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Charge Separation and Triplet Exciton Formation Pathways in Small Molecule Solar Cells as Studied by Time-resolved EPR Spectroscopy

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Abstract

Organic solar cells are a promising renewable energy technology, offering the advantages of mechanical flexibility and solution processability. An understanding of the electronic excited states and charge separation pathways in these systems is crucial if efficiencies are to be further improved. Here we use light induced electron paramagnetic resonance (LEPR) spectroscopy and density functional theory calculations (DFT) to study the electronic excited states, charge transfer (CT) dynamics and triplet exciton formation pathways in blends of the small molecule donors (DTS(FBTTh₂)₂, DTS(F₂BTTh₂)₂, DTS(PTTh₂)₂, DTG(FBTTh₂)₂ and DTG(F₂BTTh₂)₂) with the fullerene derivative PC₆₁BM. Using high frequency EPR the g-tensor of the positive polaron on the donor molecules was determined. The experimental results are compared with DFT calculations which reveal that the spin density of the polaron is distributed over a dimer or trimer. Time-resolved EPR (TR-EPR) spectra attributed to singlet CT states were identified and the polarization patterns revealed similar charge separation dynamics in the four fluorobenzothiadiazole donors, while charge separation in the DTS(PTTh₂)₂ blend is slower. Using TR-EPR we also investigated the triplet exciton formation pathways in the blend. The polarization patterns reveal that the excitons originate from both intersystem crossing (ISC) and back electron transfer (BET) processes. The DTS(PTTh₂)₂ blend was found to contain substantially more triplet excitons formed by BET than the fluorobenzothiadiazole blends. The higher BET triplet exciton population in the DTS(PTTh₂)₂ blend is in accordance with the slower charge separation dynamics observed in this blend.

Graphical Abstract

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1. Introduction

Bulk heterojunction (BHJ) organic solar cells are a promising technology for solar energy conversion due to their light weight, mechanical flexibility and solution processability. High efficiency BHJ materials have traditionally been dominated by conjugated polymer donor and fullerene acceptor blends processed from solution, which now routinely achieve power conversion efficiencies (PCE) of greater than 10 %.^{1–5} A switch from polymeric to small molecule donors offers key advantages in the design and fabrication of BHJ solar cells. Well-defined molecular structures allow easier control of energy levels and charge mobility and enable direct structure property relationships to be established.^{6–7} Synthetically, small molecules are easier to purify and have reduced batch-to-batch variation allowing greater reproducibility in device performance.⁸ Recently BHJs that incorporate solution processed small molecule donors in place of the polymer have become increasingly competitive, with PCEs of 10.1 % now reported.^{6, 9–10}

Understanding the excited states and intermediates that are involved in the charge separation process in these molecular systems is crucial if efficiency is to be further improved using rational design principles. Some basic steps of the energy and charge transport within the active layer of a BHJ cell are described in the following. In a BHJ active layer, upon photon absorption a strongly bound singlet exciton is generated which then needs to be broken apart to yield free charge carriers (called polarons or radical ions). Ideally, the photogenerated exciton quickly diffuses, reaches a donor acceptor interface, and undergoes electron transfer to yield a (primary) charge transfer (CT) state consisting of a positive and negative polaron that are coulombically bound together. This is followed by further electron and hole transfer steps (secondary electron transfer) until the polarons are fully separated. These processes are shown in a simplified manner in Figure 1 alongside other competing pathways and states that can be present in BHJ solar cells. With the exception of the short-lived singlet exciton, the excited states shown in Figure 1 contain unpaired electrons which makes electron paramagnetic resonance (EPR) spectroscopy ideally suited for their study.¹¹ EPR is exclusively sensitive to centers that contain unpaired electrons, enabling it to selectively probe only those states relevant to solar cell operation.

In this work we combine steady state and time resolved EPR spectroscopy with DFT calculations to investigate the polaron electronic structure and the charge separation and triplet exciton formation dynamics across a family of small molecule electron donors. The donor molecules are from the important and widely studied DTS family and are shown in

Figure 2.^{12–17} They are formed around an acceptor/donor/acceptor (A/D/A) core (also called push-pull) which facilitates intramolecular charge transfer, leading to low bandgaps and good absorption characteristics. The molecules utilize either dithienosilole (DTS) or dithienogermole (DTG) as the central donor unit. Fluorobenzothiadiazoles with one or two fluorine electron withdrawing groups (FBT & F₂BT respectively) and [1,2,5]thiadiazolo[3,4-*c*]pyridine (PT) comprise the three acceptor units. Combinations of these donor and acceptor units yield the five electron donating molecules investigated here.^{12–14} This family of molecules has found widespread success with reported PCEs of 6.7 % for DTS(PTTh₂)₂, 7.55 % for DTG(FBTTh₂)₂ and 8.3 % for DTS(FBTTh₂)₂ when blended with PC₇₁BM.^{12, 15–16}

Using high frequency (130 GHz) EPR we systematically characterize the positive polarons formed on the dithienosilole / dithienogermole series of molecular donors after charge separation and assign the electronic g-tensor. Polaron delocalization was investigated using hyperfine (hf) coupling sensitive Electron Nuclear Double Resonance (ENDOR) spectroscopy. The experimental g-values and hyperfine coupling constants were then compared and contrasted to the values obtained by DFT calculations. Furthermore, the charge separation dynamics and exciton formation pathways in these blends were then investigated using TR-EPR spectroscopy. By analyzing and modelling the CT and triplet exciton polarization patterns we conclude that charge separation is slowest in the DTS(PTTh₂)₂ blend which results in increased back electron transfer losses.

5. Experimental

Sample Preparation

The single molecule donors used in this study, DTS(FBTTh₂)₂, DTS(F₂BTTh₂)₂, DTS(PTTh₂)₂, DTG(FBTTh₂)₂ and DTG(F₂BTTh₂)₂ were purchased from 1-Material (Quebec, Canada). The fullerene derivative PC₆₁BM was obtained from Sigma-Aldrich (St. Louis, US). Donor-fullerene solutions were prepared under anaerobic conditions inside a N₂ drybox. A 3:2 donor/fullerene weight ratio with a total concentration of 20 mg cm⁻³ in deoxygenated chlorobenzene was used for all blends. For frozen solution samples the blend solution was added to EPR quartz tubes which were then sealed under N₂ atmosphere and quickly frozen in liquid nitrogen. Film samples were prepared by pumping on the tube using a Schlenk line which slowly removed the solvent and left a thick film coating. Samples were prepared under dimmed lighting conditions to minimize the chance of sample degradation.

