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Absence of Singlet Fission and Carrier Multiplication in a Model Conjugated Polymer: Tracking the Triplet Population through Phosphorescence

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ABSTRACT: Singlet fission, or multiple exciton generation, has been purported to occur in a variety of material systems. Given the current interest in exploiting this process in photovoltaics, we search for the direct signature of singlet fission, phosphorescence from the triplet state, in a model polymeric organic semiconductor for which photoinduced absorption experiments have implied a tripling of the intersystem crossing yield at the onset of fission. Fluorescence and phosphorescence are clearly discriminated using a picosecond gated photoluminescence excitation technique, at variable temperature. At low excitation densities, in a quasi-steady-state experiment, we detect no change of the relative triplet yield to within 4% for photon energies of almost three times the triplet energy of 2.1 eV. Identical results are obtained under nonlinear two-photon excitation. We conclude that assignments of singlet fission based on induced absorptions alone should be treated with caution and may substantially overestimate excited-state intersystem crossing yields, raising questions with regards to the applicability of the process in devices.

Einstein's theory of special relativity lays down an elementary aspect of the light−matter interaction, momentum conservation. As a consequence, the absorption and annihilation of a photon can excite only one electron at a time, irrespective of the original photon energy. The presence of matter can help to circumvent this restriction, either through quasi-classical serial effects such as impact ionization, as exploited in Geiger counters and avalanche photodiodes, or through quantum mechanical many-body correlation effects, as in the double ionization of helium.[1] In semiconductors, the related phenomenon of multiple exciton generation (MEG) is conceivable.[2] In molecules and molecular crystals, where different selection rules apply, an analogous process is given by exciton fission, the spin-allowed mechanism whereby one singlet exciton splits into two triplet excitons.[3−5] Although these processes have been known to occur, in principle, for decades, interest in such approaches to carrier multiplication has recently exploded because of the hope of raising the fundamental photovoltaic device efficiencies by increasing power conversion in the short wavelength range of the solar spectrum.[2a,5b] Obviously, it is a long way from a physical effect to improved device performance, and quantification of MEG in semiconductors and especially semiconductor nanostructures has been controversial at best,[2] since surface states can induce transient absorption signals which interfere with excitonic signatures.[2e] The biggest puzzle in the case of quantum dots lies with respect to the absence of significant multiple exciton emissive species:[2f] if a single photon does generate multiple excitons, then at the very least emission from the non-degenerate radiatively coupled biexciton should be observed. This, however, is not the case in some studies: biexciton emission is only seen under conditions of strong nonlinear optical pumping.[2f] In the case of molecular singlet fission, spectroscopy should be much more straightforward since triplet excitons possess well-defined spectral signatures and magnetic field dependencies.[3] The "smoking gun" for fission in this case is phosphorescence, radiative recombination from the triplet state. Although fission and phosphorescence are often labeled within one and the same Jablonski diagram describing molecular excitation kinetics,[5b] the two are hard to link since organic materials are typically only very weakly phosphorescent.[6] In addition, phosphorescence is usually entirely absent at room temperature, where fission is thought to be more effective.[4,5]

Here, we report on a highly sensitive search for changes in phosphorescence yield in an organic semiconductor, for which singlet fission has previously been claimed to occur at photon energies above 3.4 eV, based on photoinduced absorption (PIA) action spectra.[7] The material, ladder-type poly(*para*-phenylene) (LPPP, shown in Figure 1a) is unique in that it can be made to emit from the triplet state without perturbing the kinetics of the singlet excitations.[8] Incorporation of, on average, roughly one covalently bound palladium atom to every 10 polymer chains dramatically increases spin−orbit coupling locally. With measured triplet diffusivities on the order of 2×10^{-5} cm^2/s and lifetimes of hundreds of microseconds, triplet exciton diffusion lengths can reach several hundred nanometers, much larger than those of singlet excitons.[8b,c] Only triplet excitons are thus affected by the heavy metal sites, as indicated by the sketch in Figure 1b. The singlet kinetics, and indeed all macroscopic material properties, remain unaffected by the local increase in spin−orbit coupling when compared to the unmetalated material:[8e] intersystem crossing (ISC) is only

