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Singlet exciton lifetimes in conjugated polymer films for organic solar cells

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Abstract: The lifetime of singlet excitons in conjugated polymer films is a key factor taken into account during organic solar cell device optimization. It determines the singlet exciton diffusion lengths in polymer films and has direct impact on the charge photogeneration yields of the solar cell devices. However, very little is known about the material properties controlling the lifetimes of singlet excitons in conjugated polymer films, with most of our knowledge originating from studies of small organic molecules. Herein, we provide a brief summary of the nature of the excited states in conjugated polymer films and then present an analysis of the singlet exciton lifetimes of 16 different polymers. The exciton lifetimes of nine of the studied polymers were measured using ultrafast transient absorption spectroscopy and compared to the lifetimes of seven of the most common polymers found in the literature. A plot of the logarithm of the rate of exciton decay vs. optical bandgap for all polymers reveals a medium correlation between lifetime and bandgap, thus suggesting that the Energy Gap Law may be valid for these systems but other factors can dominate the polymer exciton lifetimes. The impact of film crystallinity on the exciton lifetime was therefore assessed for a small bandgap diketopyrrolopyrrole co-polymer. Our results show that the increase of polymer film crystallinity leads to proportionate reduction in exciton lifetime and optical bandgap that follows the Energy Gap Law.

Keywords: excited states; diffusion; energy gap law; non-radiative, ultrafast transient absorption spectroscopy.

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1. Introduction

Organic solar cells (OSC) have power conversion efficiencies that are now surpassing 11 % which is a 5 fold increase from the efficiency of the first reported OSC device 30 years ago.[1-3] However, significant further performance improvements are required for the successful translation of this technology into a commercial product. Conjugated polymers are the most widely used light harvesting materials for OSC. In the device active layer, they are normally blended with a soluble derivative of the fullerene C60 or C70 or with a high electron affinity aromatic molecule to create an electron donor-acceptor pair that has energy landscape that favors photocurrent generation. Unlike most inorganic semiconductors, the absorption of light by conjugated polymers does not lead to the direct generation of free charges, but instead coulombically bound pairs of electrons and holes are created. These so called excitons have relatively short lifetimes and limited diffusivities through the active layer.[4-6] They have binding energies that are an order of magnitude bigger than the thermal energy (kT) and for their dissociation they require an external force which in the OSC devices is provided by the molecular orbital energy offset at the D-A interface.[7]

Polymer singlet excitons are the precursors for charge photogeneration taking place at the D-A interface and despite of their importance for OSC performance, relatively little is known about their properties and how we can control them. In particular, there are no clear strategies for the optimization of the exciton lifetime and exciton diffusion in conjugated polymer films. Therefore, the aim of this article is to provide an analysis of the singlet exciton lifetimes of 16 different conjugated polymers to test the validity of the Energy Gap Law for non-radiative transitions.[8,9] The paper starts with a brief overview of our knowledge of the nature of the excited states in conjugated polymer films covering exciton diffusion and lifetimes. Then, the results from transient absorption spectroscopy measurements of the exciton lifetimes of 9 polymers are presented alongside the lifetimes of 7 popular polymers widely used for OSC fabrication. Based on this data, a weak correlation between the natural logarithm of the inverse of the exciton lifetime and the polymer bandgap is discovered. Finally, three films of the co-polymer BTT-DPP with different molecular weights were characterized to assess the impact of film crystallinity on exciton lifetime.

2. Results and Discussion

2.1. Excited states in conjugated polymers

The excited states of conjugated polymers are coulombically-bound electron-hole pairs that resemble molecular excited states.[10] They are called singlets when their spin is 0 and triplets when their spin is 1. The singlets and triplets vary broadly in properties but only singlets are populated upon polymer light absorption. This is because of the spin forbidden nature of the transition from a singlet ground state to a triplet excited state. Triplets are generated indirectly through intersystem crossing from a singlet exciton involving a spin flip or through electron-hole recombination.[11-14] Singlet and triplet excitons are both formed in OSC during device function but predominantly singlets are involved in charge photogeneration, while triplets are normally associated with undesirable recombination processes.[11-14]

Singlet excitons can be broadly classified as intrachain and interchain.[15-17] In the former, the excited state extends only over a single polymer chain and its delocalization is limited by conformational disorder and chemical defects.[18] This is typically the case for homologous polymers like P3HT but not for co-polymers in which the excited state is not evenly distributed through the polymer chain. The main reason for this is the difference in electron affinity of the co-polymerized chromophores.[19-22] For example, the absorption of light by the co-polymer SiIDT-DTBT creates an excitation with a partial charge transfer character; the electron is predominantly localized on the BT unit, while the hole is uniformly delocalized along the polymer chain up (Figure 1).[13] As a result, the exciton delocalization in this co-polymer extends only over 3 monomer units.