EPR Spectroscopy

X-band (9.8 GHz) EPR experiments were undertaken using an ELEXSYS E580 spectrometer (Bruker Biospin, Rheinstetten, Germany) that was equipped with a dielectric ring resonator (Bruker EN 4118X-MD4). All EPR measurements were performed at 50 K. Temperature control was provided by a helium gas-flow cryostat (CF935, Oxford Instruments, UK) and an ITC temperature controller (Oxford Instruments, UK). Light excitation was done directly in the resonator of the spectrometer with 532 nm laser light through an optical fiber (Nd:YAG Laser, INDI, Spectra Physics / Newport, operating at 20 Hz, and OPO, basiScan, GWU). Typical incident light intensities at the sample were 80

mW/cm² (4 mJ/pulse/cm²). For ENDOR experiments a BT01000-AlphaSA 1 kW RF amplifier (TOMCO Technologies, Stepney, Australia) was used. D-band (130 GHz) EPR measurements were carried out on custom built spectrometer,^{18–19} with optical excitation provided via an optical fiber from the above laser. Typical incident light intensities at the sample were 20 mW (1 mJ/pulse). D-band spectra were obtained in pulsed mode using a two microwave pulse sequence and monitoring the resulting electron spin echo intensity. Data processing was undertaken using Matlab 2015a (MathWorks, Natick, US). Simulations of EPR spectra were performed using the Easyspin Matlab toolbox (version 5.0.2).²⁰

DFT Calculations

The starting structures of DTS(FBTTh₂)₂, DTS(F₂BTTh₂)₂, DTS(PTTh₂)₂, DTG(FBTTh₂)₂ and DTG(F₂BTTh₂)₂ were built and optimized *in vacuo* using NWChem v 6.5.²¹ Unless noted, basis sets and functionals used for geometry optimizations were B3LYP||6–31G* which has been shown to be appropriate for positively charged polymers containing first and second row atoms.²² In all cases frequency calculations were performed to ensure, by the absence of imaginary frequencies, that the stationary points obtained in the geometry optimizations were energetic minima. EPR parameters were calculated using the computational package Orca 3.0.3.²³ Calculations of the EPR parameters employed the B3LYP functional,²⁴ the def2-TZVPP²⁵ basis set for Si, Ge, S, and the EPRII^{26–27} basis set for all other atoms. The def2-TZVPP basis set has been shown to give comparable results for magnetic resonance parameters (g tensors and hyperfine interaction tensors (A tensors)) for the type of elements under investigation. The principal g values were calculated employing the coupled perturbed Kohn–Sham equations.^{28–29}

2. Results

LEPR Spectra

LEPR was used to observe the charge separated species in blends of the dithienosilole & dithienogermole based donors with PC₆₁BM. In high efficiency solar cells the donors are routinely blended with the soluble fullerene derivative PC₇₁BM, because of its improved optical absorption over PC₆₁BM.³⁰ However PC₆₁BM is also widely used in OPV and has very similar energy levels and solubility. For this study we chose to blend the donors with PC₆₁BM since negative polarons residing on PC₇₁BM spectrally overlap with positive polarons on electron donors, making interpretation of the EPR experiments difficult.^{22, 31} In contrast, the EPR signals of the negative polarons on PC₆₁BM are partially spectrally separated from positive polarons on the donor even at the magnetic fields of X-band spectrometers. It was shown previously, that the use of PC₆₁BM instead of PC₇₁BM has negligible influence on the EPR properties of the positive polaron of the donor molecule.²²

The left panel of Figure 3 shows 9.8 GHz (X-band) continuous wave LEPR spectra of the five different donors blended with PC₆₁BM in frozen chlorobenzene solution. The spectra consist of a broad low field signal centered at $g \approx 2.0025$ and a partially overlapping narrow higher field line at $g \approx 1.9999$. Previous EPR studies on donor:fullerene blends allow the unequivocal assignment of the low field component to positive polarons (P⁺) residing on the donor and the high field signal to negative polarons (P[−]) on PC₆₁BM.^{32–35} Within the

limited resolution at X-band the P^+ signal is similar across the five donors, with integrated intensities that are 25 to 40 % of the P^- signal intensity. This is due to the longer spin relaxation times of the polaron on the donors which causes partial saturation at cryogenic temperatures. LEPR spectra of films were similar to the solution spectra and therefore not shown. In order to resolve the principal values of the g-tensor and completely spectrally separate the P^+ signal of each donor from the fullerene signal we performed pulsed LEPR at 130 GHz (D-band) which are shown in the right panel.

At D-band the P^+ and P^- signals are now completely spectrally separated and the principal values of the P^+ and P^- g-tensors can be resolved. The g-tensor of the P^- on PC₆₁BM was invariant across the five blends with principal values of $g_x = 2.0006$, $g_y = 2.0004$, $g_z = 1.9989$ which is in good agreement to previously reported values.^{22, 31, 33, 36–37} The g-tensors of the positive polaron on the five donor molecules are summarized in Table 1. Comparing the four fluorobenzothiadiazole containing donors, it is clear that the g-tensor is largely insensitive to the replacement of silicon with germanium. There is only a small shift in g_y to higher values in the germanium analogues (about 0.0002), which shows the choice of the central heteroatom has little influence on the electronic properties of the molecule. Similarly, the number of fluorine substituents on the fluorobenzothiadiazole units appears to have no influence on the g-tensor. The g-tensor of DTS(PTTh₂)₂ is less anisotropic than the tensor of the fluorobenzothiadiazole donors with a slightly higher g_z component of 2.0020.