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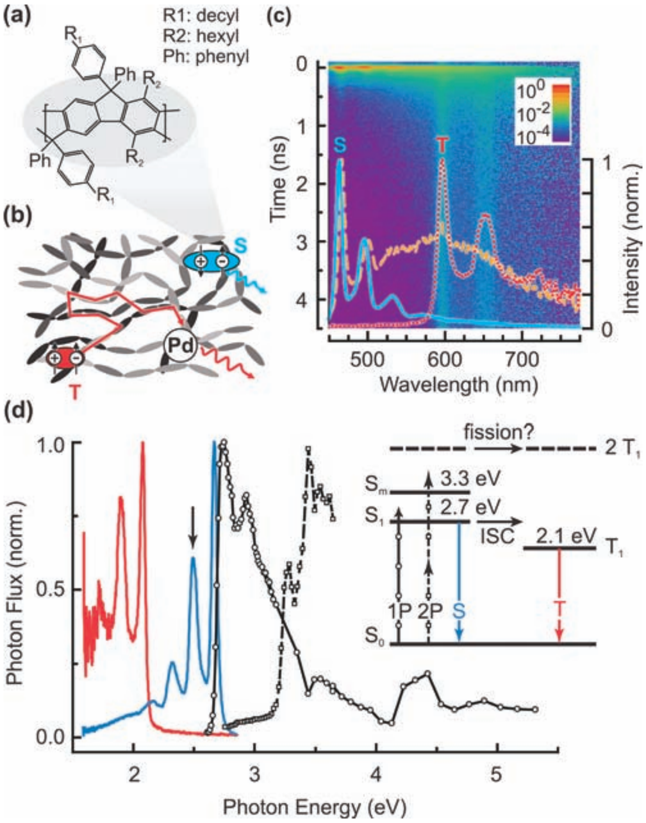

Figure 1. (a) Structure of the conjugated polymer phenyl-substituted ladder-type poly(*para*-phenylene), LPPP (R1: decyl, R2: hexyl). (b) A small concentration of Pd atoms exists within the polymer, corresponding to roughly one atom per ten chains. Since the diffusion length of triplet excitons (red) is greater than that of singlets (blue), enhanced intersystem crossing due to increased local spin−orbit coupling occurs primarily in the triplet excited state, enabling diffusion-driven phosphorescence.[8] (c) Emission dynamics of the polymer film exhibiting the transient fluorescence (S, blue solid line), defect-related emission (yellow dashed line), and the quasi-static phosphorescence (T, red dotted line). (d) Jablonski diagram sketching the relevant energy levels and transitions with the corresponding excitation (black solid line: one-photon UV excitation; black dashed line: two-photon IR excitation) and emission spectra (blue: singlet; red: triplet). All spectra were recorded at a temperature of 30 K.

enhanced from the triplet and not from the singlet excited state. As a consequence, steady-state phosphorescence can even be seen at room temperature under the condition of electrical excitation,[8a] where 75% of the random spin radical encounters pair in the triplet state. Under optical excitation, phosphorescence is over 2 orders of magnitude weaker and can only be visualized in a gated detection configuration. Since the singlet exciton lifetime is on the order of 100 ps, we employed a synchro-scan streak camera to gate the phosphorescence emission as a function of excitation wavelength: picosecond-gated photoluminescence (PL) excitation (PLE) spectroscopy. A frequency-doubled or -tripled tunable mode-locked Ti:sapphire laser was used to excite ~100 nm thin films of the polymer spin-coated on a quartz substrate and mounted to the cold-finger of a liquid-helium cryostat, under vacuum. The phosphorescence decay is driven by diffusion to the palladium sites and hence follows a power law on the microsecond time scale.[8b] Under optical excitation and gating at 80 MHz repetition rate, the phosphorescence therefore appears static.

Figure 1c shows a stitched streak image covering 4.5 ns of luminescence decay at a 5 ps time resolution. It displays the singlet decay at 460 nm and the steady-state phosphorescence background at 600 nm, recorded at 30 K. The overlaid spectra were integrated between −50 and 50 ps (blue) for singlet emission, −50 and 150 ps (yellow) for mixed singlet and keto defect-related emission,[8a] and 3 and 5 ns (red) for the triplet emission.

The static triplet peak is more than 100 times weaker in intensity than the singlet maximum. Panel d summarizes the electronic energy levels and the corresponding transition spectra, obtained with the PLE setup. Emission from vibronically relaxed singlet states was excited by one-photon (1P, solid line) and two-photon (2P, dashed line) processes and allowed for the collection of the corresponding PLE spectra by pointwise scanning of the excitation wavelength while observing the singlet emission at 2.5 eV. In agreement with prior reports, the polymer backbone's rigidity enforces symmetry selection rules, such that 2P excitation of the even-parity S_1 state is negligible.[9] The lowest odd-parity state S_m excited by 2P absorption has an energy 0.6 eV above S_1 and displays a vibronic progression of slightly smaller spacing (0.174 eV) compared to 1P excitation (0.193 eV), in line with the results reported for methylated LPPP in ref 9. Excitation and emission spectra exhibit near-mirror symmetry, with the PL spectrum appearing slightly narrower due to excited state relaxation in the inhomogeneous energetic distribution of molecules. The triplet emission spectrum displays a small shift in Franck−Condon factors due to the more localized nature of triplets compared to singlets.[10] Our setup enabled us to tune the excitation energy from 1.15 to 1.82 eV (1080−680 nm, 2P excitation), and from 2.4 to 5.5 eV (517−227 nm, 1P excitation).