Figure 1. Charge density isosurface of the electron and hole natural transition orbitals of the lowest energy electronically excited state in the trimer of SiIDT-DTBT. Calculations were performed by TD-DFT B3LYP/6-31g* and are taken with permission from reference [13].

In addition to intrachain excited states, many conjugated polymers including co-polymers form interchain excited states that can be thought of as Frenkel excitons.[23] These occur frequently in molecular crystals and crystalline polymer films as a result of strong electronic interactions between the neighboring chromphores.[24] The Frenkel exciton is a strongly bound electron-hole particle that has no net dipole moment and distinctive optical properties, such as well-defined vibronic peaks and strong 0-0 transitions, which allow for an easy identification of high order in thin polymer films.[25]

Another type of interchain excited states that has been observed in polymer films is the excimer that is an excited state complex of two stacked chromophores formed dynamically through molecular rearrangements after light absorption.[10] The excimer cannot be directly excited through light absorption and is identified by its distinctively broad and featureless emission spectrum that is red-shifted from the monomer emission. Excimers are frequently observed in solutions of aromatic molecules, where solvent and molecular geometrical rearrangements are possible. In thin polymer films however the movement of the chromophores from the polymer chain is highly restricted due to steric hindrance caused by dense polymer packing. Despite of this, excimer formation still takes place in such films and on surprisingly fast timescales (picoseconds), possibly because of the existence of pre-associated complexes that require only a small geometrical reorganization. It has been demonstrated that the yield of excimers in polymer film can be significant reaching up to 30% for highly crystalline P3HT domains.

Rumbles et al have also pointed out that in addition to excimers and excitons, often polymer films generate low yield relatively long-lived polaron states. These are electrons or holes that are coupled to the molecular vibrations and are able to diffuse through the film.[10,26] Because of their low yields, these will not be further discussed in this article. Instead, we will focus on the intrachain and interchain excited states which we will call excitons for simplicity. We note that excimers and excitons and even polarons are often difficult to distinguish spectroscopically. Therefore, in the studies of excited state diffusion in polymer films these are generally referred to as excitons.

2.2. Exciton diffusion in polymer films

Singlet exciton diffusion is one of the key material parameters that determine OSC device performance. It can be described as the migration of energy through a film via series of energy transfer steps. In its simplest form, each step can be understood as a dipole-dipole induced non-radiative energy transfer process that is best described by the Forster Resonance Energy Transfer mechanism. Therefore, the efficiency of exciton diffusion will depend on the spectral overlap between the absorption and emission of the donor and acceptor chromophores, the orientation between their transition dipole moments and the distance between them. [review Blom] Due to high film disorder the density of exciton states in polymer films is often very high, which often causes polymer excitons to diffuse via energy downhill migration especially in more disordered materials and at low temperatures. In this type of diffusion, the rate of energy transfer differs for each consecutive step and it depends on the number of accessible states and their spatial separation, resulting in the slowing down of the excitons with time. Another mechanism of exciton diffusion is through temperature-activated hoping which has been shown to dominate the exciton diffusion in higher crystallinity polymers, like MDMO-PPV, which generally have narrower density of exciton states. This type of exciton diffusion is thought to be more effective but examples of demonstrated improved diffusion lengths with higher polymer crystallinity are limited. Instead, Blom et al. have recently shown that exciton diffusion is predominantly limited by the number of trap states (loosely defined, as impurities, morphological and chemical defects) in the thin organic film rather than other material properties. However, further work is required to provide insights into the nature of the trap states and the possibility for their removal from the film for improved exciton diffusion. A more detailed description of the possible mechanisms of exciton diffusion can be found in a couple of recent review articles by Blom et al and Ohkita et al.

In the OSC literature, the most widely cited figure of merit for exciton diffusion is the exciton diffusion length (L_D) that is defined as the root mean square of the spatial exciton displacement from its origin, prior to its recombination to ground state. It is given with the following expression:

$$L_D = \sqrt{2ZD\tau} \tag{1}$$

where Z is equal to 1,2 or 3 for the number of dimensions the exciton can travel, D is the diffusivity of the films expressed with units cm^2s^{-1} and τ is the exciton lifetime.