Hyperfine Interactions in the positive polaron

The delocalization of the positive polaron over the molecule can be observed by probing the coupling of the unpaired electron spin to magnetic nuclei in the molecule through the hyperfine interaction. The magnetic nuclei of interest in the blends under study are ¹H and ¹⁴N in all five donor molecules and ¹⁹F in the four fluorobenzothiadiazole containing donor molecules. The strength of the hf-coupling between the polaron and the nuclei provides information on the delocalization of the polaron over the molecule, with a more localized polaron resulting in larger hyperfine interaction. Solvent and PC₆₁BM side chain ¹H in close vicinity to the positive polaron are only weakly dipolar coupled and thus can be disregarded for the following analysis.²² To determine the hf-couplings, which were not resolved in the EPR spectra at X-band or D-band, we performed pulsed X-Band electron nuclear double resonance (ENDOR) spectroscopy. The ENDOR spectra were measured using Davies³⁸ and Mims³⁹ pulse sequences.⁴⁰ The Mims ENDOR spectra of the P^+ in the five blends are shown in Figure 4 alongside the P^- spectrum of the DTS(FBTTh₂)₂ blend. The Davies ENDOR spectra had similar lineshape to the Mims spectra but lower signal to noise (data not shown). The P^+ ENDOR spectra are dominated by signals of weakly coupled protons, centered on the proton Larmor frequency (14.8 MHz at 347 mT) and consist of two broad overlapping peaks with a sharper peak in the center at the Larmor frequency. The broad peaks correspond essentially to the P^+ ENDOR spectrum while the weaker sharp peak stems mostly from a small fraction of PC₆₁BM⁻ molecules that were excited by MW pulses due to the not completely selective pulse sequence. Reciprocally the PC₆₁BM⁻ ENDOR spectrum has a strong central peak and weak broad wings. We have observed similar types of ENDOR spectra in our previous study of polymers blended with PC₆₁BM.²² The four fluorobenzothiadiazole donor spectra are slightly asymmetric with respect to the ¹H Larmor

frequency of 14.8 MHz, which is attributed to coupling to ^{19}F nuclei with a Larmor frequency of 13.9 MHz. It can be seen that the ^{19}F contribution is more pronounced for the difluorinated donors. The coupling to ^{19}F indicates that some unpaired spin density is delocalized over the fluorine substituents. This spin density is visible in all calculated spin density plots (see DFT Section Figures 7 and S3).

The larger the electron spin density at a nucleus the greater the strength of the (isotropic) hyperfine coupling to that nucleus. Increasing the delocalization of the polaron therefore lowers the largest detected hf-coupling which corresponds to a narrowing of the ENDOR spectrum. In first approximation, the width of the ENDOR spectrum is inversely proportional to the delocalization of the polaron over more monomeric units (width of ENDOR spectrum proportional to $1/n$, n number of identical monomeric units). However, the case is not that simple for these small donor molecules. Since all five molecules are of essentially identical size and have non-identical subunits, changes in hf may indicate redistribution inside the molecule. The best indicator of polaron delocalization and redistribution are proton hyperfine couplings. It can be seen that the ENDOR spectra of the four fluorobenzothiadiazole blends are similar in width, with a FWHM of 2.4 ± 0.2 MHz indicating that the polaron delocalization is largely insensitive to the choice of heteroatom (Si, Ge) and number of fluorine substituents (1 or 2 per benzothiadiazole). The DTS(PTTh₂)₂ spectrum is slightly broader with a FWHM of 3.0 ± 0.1 MHz suggesting that the polaron is differently distributed on this donor molecule. The ENDOR spectra of film samples exhibited similar widths to those in frozen solution (not shown) Further conclusions can be made with the help of the DFT calculations which are discussed later.

Radical Pair Spectra

To get an insight into the dynamics of charge separation we performed direct detection time resolved EPR spectroscopy (TR-EPR), where the EPR signal is recorded as a function of time after the laser flash without field modulation.⁴¹ The first step in charge separation is dissociation of photogenerated excitons by electron transfer to yield the primary CT state. This is followed by subsequent electron and hole transfer steps until the electron and hole are fully separated. The time resolution of TR-EPR is around 100 ns, which is significantly lower than ultrafast optical spectroscopy methods techniques. TR-EPR is therefore too slow to directly monitor many of the processes occurring in bulk heterojunction films such as the separation of the primary CT state which dissociates on a sub ns timescale.⁴² However it can detect the subsequent longer lived CT states formed during charge separation. These subsequent CT states are termed intermediate if they are too short lived to be observed using TR-EPR and secondary if long lived and observable by TR-EPR. The line shape of the secondary CT states can be influenced by spin evolution during the primary and intermediate CT state(s), thus allowing the earlier dynamics to be indirectly monitored. The TR-EPR spectra of the five blends in frozen solution, captured 500 ns after the laser flash at a temperature of 50 K, are shown in Figure 5. Since the TR-EPR spectra were recorded using direct detection without field modulation, the positive and negative peaks correspond directly to absorption and emission respectively, which arises from the non-Boltzmann electron spin polarization. Electron spin polarization originating from radical pairs in OPV blends,^{43–46} is most commonly interpreted using the spin-correlated radical pair (SCR-P)

model.^{47–49} The SCR model rests on the assumption that starting from a singlet precursor exciton the primary and intermediate CT states separate sufficiently rapidly so that there is no time for spin mixing to occur and thus no spin polarization build up during charge separation. Instead the spin polarization wholly arises from magnetic interactions between the spins in the observable secondary CT states, generating an EAEA spin-polarization pattern (alternating emission and absorption lines).⁴⁴

As can be seen from Figure 5 the four fluorobenzothiadiazole donor blends exhibit a distorted EAEA spectrum while the DTS(PTTh₂)₂ blend is closer to EA. According to the SCR model, an EAEA polarization pattern should be observed. An explanation for the deviation from EAEA pattern of the fluorobenzothiadiazole spectra and the apparent EA spectrum of DTS(PTTh₂)₂ is the existence of sufficiently long lived primary or intermediate CT states, where spin polarization can build up during charge separation via singlet-triplet mixing which creates a non-Boltzmann population that carries over to the observable secondary CT states. This mechanism for spin polarization is commonly known as chemically induced dynamic electron polarization (CIDEP).^{50–57} A “pure” CIDEP spectrum, which would arise if there was no magnetic interactions in the secondary CT state, is known to exhibit an EA polarization pattern if the precursor state was singlet.⁵⁷ The presence of a long lived intermediate CT state therefore distorts the polarization pattern from EAEA towards EA and the longer the lifetime of the intermediate state the greater the distortion.^{58–60} Applying this reasoning to the spectra in Figure 5 leads to the conclusion that charge separation in the four fluorobenzothiadiazole donors occurs on the same timescale since they exhibit similar polarization patterns. In contrast, charge separation in DTS(PTTh₂)₂ is slower as the spectrum is strongly distorted towards EA, indicating the presence of a long lived primary or intermediate CT state.