The question, indicated in the Jablonski diagram, is therefore whether under any of these excitation conditions a change in relative triplet intensity becomes discernible. Luminescence experiments tend to be much more sensitive than absorption measurements since they are, in principle, background-free. Further, PIA requires much higher intensities than PL, since a transient excited state has to be populated to induce the absorption. Under the conditions employed in our experiments, with excitation densities of less than 50 mW/cm^2 and pulse energies of 0.5 pJ, PIA is barely able to resolve a triplet absorption.[11] We can therefore probe singlet and triplet densities in a situation which more reasonably relates to a real photovoltaic device than in the case of conventional PIA spectroscopy. The gated phosphorescence detection is sensitive to changes in triplet yield of down to 4%. Therefore, a fission yield of this order is detectable.

Figure 2a shows the phosphorescence to fluorescence ratio as a function of excitation photon energy, for one-photon (blue, red) and two-photon (purple, shifted to twice the photon energy) excitation. Emission spectra were acquired under conditions of constant fluorescence intensity, corresponding to an excitation intensity of 30 mW/cm^2 at 2.8 eV (1P) and 64 W/cm^2 at 1.7 eV (2P). For quantification of the relative fluorescence to phosphorescence intensity, residual long-lived defect emission[8a] was subtracted from the triplet spectra by taking into account the keto emission spectrum known from intermediate-time spectra (Figure 1c), which usually only contributes less than 10% to the measurement signal in the 3−5 ns range. The accuracy of measurements under 2P excitation suffered from local sample heating effects due to the large laser

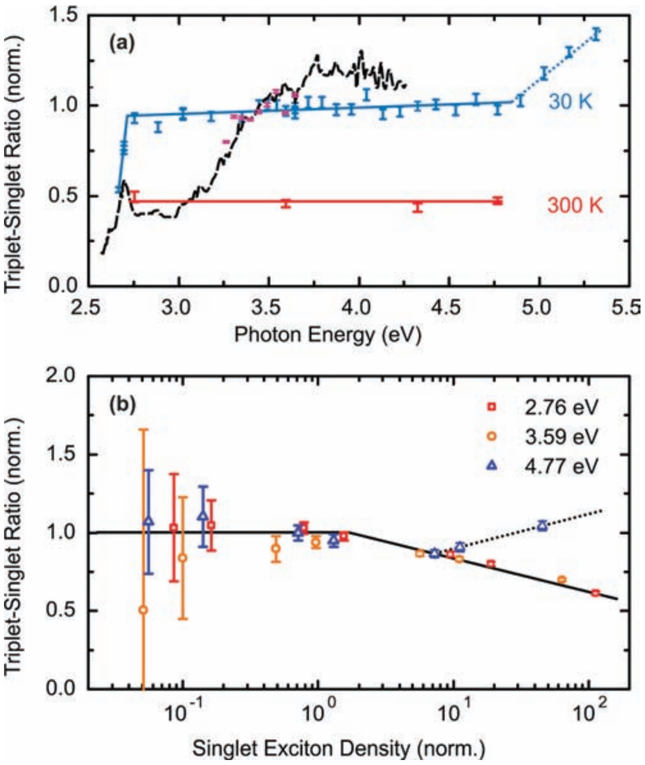

Figure 2. (a) Ratio of phosphorescence to fluorescence as a function of photon energy under one-photon excitation at 30 K (blue) and 300 K (red); straight lines are guides to the eye. The ratio extracted under two-photon excitation (purple) at 30 K is plotted as a function of twice the original photon energy. The relative triplet yield as extracted from PIA measurements in ref 7 is superimposed on the graph (dashed line), normalized at 3.4 eV. (b) Phosphorescence to fluorescence ratio at 30 K as a function of singlet exciton density, plotted for different excitation photon energies. The singlet density is normalized to an excitation intensity of 75 mW/cm^2 at 3.59 eV. Straight lines are guides to the eye.

powers, and the error bars shown only indicate the spectrometric error. In contrast to previous reports based on PIA,[7] no change of the triplet yield >4% is discernible up to a photon energy of 5.0 eV, confirming preliminary phosphorescence studies which were limited in spectral range.[6b] No effect of temperature is seen, other than to slightly shift the flat phosphorescence to fluorescence ratio. The earlier PIA data[7] are superimposed on the graph and show a distinct step at 3.4 eV, which, as noted previously,[6b] is 0.6 eV below the energy required to form two triplets (see Figure 1d). The absence of a rise in phosphorescence also demonstrates that the yield of nongeminate (free) carriers is independent of photon energy, since these charges would recombine preferentially in the triplet channel and thus increase phosphorescence: there is no photon energy-dependent carrier multiplication.