The singlet exciton diffusion lengths of many polymers have been reported to vary between 3 and 20 nm. These values are an order of magnitude smaller than the light absorption depth of typical polymer films, which is the key limiting factor for the development of bi-layer OSC devices. Therefore, the photoactive layer of the majority of OSC devices is a fine blend of polymer and fullerene that ensures sufficiently high density of a polymer-fullerene interface for high exciton dissociation yields. In fact, many of the high performance OSC have blend structures that are optimized for near unity exciton dissociation yields (e.g. PCDTBT:PCBM and PTB7:PCBM) in which the polymer and fullerene mixing is very high, on the nanometer length scale. On the contrary to these, more crystalline and relatively low miscibility polymers, such as P3HT and DPP-T-TT exhibit 20-40% photocurrent losses due to poor exciton dissociation. These are caused by coarser film structures with high polymer and fullerene phase separation. It is worth mentioning that the current highest performing OSC have less than optimal polymer exciton dissociation yields, but compensate with high fill factors and open circuit voltages due to excellent charge transport properties and well aligned energy levels. It can therefore be concluded that the interplay between exciton dissociation and charge transport is very important for OSC performance. Therefore, the possibility for systematic improvements of the exciton diffusion lengths of a material can provide a new pathway to device performance enhancements.

2.3. Exciton lifetimes

As shown in equation 1, the exciton lifetime is one of two parameters that determines the polymer exciton diffusion lengths. Longer exciton lifetimes can be translated into longer diffusion lengths. Nevertheless, our ability to control the polymer exciton lifetime, either synthetically or via material processing is currently very limited. The lifetime of singlet excitons is determined by both radiative and non-radiative photophysical processes and can be expressed with the following equation:

$$\tau_{AVE} = 1(k_R + k_{NR}), \tag{2}$$

where τ_{AVE} is the measured lifetime, k_R is the rate of radiative decay and k_{NR} is the average rate of non-radiative recombination decay. The exciton lifetime is also directly related to the fluorescence quantum yield (QY) via the equation:

$$QY = k_R / (k_R + k_{NR}), \tag{3}$$

In the case of multi-atomic molecules τ_{AVE} is normally dominated by the rate of non-radiative recombination decay. As a result, large molecular complexes and polymers usually have very low

QY. For example, the QY of the thin films of the benchmark polymers P3HT, PTB7 and MEH-PPV are < 1%, although there are also some exceptions to this empirical observation, as seen for PFO (QY of 53%). The dominance of the non-radiative photophysical processes is further enhanced in thin films, which is evident in experiments comparing the exciton lifetime and QY of polymers in solution and films. Therefore, for the rest of this manuscript we will focus on examining the non-radiative decay of polymer singlet excitons in conjugated polymer films.

Non-radiative electronic transitions include internal conversion, intersystem crossing, electron transfer and electron-hole recombination. It is generally known that the rate constant of these processes depend on the energy gap between the initial and final states involved. This is well demonstrated in the Marcus Theory of non-adiabatic electron transfer and in the Energy Gap Law. The latter describes the rate of unimolecular non-radiative decay between two weakly coupled electronic states (the states undergo small changes in their equilibrium geometries during their transition). The Energy Gap Law is therefore directly related to the rate of exciton decay to ground state in organic materials (inversely proportional to the exciton lifetime). It can be most simply presented as:

$$k_{NR} \alpha \exp(-\gamma\Delta E), \tag{4}$$

where γ is a molecular parameter that includes the highest energy vibrational mode involved in the non-radiative transition and ΔE is the energy difference between the potential minima of the lowest excited state and the ground state.

The Energy Gap Law has been successfully applied to describe the non-radiative transitions in variety of systems including aromatic molecules, heavy atom complexes and rare earth ions, as well as triplet exciton decays in conjugated polymer films. Nevertheless, the validity of this law has not been tested for singlet exciton lifetimes in conjugated polymer films. We therefore collected the exciton lifetimes for sixteen conjugated polymers that have been used for OSC fabrication to study the relationship between polymer bandgap and exciton lifetime, if any. The structures of the polymers are presented in the SI and include some of the most widely studied polymers to date.