Triplet Excitons

To get a more complete picture of charge separation kinetics in these blends we also investigated triplet excitons, which exhibit very characteristic EPR signatures. High populations of triplet excitons are a good indicator of inefficient charge separation in donor acceptor blends. Singlet excitons photogenerated in the donor or the acceptor phase that fail to reach the interface can undergo ISC to triplets, which is a terminal loss mechanism. Additionally back electron transfer (BET) from interfacial triplet CT states yields triplet excitons in the donor phase, which also reduces device efficiency.^{61–62} While optical spectroscopy is capable of detecting the existence of triplets, it is insensitive to their origin. TR-EPR is uniquely positioned to study triplet excitons, as it is capable of identifying the mechanism of triplet generation, ISC or BET. In addition, EPR is sensitive to the extent of the exciton delocalization. The width of a triplet exciton EPR spectrum (Figure 6) is much larger than the weakly bound CT states shown in Figure 5 or the fully separated polarons shown in Figure 3, allowing the triplet exciton signature to be easily distinguished. The spectra of DTS(FBTTh₂)₂ and DTS(PTTh₂)₂ captured 500 ns after the laser flash at a temperature of 50 K in both frozen chlorobenzene solution (left panel) and solution cast films (right panel) are shown in Figure 6. The DTS(FBTTh₂)₂ spectra can be considered representative of the four fluorobenzothiadiazole donors which all yielded similar spectra (Supporting Information Figures S1 & S2).

The frozen solution TR-EPR spectra consist of two overlapping triplet signals with approximately equal intensity and widths of about 25 mT (≈ 700 MHz) and 90 mT (≈ 2500 MHz). Previous studies of triplet excitons in donor/fullerene blends allow us to assign the narrow 25 mT signal to triplet excitons residing on PC₆₁BM and the 90 mT signal to triplet excitons on the donor.^{37, 44, 63–64} The width of the triplet spectrum is determined by the zero field splitting (ZFS) tensor describing the energetics of the three triplet sublevels, where D_x , D_y and D_z are the eigenvalues of the ZFS tensor. Since the ZFS tensor is traceless ($D_x + D_y + D_z = 0$), the splitting can be described by only two parameters D and E .⁶⁵

$$D = -\frac{3}{2}D_z \quad E = \frac{1}{2}(D_y - D_x) \quad (1)$$

The parameter D represents the strength of the dipolar coupling and increases in magnitude with decreasing exciton delocalization while the magnitude of E represents the deviation of the exciton delocalization from axial symmetry. The sign of D cannot usually be determined from EPR spectroscopy, instead the magnitude is obtained. ZFS parameters obtained from spectral simulations of the frozen solution spectra are detailed in Table 2. The choice of heteroatom, Si or Ge, does not appreciably influence the ZFS. There is a subtle variation in ZFS with choice of electron withdrawing groups, with difluorinated donors having the largest $|D|$ value followed by monofluorinated and then [1,2,5]thiadiazolo[3,4-c]pyridine which does not contain any fluorine. The general similarity of ZFS across the five donor molecules suggests that the triplet exciton delocalization is largely insensitive to the small changes in molecular structure and the presence of Si or Ge. The ZFS of the triplet exciton on the donor is in agreement to that determined by PLDMR on DTS(FBTTh₂)₂.⁶⁶ The ZFS parameters of triplet excitons on the PC₆₁BM are similar to previously reported values.^{37, 44, 63}

The two routes of triplet exciton formation in a BHJ are intersystem crossing (ISC) from the singlet exciton and back electron transfer (BET), also called the RP triplet or S-T₀ triplet, from the triplet CT state as shown in Figure 1. The ability of TR-EPR to distinguish the ISC and BET triplet exciton relies on the fact that population of the triplet sublevels is different for each pathway; both mechanisms result in non-Boltzmann population leading to spin polarized EPR spectra exhibiting emissive and absorptive components. The spin-polarization of ISC triplets is either AAAEEE, EEAEAA or their inverses. In contrast BET from the triplet CT state populates the $|T_0\rangle$ sublevel directly. For a negative D , the excess in the $|T_0\rangle$ sublevel leads to an EAAEEA pattern. For a positive D , the excess in the $|T_0\rangle$ sublevel leads to an AEEAAE pattern. These patterns are unique to BET triplet excitons and cannot be generated by ISC.^{67–70}

In frozen solution blends the triplet exciton residing on PC₆₁BM has an AAAEEE pattern and can be accurately simulated using only the ISC mechanism (blue line). The spectra of the triplet exciton on the donor have the overall EEEAAA or EEAEAA pattern that is indicative of an ISC triplet exciton, however simulations using the ISC mechanism (green line) alone could not accurately reproduce the experimental spectra. Since the samples are

flash frozen chlorobenzene solutions the orientation of the molecules with respect to the magnetic field should be random and the deviation of the experimental spectra from the ISC simulation cannot be explained by partial orientation effects. Instead the deviation from ISC is attributed to a minority of BET triplet exciton (orange line). The combination of an ISC and a BET triplet exciton yields simulated spectra (red line) that are in excellent agreement to the experimental data. The spectral weight of BET component required to fit the spectra was similar across the four fluorobenzothiadiazole donors and varied between 13 and 15 %. In contrast the DTS(PTTh₂)₂ simulation required a substantially larger BET component of 29 %. This indicates that back electron transfer occurs more readily in the DTS(PTTh₂)₂ blend.