To demonstrate the linearity and stability of the material, we varied the excitation intensity by 3 orders of magnitude between 5 mW/cm^2 and 5 W/cm^2, as shown in Figure 2b, for three different excitation photon energies. Both the singlet and triplet emission intensities are roughly linear with excitation power, so that the ratio appears constant. Sweeps up and down in excitation power are reproducible. At high powers, triplet—triplet annihilation (TTA) is seen to reduce the relative phosphorescence yield with increasing laser power. This observation excludes the occurrence of singlet—singlet annihilation. At low excitation powers, TTA is only effective at room temperature (see Figure 2a), where it lowers the apparent triplet/singlet ratio by about a factor of 2. At excitation energies exceeding 4.8 eV, changes in phosphorescence intensity are no longer fully reversible even at low excitation power (dotted lines in Figure 2); this photon energy approaches the ionization energy of the molecule and likely induces photochemical changes.

LPPP is not an ideal system to search for singlet fission since its singlet level lies 1.3 eV below the corresponding energy of two triplets and fission would therefore have to compete with internal conversion.[5b] However, LPPP does constitute a model multichromophoric macromolecule,[12] with well-defined closely spaced chromophores which could readily accommodate two distinct triplet excitons to prevent renewed conversion of two triplets to an excited singlet.[5b] The fact that PIA suggests a tripling of the ISC yield at the proposed onset of fission,[7] whereas our linear excitation technique clearly shows no change in ISC, implies that the interpretation of PIA spectral signatures is not always straightforward. High excitation densities may lead to the formation of charge-separated states, which themselves can feed triplet excitons.[11] A clear illustration of this mechanism has been given by the electric field modulation of phosphorescence which is observed in LPPP at high pulse energies.[8e] In addition, PL optically detected magnetic resonance unambiguously reveals the presence of spin-1/2 radical species as a result of photoexcitation in conjugated polymers,[13] which add additional absorption features.[10b,13c] It is therefore not trivial for a PIA experiment alone to discriminate between pure excitonic processes, radical-pair mechanisms, and a degradation phenomenon as that exemplified in Figure 2b.

We note that specifically with regards to determining ISC yields, PIA and similar nonlinear optical methods have yielded results hard to reconcile with other observations. For example, much effort was invested in measuring the ISC yield in polymer light-emitting diodes in order to compute the singlet to triplet ratio in carrier pair recombination. Yields of over 10% were inferred for materials such as a polyfluorene derivative.[14] However, given the triplet lifetime of polyfluorene of 1 s at 4 K,[6b] such a high yield would make it impossible to perform single molecule fluorescence spectroscopy on polyfluorenes. In contrast, in excess of 10 000 photons are detected on average from a single molecule per second at low temperatures due to repeated cycling between the singlet ground and excited state, implying that the intrinsic ISC yield must be very low.[15]

Given the discrepancy between our results and previous conclusions regarding fission drawn from PIA we urge caution in interpreting signatures of singlet fission without probing the triplet density by direct quantitative means, such as by spin resonance or phosphorescence. With regards to claims of fission and MEG in photodiodes, we note that it can be hard to discriminate between traditional impact ionization, disorder related effects, and real fission in direct measurements of current.[16,17] A possible interpretation of our results is that, even if singlet fission does occur, the triplets remain correlated and cannot move apart,[4a] in spite of the multichromophoric nature of the polymer.[12] In this case, the triplets would still contribute to transient absorption, but since they could not migrate through the polymer film (Figure 1b), they would not enhance phosphorescence. Such immobile triplets generated through fission would be irrelevant to the operation of photovoltaic devices. Since, however, indications of fission processes do appear to exist in acene-based devices,[18] it is not clear why triplets would remain correlated in some materials (e.g., polymers) and uncorrelated in others (e.g., acenes).

We tentatively generalize our results by concluding that singlet fission appears to be extremely unlikely in multichromophoric aggregates in which the singlet energy lies significantly below twice the triplet energy. We recently demonstrated the ability to shrink the singlet−triplet gap by chemical design by exploiting different localization lengths for the two species and monitoring the gap by simultaneous fluorescence and phosphorescence.[19] By increasing delocalization of the triplet, it may be possible to engineer the gap in the opposite direction, which may after all provide a route to exciton fission in conjugated polymers with the ability to monitor the yield directly through phosphorescence.

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