Table 1 presents the abbreviations of the polymer names, their optical bandgaps and exciton lifetimes as measured in thin films. The exciton lifetimes of the first nine polymer films were estimated using high sensitivity ultrafast transient absorption spectroscopy. In all measurements, the light excitation densities were kept sufficiently low to avoid non-linear response from the samples. The exciton lifetimes were extracted by exponential fitting of the singlet exciton absorption band present in the NIR for all polymers. In the case of multi-exponential decays, the average exciton lifetimes were estimated by calculating the weighted average of all time constants received from the fits. Any long-lived signals arising from polaron or triplet-triplet state absorption were excluded from the fitting analyses. In order to expand the number of data points and compare our results to previously published values, the lifetimes of seven more polymers were taken from the literature. These include some of the most widely studied polymers to date: P3HT, PCDTBT, PCPDTBT, PFO, PTB7 and MEH-PPV. It is worth noting that polymer exciton lifetimes published in literature vary widely, probably because of differences in the source of the polymers and their film processing conditions. Another possible source of error is the difference in the spectroscopic techniques used and the experimental conditions. This variation in lifetimes is taken into account in the analysis of the exciton lifetimes.

Table 1. Optical bandgaps and exciton lifetimes of the polymers characterized in this study. The structures of the polymers are included in the SI. (a) lifetimes measured using transient absorption spectroscopy (b) average lifetimes found from published work, measured via ether transient absorption or fluorescence spectroscopy.

Polymer	Optical bandgap eV	Exciton lifetime Ps
BTT-DPP	1.33	18±0.9[a]
DPP-TT-T	1.38	38.1±1.2[a]
SiIDT-BT	1.80	112±4.0[a]
SiIDT-2FBT	1.80	175.3±6.7[a]
Bu-GeDT	1.89	97.8±5.8[a]
Bu-SiDT	1.90	106.8±11.3[a]
APFO-3	1.93	399. 6±82.7[a]
SiIDT-TPD	2.00	107.8[a]
TTP	2.60	127±4.7[a]
PCPDTBT	1.43	78[b]
PCDTBT	1.86	463±193[b]
PBTTT	1.90	175[b]
P3HT	1.95	422±150[b]
MEH-PPV	2.11	210±79[b]
PFO	2.80	430[b]

Figure 2 presents a plot of the natural logarithm of the inverse of the exciton lifetime vs. the optical bandgap of all thin polymer films presented in Table 1, which allows us to test the validity of the Energy Gap Law for the polymers studied here. The exciton lifetime of PFO included in the figure is corrected using Equation 2 for the high QY of this polymer (53 %); it therefore represents the non-radiative recombination decay of the PFO singlet exciton. A similar correction was carried out for PCDTBT (QY of 6%), although the received non-radiative decay constant is well within the standard deviation of the lifetimes measured for this polymer. The scatter data in Figure 2 was fitted to a line function which yielded a low adjusted root square value of 0.45, which reflects the high variation in exciton lifetimes. Relatively high Pearson's correlation of -0.69 is received from the fit, which allows us to suggest that the polymers studied here follow the Energy Gap Law. In agreement with this is the negative correlation between the rate of decay and the optical bandgap, which means that smaller polymer bandgaps result in shorter exciton lifetime. However, further experimental work is required to confirm the validity of this conclusion.

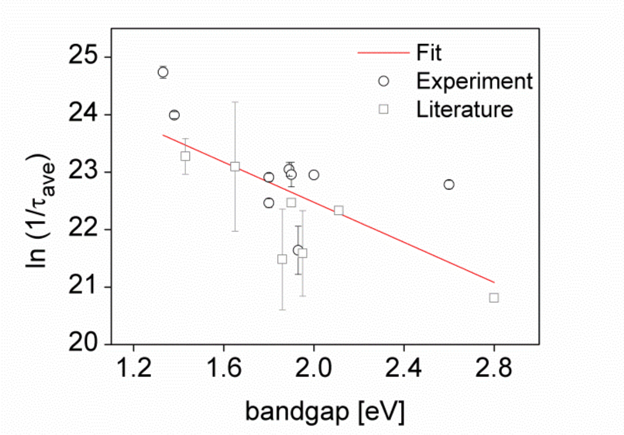

Figure 2. The natural logarithm of the rate of singlet exciton decay plotted as a function of optical bandgap for 16 conjugated polymer films included in Table 1. The open circles represent the experimentally determined rates of exciton decay of polymer films studied herein, estimated using ultrafast transient absorption spectroscopy. The error bars represent the square root of the mean residual variance of the exciton lifetime as received from the exponential fits of the exciton decays. The open squares represent the rates of exciton decay for popular polymers as extracted from the literate. The error bars are the standard deviation of the exciton lifetimes found in the literature for each polymer. The red line is the best fit straight line to all data points showing negative slope.