In film samples triplet excitons on the donor yielded similar spectra to those in frozen solution. The most notable difference between the frozen solution and film spectra is the absence of the ISC PC₆₁BM triplet in the film. While direct excitation of isolated PC₆₁BM molecules followed by ISC can in principle explain the presence of PC₆₁BM triplets in frozen solution, it has to be considered that PC₆₁BM has a low absorption coefficient and other mechanisms could contribute to PC₆₁BM triplet generation. For example, singlet excitons generated on the donor molecules may undergo long-range Förster resonance energy transfer (FRET) to the PC₆₁BM which can then undergo ISC. In the film the donor and acceptor molecules are more closely packed and FRET to PC₆₁BM will be suppressed in favor of charge transfer, resulting in a lack of PC₆₁BM triplets in the film.

The spectral simulation of the triplet exciton is more complicated for the film samples than for the frozen solutions. In the DTS(PTTh₂)₂ film the addition of a BET component again improves the fit of the simulation. However in contrast to the solution case, the addition of the BET component actually exacerbates the fit of the four fluorobenzothiadiazole donors and the ISC mechanism alone also proved incapable of reproducing the experimental spectra (data not shown). This discrepancy between the solution and film spectral fits is likely due to partial orientation effects. The simulations of the frozen solution samples used a full powder average but if the molecules are partially ordered in the film this approach will yield erroneous results. The donor family under study is known to exhibit extensive crystalline phases and the slow solvent evaporation used to prepare the films would enable crystallite growth^{12, 71}. It has also been shown that films of the polymer PCDTBT fabricated using similar methods to those employed here exhibited partial orientation effects in the triplet exciton TR-EPR spectrum.⁷²

To account for partial orientation in the simulation, a Gaussian distribution was used to weight the preferred orientations of the molecules. The spectra of the four fluorobenzothiadiazole donor molecules could be accurately simulated using the ISC mechanism with partial orientation given by weighting the Euler angle θ , with a $\sigma = 1.4$ Gaussian distribution. The simulation for DTS(FBTTh₂)₂ is shown in Figure 6 and can be considered prototypical for the fluorobenzothiadiazole donors. The steric structure of DTS(PTTh₂)₂ is very similar to the fluorobenzothiadiazole donors and it would be expected to orientate in a similar manner. However simulating the DTS(PTTh₂)₂ solely using the ISC mechanism requires a partial orientation distribution that is orthogonal to that used for the fluorobenzothiadiazole donor molecules. This drastic difference in alignment of near

identical molecules is highly unlikely to occur. Instead we treat the fluorobenzothiadiazole orientation distribution as a global fitting parameter and apply it to the DTS(PTTh₂)₂ simulation. Using this distribution the DTS(PTTh₂)₂ experimental data was accurately simulated with the inclusion of a 30 % BET triplet exciton contribution. A small amount of BET exciton component is likely also present in the fluorobenzothiadiazole blend spectra, but is difficult to accurately determine due to the number of free parameters in the simulation. To summarize, in both film and frozen solution samples there is significantly more BET occurring in the DTS(PTTh₂)₂ blend than in the fluorobenzothiadiazole blends. The higher proportion of BET excitons observed in the DTS(PTTh₂)₂ blends is supported by the slower charge separation in the DTS(PTTh₂)₂ blend inferred from the spin polarization patterns of the radical pair spectra. A longer CT lifetime would result in increased S-T₀ mixing and a higher population of triplet CT states that can undergo BET to generate a triplet exciton on the donor.

Density Functional Theory Calculations

In order to further investigate the electronic properties of these small molecule donors, Density Functional Theory (DFT) calculations were performed. These calculations provide vital information concerning the energies of the various potential conformers, distribution of the unpaired spin density over the positive polaron, and magnetic resonance parameters like g-values. In return, experimentally obtained magnetic resonance parameters can be directly compared with the calculated ones and thus act as a control if the structural model and level of theory were chosen appropriately.

From the spin density plots for the positive polaron state (radical cation) of the donor molecules (DTS(FBTTh₂)₂ shown in Figure 7; others in Supporting Information Figure S3), it is apparent that essentially no spin density resides on either the central Si or the central Ge. For example, in DTS(FBTTh₂)₂ less than 1% of the total Mulliken spin population is assigned to the Si atom compared to 45% on the central DTS unit (see Table S3). The lack of spin density on these atoms suggests that there should be little difference due to electronic effects when comparing DTS and DTG structures, unless replacing silicon with germanium results in significant structural rearrangement. Overlaying the Si/Ge paired structures (Supporting Information Figure S4) confirms that there is indeed little difference when Si is replaced with Ge. The Ge-C distance is slightly larger (1.99 Å) than the Si-C distance (1.90 Å) but this has only minor effects on the rest of the central dithienosilole/dithienogermole with C-S differences of less than 0.002 Å. The overall RMSD is less than 0.5 Å between DTS(FBTTh₂)₂ and DTG(FBTTh₂)₂. The lack of electronic effects upon change from Si to Ge is in agreement with the experimental results that show little sensitivity to the Si-based structures vs the Ge-based ones. While the overall spin density plots are very similar for all five structures (Supporting Information Figure S3), the non-fluorinated molecule, DTS(PTTh₂)₂ exhibits slightly larger ¹H hyperfine coupling constants on both the thiophene functional units (Supporting Information Table S2). Additionally, analysis of the calculated ¹H hyperfine couplings reveals that the isotropic couplings are not spread evenly over both ¹H on the thiophene units. For a given pair on a thiophene unit, the largest isotropic couplings are due to the proton closer to the center of molecule (see also Figure 7 which shows the high spin density on the carbon atoms the hydrogen is bound to). In the non-

fluorinated donor molecule these hyperfine couplings are approximately 30% larger than the isotropic hyperfine couplings of these protons in the four other donor molecules (the larger isotropic hyperfine couplings in the other four donor molecules are similar with respect to each other). The introduction of fluorine in the FBT unit causes a shift of spin density distribution to the outer thiophene units causing a significant change in hfc. While the FBT and the central unit also experience a change in spin density distribution, the smaller magnitude of hfc makes it harder to observe experimentally. These findings explain nicely the experimentally observed larger hyperfine couplings of DTS(PTTh₂)₂ in the ENDOR spectra. These subtle differences are clearly detected in the magnetic resonance parameters but are not easily obtained by visual inspection of the spin density plots.

