiat and R.H. Friend and acknowledge support from ANR SPINEX and Labex ANR-10-LABX-0039-PALM. L.R. Weiss acknowledges support from the Clare College Junior Research Fellowship.

Author Contributions The data were measured and analyzed by K.M.Y., L.R.W., and A.D.C. J.E.A. provided materials. All authors contributed to planning the experiment, discussions and the preparation of the manuscript.

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Methods Optically detected magnetic resonance is performed 532 nm CW laser illumination via 1 mm-diameter optical fiber (Fig. 1a) in liquid helium at 4 K. An amplitude modulated microwave field (B$_1$) in a frequency range 0 – 9 GHz was applied using a broadband copper stripline. The sample holder was fixed inside a superconducting solenoid. Photoluminescence was collected (via the same optical fiber and avalanche photodiode) to detect the microwave-induced change in photoluminescence (ODMR) as a function of both microwave frequency and static magnetic field (B$_0$) with B$_0$ $\perp$ B$_1$. 