According to the Energy Gap Law, the slope of the linear fit (γ) depends on the geometrical rearrangements experienced by the polymers during their non-radiative decay from the excited to the ground state. It also includes the maximum energy vibration involved in the decay. Considering the relatively low confidence in the fit in Figure 2, a low value of γ (-1.7 ± 0.5 eV^{-1}) is extracted; thus, suggesting that for the studied materials the singlet exciton decay to ground state involves a high distortion of the polymer equilibrium geometries. (Friend+Kohler). This result is not surprising based on the relatively high Stokes shifts observed in conjugated polymers due to their high disorder. It also provides a possible reasoning for the large variation in exciton lifetimes seen here, possibly originating from differences in film crystallinity, although no obvious trends between film crystallinity and exciton lifetime can be observed in Figure 2.

Table 2. Optical bandgaps and exciton lifetimes of BTT-DPP polymer films with differing number average molecular weights in kg.mol^{-1} (included in the the table).

Polymer name	Optical bandgap / eV	Exciton lifetime / ps
BTT-DPP 90 kg.mol^{-1}	1.37	16.5±1.3
BTT-DPP 73 kg.mol^{-1}	1.34	15.3±0.9
BTT-DPP 22 kg.mol^{-1}	1.32	13.5±1.2

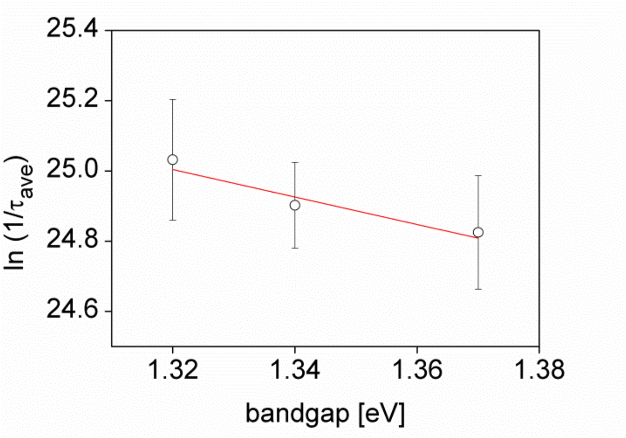

Figure 3. The natural logarithm of the rate of singlet exciton decay plotted as a function of optical bandgap for 3 BTT-DPP polymers with different molecular weight and film crystallinity. The open circles represent the experimentally determined rates of exciton decay of polymer films studied herein, estimated using ultrafast transient absorption spectroscopy. The error bars represent the square root of the mean residual variance of the exciton lifetime as received from the exponential fits of the exciton decays. The red line is the best fit straight line to all data points showing a negative slope with a value of -3.9 ±1.3 eV^{-1}.

To test the importance of film crystallinity on the exciton lifetime, three BTT-DPP polymers with differing molecular weights were studied using transient absorption spectroscopy. Previously published WAXS measurements have indicated that the crystallinity of the BTT-DPP films increases with the decrease in molecular weight of the polymer; hence, the smaller molecular weight polymers produce more crystalline films. According to Table 2, the lifetime of the singlet excitons in the three BTT-DPP films also decreases with increasing film crystallinity. Furthermore, a careful examination of the absorption spectra of the films (Figure 3a) reveals that the changes in film crystallinity with molecular weight impact not only the exciton lifetime but also the optical bandgap of the polymers. This result is not surprising in lights of recent reports showing that morphological changes of organic films impact their molecular orbital energetics. In Figure 3, we include an Energy Gap Law plot of the natural logarithm of the inverse of the exciton lifetime of the BTT-DPP films as a function of optical bandgap. The data was successfully fitted with a linear function producing a high confidence fit with Pearson's correlation of -0.95155 and high adjusted root square value of 0.81089. The fit also estimated a gradient of -3.9 ±1.3 eV^{-1} which is in a good agreement with previously published values for molecules and polymers. This indicates relatively small displacement of molecular geometry between the excited and ground states for this polymer. On the basis of these results, it is possible to conclude that the changes in BTT-DPP film crystallinity cause a change in both polymer exciton lifetime and optical bandgap that follow the Energy Gap Law.