The spin density plots also show minimal spin density on both the hexyl substituent on the terminal thiophene groups and the 2-ethyl hexyl substituent on the Si/Ge central atom. To confirm that this was not an effect of the alkyl conformation, several model structures with trimmed alkyl chains were optimized. Converting the hexyl chain to an ethyl group or even a methyl group had very small effects on the g-values (less than 0.0001) and, as shown in Table 3, generally no effect. Likewise, while changing the conformation of the hexyl chain from a linear form to a curved form increased the overall energy of the conformation, it did not change the g-values by more than 0.0001. In addition, we investigated the effect of the Si/Ge alkyl substituent by calculating several model compounds. Again, reducing the 2-ethyl hexyl group to 2-methyl propyl resulted in g-value changes of less than 0.0002. Reducing the substituent completely to a hydrogen atom results in a minor shift of 0.0002.

While the alkyl substituents seem to have little effect on the electronic structure, the actual conformation of the molecule has a much more pronounced effect on the g-values. In particular, we investigated the effect of changing the conformations around the thiophene-thiophene linkages and between the thiophene and central unit. The two low energy conformations around these bonds are labelled *cis* (sulfur atoms on the same side) and *trans* (sulfur atoms on opposite sides). For example, the molecules drawn in Figure 2 would be all *trans* or TTTTTT notation in Table 4. For all molecules investigated, the all-*trans* conformation (TTTTTT) had the smallest g-tensor anisotropy, i.e. largest g_z values and the smallest g_x . Molecules including *cis* conformations, even of just the thiophene units, had significantly different values than the all *trans* conformer. While for all molecules the all *trans* conformation appears to be the lowest in energy, the other conformations are energetically accessible. Calculations show that less than 1 kcal/mol separates all *cis* and all *trans* conformer for DTS(PTTh₂)₂. For DTG(FBTTh₂)₂, the energy difference between the all *trans* and the other conformers is larger (2.8 kcal/mol for the CCCTCT conformer) but still not large enough to definitively select one conformer over the other.

As shown in Table 5, neither the all *cis* nor the all *trans* molecules reproduce the experimental g-values well. The calculations do reproduce the experimental insensitivity to replacing the Si with Ge or one fluorine atom with two resulting in almost identical g-values for all molecules. Interestingly, the calculations using all *trans* molecules generally replicate the g_z and g_y values while underestimating g_x (see rows 3 and 8 in Table 5). The other conformations replicate the g_x and g_y values while underestimating the g_z significantly (compare rows 4 and 9 in Table 5). For all molecules, the g_z axis runs parallel to the longest

molecular axis while g_x is parallel to the short molecular principal axis (Figure 7). When optimizing the molecular structures with various functionals (BP86, B3LYP, TPSSH) no significant changes to the values were found (Supporting Information Table S4). This is not surprising, as the geometries of these organic systems should be adequately modeled with the 6-31G* basis set and the B3LYP functional. Since the g-tensor calculations of such molecules are typically quite successful, the question of the disagreement between experiment and theory remained.

Prior research work has indicated that DTS(FBTTh₂)₂ aggregates into dimers as concentrated solutions are cooled.⁷³ Similar behavior was found in thin films. Since the experimental conditions of our EPR measurements more closely resemble the low temperature, concentrated solutions of Köhler et al.'s work,⁷³ computational models of dimer complexes with an overall +1 charge were built. As shown in Table 6, for the cis conformation, the dimer results show significantly improved agreement for the g_x values while the dimer/trans conformation improves the g_z values as compared to experiment. The orientation of the g tensor axis remains the same as it is in the monomer examples (Supporting Information Figure S6). A dimer with one molecule in the cis conformation and one in trans (Table 7) slightly improves the agreement, but still underestimates g_z . These results hold for all molecules investigated (see Table 7). For all systems, the E^1 is quite negative indicating that at least in the gas phase, these complexes are stable, in agreement with prior spectroscopic results.⁷³ Figure 8 shows the model DTS(FBTTh₂)₂ dimer. The spin density is spread evenly between the two monomers that are approximately 4 Å apart at their closest point.

Since the dimers improved the agreement between calculation and experiment and the spectroscopic results suggest various levels of aggregation were possible, a trimer of DTS(F₂BTTh₂)₂ was constructed. Since it was possible that the bulky 2-ethyl hexyl groups would make such stacking sterically unfavorable, the trimer was optimized with the full structure of the small molecule donor. The optimized structure for the DTS(F₂BTTh₂)₂ trimer is shown in Figure 9. Energetically, the trimer was also very stable in the gas phase, although the individual monomers were not as parallel as in the dimer. The spacing between the top two monomers was very similar to the dimer (4.2 Å apart), while the plane of the third monomer was 4.5–5.5 Å from the middle unit. The calculated g-values (2.0010, 2.0027, 2.0038) are very similar to the all cis dimer and the g tensor axes remain constant (Supporting Information Figure S7). Similar to both the monomer and the dimer, the spin density was spread amongst all three monomers and delocalized across the entire backbone although the most distant (bottom) monomer shows slightly less spin density on the outer units. As the spin density is distributed over the constituent molecules, the isotropic ¹H hyperfine coupling constants of the dimer and trimer are approximately one half and one third of the monomer values, respectively (Supporting Information Table S2). Using these calculated coupling constants, the ¹H ENDOR spectrum of the monomer, dimer and trimer of DTS(F₂BTTh₂)₂ were simulated (Supporting Information Figure S8) and compared to the experimentally obtained spectrum. The simulation using the monomer coupling constants

¹Energy of optimized dimer – 2 x Energy of the independently optimized monomer.

results in significant overestimation of the ENDOR spectrum width, while the simulations using the dimer and trimer values are in much better agreement to the experimental spectrum. The agreement between the dimer and trimer coupling constants and the ENDOR spectra lends further support to the proposal that the positive polaron is delocalized over more than one molecule. The ENDOR spectra recorded using film samples were of approximately equal width to those obtained from frozen solution which suggests the positive polaron is delocalized to a similar degree in the film. The delocalization of the positive polaron across several molecules will reduce the Coulomb binding energy in the CT state, which is beneficial for efficient charge separation.