The results presented herein have a particular significance for the development of materials for OSC, especially in lights of the extensive number of small bandgap materials with absorption up to and beyond 900 nanometres reported over the past 5 years. They suggest that smaller bandgap polymers should naturally exhibit shorter exciton lifetimes compared to the higher bandgap polymers due to an increase in their rate of non-radiative exciton decay to ground state, following the Energy Gap Law. It is clear however that the exciton lifetime data shown in Figure 2 generates a high variance plot with a relatively low confidence linear fit. There are multiple possible reasons behind this result, of which the most obvious ones are the diversity in chemical structures between the polymers used, the presence of different heteroatoms in their structures and the differences in film order/crystallinity. These may lead to the population of very different in nature excited states that may result in different exciton lifetimes, as discussed in Section 2.1. Our comparison of the exciton lifetime of the polymer BTT-DPP as a function of film crystallinity shows clearly that film crystallinity can be used as a tool to control the exciton lifetime in polymer films, as more crystalline films exhibit shorter lifetimes. Our results however indicate that the cause of the change in exciton lifetime is the reduction of polymer bandgap in the more crystalline films.

2. Materials and Methods

The materials studied herein have been synthesized via established synthetic procedures and their optical properties characterized elsewhere.

BTTDPP[27]:Poly[(5-decylbenzo[1,2-b:3,4-b':5,6-d'']trithiophene-2,8-diyl)-alt-co-(3,6-bis(2-thienyl)-2,5-dihydro-2,5-di(2-octyldodecyl)pyrrolo[3,4c]pyrrolo-1,4-dione-5,5'-diyl)]
DPP-TT-T[20]: Poly[[2,5-bis(2-octyldodecyl)-2,3,5,6-tetrahydro-3,6-dioxopyrrolo[3,4-c]pyrrole-1,4-diyl]- alt –[[2,2′-(2,5-thiophene)bis-thieno[3,2-b]thiophen]-5,5′-diyl]]
SiIDT-BT[28]: silaindacenodithiophene, benzo[*c*][1,2,5]thiadiazole
SiIDT-2FBT[29]: silaindacenodithiophene, 5,6-difluorobenzo[*c*][1,2,5]thiadiazole
Bu-GeDT[30]: Poly(3,5-didodecyl)-4,4′-di-n-butyldithieno[3,2-b:2′,3′-d]-germole)-2,6-diyl-alt-(2,2′-bithiophene)-5,5′-diyl)
Bu-SiDT[30]: Poly(3,5-didodecyl)-4,4′-di-n-butyldithieno[3,2-b:2′,3′-d]silole)-2,6-diyl-alt-(2,2′-bithiophene)-5,5′-diyl)
SiIDT-TPD synthesis is provided in the SI. TTP[31]: poly(phenyl-bithiophene)

The thin polymer films were fabricated via spin-coating from chlorobenzene or di-chlorobenzene solutions on glass substrates. The absorption spectra of the films were measured with a PerkinElmer Lambda 25 spectrometer in air. The optical bandgaps of the films were estimated from the onset of the lowest absorption peak.

Femtosecond transient absorption spectroscopy was carried out using a commercially available transient absorption spectrometer, HELIOS (Ultrafast systems). Samples were excited with a light pulse with a wavelength matching the lowest energy absorption maxima of the polymers. The excitation was generate by an optical parametric amplifier, TOPAS (Light conversion) seeded from the output of an 800 nm, ~100 femtosecond, 1KHz Solstice Ti:Sapphire regenerative amplifier (Newport Ltd). The probe pulses were generated in a sapphire plate and detected with Si or InGaAs CMOS cameras. All spectroscopy measurements were carried out at low excitation densities to avoid exciton-exciton annihilation processes and their lifetimes estimated via exponential fits.

Supplementary Materials: The following are available online at www.mdpi.com/link, Figure S1: title, Table S1: title, Video S1: title.

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Conflicts of Interest: The author declares no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

References

References must be numbered in order of appearance in the text (including citations in tables and legends) and listed individually at the end of the manuscript. We recommend preparing the references with a bibliography software package, such as EndNote, ReferenceManager or Zotero to avoid typing mistakes and duplicated references.

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In the text, reference numbers should be placed in square brackets [ ], and placed before the punctuation; for example [1], [1–3] or [1,3]. For embedded citations in the text with pagination, use both parentheses and brackets to indicate the reference number and page numbers; for example [5] (p. 10), or [6] (pp. 101–105).

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