In summary the DFT calculations show improved agreement with the experimental g-values for stacked dimer and trimer conformations. As there are multiple possibilities for both the conformation of the individual monomers and the actual stacking geometry, we cannot definitively select a single structure as being predominantly present in the experiment. However, the improved agreement for the dimer and trimer as compared to the monomer coupled with the prior work,⁷³ suggests such aggregates are present in our sample. Furthermore, the dimers and trimer maintain the spin density patterns shown in the monomers: no spin density on the silicon or germanium, no spin density on the alkyl substituents on the thiophenes or metals, but spin density on the fluorine atoms.

4. Conclusion

The charge-separated and excited states of five low band-gap small molecule donors, containing dithienosilole (DTS) or dithienogermole (DTG) as central unit, blended with PC₆₁BM were investigated using EPR, ENDOR and TR-EPR spectroscopy. Through EPR and ENDOR the photoinduced charge separated states that are formed in the blends were characterized, and electronic g-tensor and hyperfine couplings of these small molecule donors reported for the first time. Using TR-EPR spectroscopy insight was obtained about the efficiency of charge separation including the secondary CT states and triplet exciton formation pathways. Analysis of the polarization patterns of the TR-EPR CT spectra revealed that charge separation in the DTS(PTTh₂)₂ blend is slower than in the four fluorobenzothiadiazole donor blends and involves a longer lived primary or intermediate CT state. From the TR-EPR triplet exciton spectra we identified the presence of BET triplet excitons in all the blends and demonstrated that they occur more readily in the DTS(PTTh₂)₂ blend. The higher occurrence of BET triplet excitons correlates with the slower charge separation in the DTS(PTTh₂)₂ blend, since the longer life time of the CT states in the DTS(PTTh₂)₂ blend allows greater S-T₀ mixing to occur resulting in a higher incidence of BET to triplet excitons on the donor. This loss mechanism could be a contributing factor in the lower device efficiencies reported for the DTS(PTTh₂)₂ blend compared with those of DTS(FBTTh₂)₂ and DTG(FBTTh₂)₂.^{12, 15–16} These combined results confirm the important role of spin dynamics to control charge separation processes in OPVs and power of advanced EPR spectroscopy in characterization of OPV materials. DFT calculations indicated that a variety of conformations with very similar energetics are possible. The choice of conformation had a significant impact on the g_x and g_z values while all magnetic resonance parameters were largely independent of the alkyl substituents on the thiophene units, the alkyl substituents on the central core structure, and the presence of silicon versus

germanium. This is due to the very small amount of electron spin density on these portions of the molecules. Furthermore, in agreement with prior experimental evidence, dimeric and trimeric models with an overall +1 charge significantly improve agreement between calculation and experiment. In the dimer and trimer models, the spin density is distributed across all monomer units. The delocalization of the positive polaron across several molecules may aid charge separation in these systems. In addition it demonstrates how crucial the comparison with experiment is, since it helps to choose the proper structural model for the calculations. This study makes clear that for future computational studies, the possibility of dimeric or multimeric structures in the experiment have to be taken into account when modelling the polaron electronic structure in small molecule organic semiconductors.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Pathways to selected excited states present in a bulk heterojunction solar cell starting from an optically generated singlet exciton. The donor levels are shown in red and the acceptor in blue.

Figure 2. Structures of the small molecule electron donors and the fullerene derivative PC₆₁BM electron acceptor.

Figure 3.

Light induced EPR (LEPR) spectra from photogenerated polarons in dithienosilole & dithienogermole based donors blended with PC₆₁BM in frozen chlorobenzene solution at T = 50 K. Left panel: Continuous wave X-band (9.8 GHz) LEPR spectra. The field modulation leads to derivative-type line shapes. Right panel: Pulsed D-band (130 GHz) LEPR spectra. The absorptive spectra have been pseudomodulated to yield derivative-type line shapes. The experimental spectra (black) are shown alongside theoretical simulations of the positive polaron residing on the donor (green), negative polaron on the PC₆₁BM (blue) and the superposition of both (red). Spectra were corrected to account for small differences in microwave frequency.

Figure 4.

Light induced X-band Mims ENDOR spectra of dithienosilole & dithienogermole based donors blended with PC₆₁BM in frozen chlorobenzene solution at T = 50 K. The five upper spectra were measured 0.1 mT below the maximum of the pulsed EPR donor signal while the lowest spectrum was measured at the maximum of the PC₆₁BM signal. The arrows mark the Larmor frequency of ¹H and ¹⁹F at a magnetic field of 347 mT. The pulsed method results in absorptive line shapes.

Figure 5.

Continuous wave direct detection TR-EPR spectra of radical pairs in dithienosilole & dithienogermole based donors blended with PC₆₁BM in frozen chlorobenzene solution at T = 50 K. The spectra were captured 500 ns after the laser flash and integrated over a 100 ns period to improve S/N. Positive peaks correspond to absorption (A) and negative to emission (E). Spectra have been background subtracted to remove the broad underlying triplet component and their positions corrected to account for changes in microwave frequency.

Figure 6.

Continuous wave direct detection TR-EPR spectra of triplet excitons in dithienosilole & dithienogermole based donors blended with PC₆₁BM at T = 50 K. Spectra were captured 500 ns after the laser flash and integrated over a 100 ns period to improve S/N. Positive peaks correspond to absorption (A) and negative to emission (E). Left panel: TR-EPR of blends in frozen chlorobenzene solution. Right panel: TR-EPR spectra of solution cast blend films. The experimental data (black) are shown alongside theoretical simulations of the ISC triplet exciton residing on the donor (green), BET triplet exciton residing on the donor (orange), ISC triplet exciton residing on PC₆₁BM (blue) and the superposition of these three contributions (red).

Figure 7. Optimized structure of DTS(FBTTh₂)₂ cation radical (positive polaron) in the trans conformation. The spin density iso-surface is shown at 0.001 e/a₀³. The orientation for the g-tensor axes are shown, with g_x and g_z in the plane, and g_y perpendicular to the molecular plane.

Figure 8.

Top (left) and side (right) views of DTS(FBTTh₂)₂ dimer with an overall +1 charge showing spin density isosurface at 0.001 e/a₀³.

Figure 9.

Top (left) and side (right) views of DTS(F₂BTTh₂)₂ trimer with an overall +1 charge showing spin density isosurface at 0.001 e/a₀³.

Table 1

Principal Values of the g-tensors of the Polarons

molecule	g_x	g_y	g_z^a
DTS(FBTTh ₂) ₂ ⁺	2.0035	2.0024	2.0017
DTS(F ₂ BTTh ₂) ₂ ⁺	2.0035	2.0023	2.0016
DTG(FBTTh ₂) ₂ ⁺	2.0034	2.0026	2.0016
DTG(F ₂ BTTh ₂) ₂ ⁺	2.0034	2.0027	2.0016
DTS(PTTh ₂) ₂ ⁺	2.0034	2.0024	2.0020
PC ₆₁ BM ⁻	2.0006	2.0004	1.9989

The relative error in the g-tensor values is ± 0.0002 .

^aThe large g-strain for g_z in PC₆₁BM⁻ results in a larger error of ± 0.0004 .

Table 2

Zero Field Splitting Parameters of Triplet Excitons

molecule	D (MHz) ^a	E (MHz) ^a
DTS(FBTTh ₂) ₂	1150	143
DTS(F ₂ BTTh ₂) ₂	1190	160
DTG(FBTTh ₂) ₂	1145	142
DTG(F ₂ BTTh ₂) ₂	1185	155
DTS(PTTh ₂) ₂	1130	130
PC ₆₁ BM	280	30

^aThe error in the ZFS parameters is ± 5 %.

Table 3

g-values of DTS(FBTTH₂)₂ cation radical as obtained by DFT calculations.^a

Si/Ge substituent	thiophene substituent	g _z	g _y	g _x
2-methyl propyl	methyl	2.0012	2.0023	2.0025
2-methyl propyl	ethyl	2.0012	2.0023	2.0025
2-methyl propyl	hexyl	2.0012	2.0022	2.0025
2-ethyl butyl	ethyl	2.0012	2.0022	2.0025
2-ethyl hexyl	ethyl	2.0012	2.0023	2.0025

^a All rotatable bonds are in the trans conformation. Optimized using the B3LYP functional and a 6-31G* basis set.

Table 4

Effect of Conformational Change on the g-values

molecule	conformation ^a	g _z	g _y	g _x
DTS(PTTh ₂) ₂	CCCCC	1.9998	2.0024	2.0036
	TTTTT	2.0015	2.0021	2.0023
DTG(FBTTh ₂) ₂	CCCTCT	2.0006	2.0025	2.0028
	CCCTTC	2.0004	2.0025	2.0030
	CTTCTC	2.0005	2.0026	2.0031
	TCCTCC	2.0006	2.0025	2.0028
	TTTTTT	2.0011	2.0024	2.0025

^aBoth the DTS(PTTh₂)₂ cation radical and the DTG(FBTTh₂)₂ cation radical were optimized using B3LYP||6–31G*.

Table 5

Calculated g-values for the Five Donor Molecules.^a

molecule	central substituent	thiophene substituent	conformation	g _x	g _y	g _z
DTS(PTTh ₂) ₂	Methyl	2-methyl propyl	TTTTTT	2.0015	2.0021	2.0023
DTS(PTTh ₂) ₂	Methyl	2-methyl propyl	TTCTTT	2.0008	2.0023	2.0029
DTS(FBTTh ₂) ₂	2-ethyl hexyl	hexyl	TTTTTT	2.0012	2.0022	2.0025
DTS(FBTTh ₂) ₂	2-ethyl hexyl	hexyl	CCCCCC	2.0008	2.0023	2.0029
DTS(F ₂ BTTh ₂) ₂	2-ethyl hexyl	hexyl	TTTTTT	2.0012	2.0023	2.0023
DTG(FBTTh ₂) ₂	2-ethyl hexyl	hexyl	TTTTTT	2.0007	2.0024	2.0028
DTG(FBTTh ₂) ₂	1-ethyl pentyl	hexyl	CCCTCT	2.0006	2.0025	2.0028
DTG(F ₂ BTTh ₂) ₂	2-ethyl hexyl	hexyl	TTTTTT	2.0011	2.0023	2.0024
DTG(F ₂ BTTh ₂) ₂	2-ethyl butyl	ethyl	CCCCCC	2.0002	2.0024	2.0033

^a All results are from conformations optimized using the B3LYP functional and the 6-31G* basis set. The EPR parameters were calculated using the B3LYP functional and the EPRII basis set for first row atoms and def2-TZVPP for heavier (S, Si, Ge) atoms. Conformations are defined as cis/trans (C/T) in terms of the sulfur atoms.

Table 6

Calculated g-values for DTS(FBTTh₂)₂ with an Overall +1 Charge.^a

g	dimer/cis	monomer/cis	dimer/trans	monomer/trans	expt'l
g_z	2.0007	2.0008	2.0017	2.0012	2.0017
g_y	2.0025	2.0023	2.0024	2.0022	2.0024
g_x	2.0038	2.0029	2.0028	2.0025	2.0035

^a All results are from conformations optimized using the B3LYP functional and the 6-31G* basis set with ethyl thiophene substituents and isopropyl substituents on the central silicon atom. The EPR parameters were calculated using the B3LYP functional and the EPRII basis set for first row atoms and def2-TZVPP for heavier (S, Si) atoms.

Table 7

Calculated g-values for Dimer Molecules with an Overall +1 Charge.^a

molecule	conformation	g _z	g _y	g _x
DTS(FBTTh ₂) ₂	all cis	2.0007	2.0025	2.0038
DTS(FBTTh ₂) ₂	all trans	2.0017	2.0024	2.0028
DTS(F ₂ BTTh ₂) ₂	all cis	2.0007	2.0025	2.0040
DTS(F ₂ BTTh ₂) ₂	cis/trans	2.0009	2.0025	2.0035
DTG(FBTTh ₂) ₂	all cis	2.0005	2.0026	2.0037
DTG(F ₂ BTTh ₂) ₂	all cis	2.0006	2.0027	2.0040

^a All results are from conformations optimized using the B3LYP functional and the 6-31G* basis set with ethyl thiophene substituents and 2-methyl propyl on the Si/Ge atom. The EPR parameters were calculated using the B3LYP functional and the EPRII basis set for first row atoms and def2-TZVPP for heavier (S, Si, Ge) atoms