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Generating Triplets in Organic Semiconductor Tetracene upon Photoexcitation of Transition Metal Dichalcogenide ReS₂

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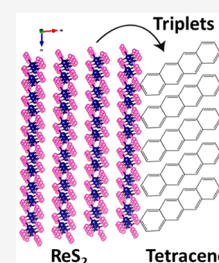
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ABSTRACT: We studied the dynamics of transfer of photoexcited electronic states in a bilayer of the two-dimensional transition metal dichalcogenide ReS₂ and tetracene, with the aim to produce triplets in the latter. This material combination was used as the band gap of ReS₂ (1.5 eV) is slightly larger than the triplet energy of tetracene (1.25 eV). Using time-resolved optical absorption spectroscopy, transfer of photoexcited states from ReS₂ to triplet states in tetracene was found to occur within 5 ps with an efficiency near 38%. This result opens up new possibilities for heterostructure design of two-dimensional materials with suitable organics to produce long-lived triplets. Triplets are of interest as sensitizers in a wide variety of applications including optoelectronics, photovoltaics, photocatalysis, and photon upconversion.



Charge and exciton transfer across heterointerfaces of organic/inorganic semiconductors is both a fundamentally interesting and technologically relevant process for photovoltaics, photocatalysis, and optoelectronics.^{1–9} Transfer of triplet excitons across such heterointerfaces is of interest as the long triplet lifetimes are advantageous for exciton harvesting and photon upconversion. Thompson et al. and Tabachnyk et al. reported transfer of triplet excitons from organic singlet fission molecules to Pb-chalcogenide nanocrystals.^{10,11} This result was complemented by Mongin et al., who demonstrated reverse triplet transfer from inorganic CdSe nanocrystals to organic surface ligands.¹² To date, triplet transfer has been found to occur in various systems of inorganic nanocrystals and organic molecules, including recently developed perovskite nanocrystals.^{13–20} Bulk metal halide perovskites absorbing in the near-infrared have also been utilized as a sensitizer to transfer triplets to organic molecules for triplet–triplet annihilation upconversion.^{21,22}

Two-dimensional van der Waals materials, such as transition metal dichalcogenides (TMDCs), are promising for near-infrared light harvesting followed by transfer of photoexcited electronic states (excitons or free charges) to organic molecules. Two-dimensional TMDC layers can be stacked on top of each other and can be mutually bonded through weak van der Waals interactions. Charge transfer across TMDC/organic interfaces has been demonstrated.^{1,23–28} Singlet exciton energy transfer from monolayer-WS₂ to emissive PbS/CdS nanocrystals has been reported.²⁹ Kafle et al. studied the zinc phthalocyanine (ZnPc)–molybdenum disulfide (MoS₂) heterointerface, where photoexcitation of ZnPc results in ultrafast electron transfer to MoS₂, creating a charge-separated state. Due to strong spin–orbit coupling in TMDCs, the electron spin flips, which results in back electron transfer from MoS₂ forming a triplet exciton in ZnPc.³⁰

However, to our knowledge, the process where photoexcitation of a TMDC yields triplets in an adjacent organic layer has not been reported yet.

Here, we demonstrate ultrafast (~5 ps) transfer of photoexcited electronic states from the near-infrared absorbing TMDC semiconductor ReS₂ (exciton energy of 1.5 eV) to triplet states in tetracene (energy at 1.25 eV)^{31,32} in a solid-film bilayer through transient optical absorption spectroscopy. Upon photoexcitation of ReS₂, we found distinct signatures of triplets in tetracene that confirm transfer of photoexcited states across the ReS₂/tetracene heterointerface. This advocates the applicability of TMDCs, such as ReS₂, as a near-infrared triplet sensitizer of organic molecules.

Flakes of ReS₂ were obtained by liquid-phase exfoliation, as reported in our previous paper.³³ The ReS₂ flakes have a thickness of 4 ± 2 monolayers and average lateral sizes of 75 nm (Figure S1, SI). We refer to Figure 1 and the SI for additional details. A dispersion of ReS₂ flakes dispersed in *N*-methyl-2-pyrrolidone (NMP) was drop-cast on a quartz substrate, and the NMP was evaporated under a nitrogen atmosphere inside a glovebox to form a film. A ReS₂/tetracene bilayer was obtained by deposition of tetracene on top of a ReS₂ film through thermal evaporation. Figure 1 shows the optical absorption spectra of tetracene, ReS₂, and the ReS₂/tetracene bilayer. Pure tetracene has a structured absorption spectrum in which the lowest energy singlet–exciton split at

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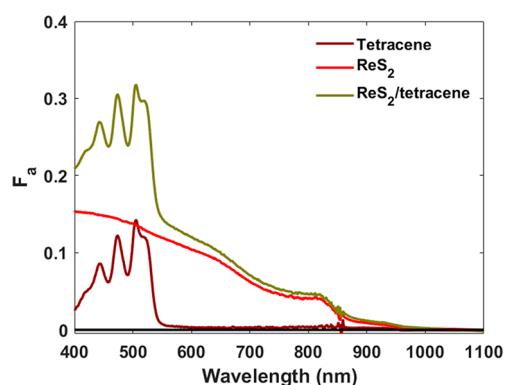


Figure 1. Optical absorption spectra in terms of fraction absorbed photons (F_a) of tetracene, ReS_2 , and $\text{ReS}_2/\text{tetracene}$ films.

505 and 520 nm (Davydov splitting).^{34,35} ReS_2 has a first excitonic absorption near 825 nm (Figure 1). The bilayer clearly shows the features associated with the individual components.

To monitor the dynamics of exciton or charge transfer from ReS_2 to tetracene, broadband (500–900 nm) femtosecond transient absorption (TA) spectroscopy was utilized. The experimental setup has been described elsewhere.³⁶ Here, we monitor the pump-induced changes in the absorption of the probe pulse ($\Delta A = A_{\text{pump on}} - A_{\text{pump off}}$, where A is the absorbance) as a function of pump–probe delay time at different probe photon energies. The TA signal can exhibit negative ΔA signals due to depletion of the ground state (ground state bleach, GSB) and/or stimulated emission (SE) from excitons. Also, photoinduced absorption (PIA) or positive ΔA in TA can arise when pump-generated charge carriers and/or excitons get excited further by absorbing probe photons. The ΔA signal can be expressed as

$$\frac{|\Delta A|}{I_0 F_a} = \varphi \frac{\sigma_B}{\ln 10} \quad (1)$$

where I_0 is the number of incident photons per unit area, F_a is the fraction absorbed pump photons in the sample, φ is the quantum yield of charges/excitons, and σ_B is the cross-section of bleach or photoinduced absorption.

Below, we first discuss the origin of the pump-induced changes in the absorption of the probe pulse for pure tetracene. We identify wavelength regions in terms of GSB/SE and PIA corresponding to singlets and triplets. That knowledge is used to interpret the TA results $\text{ReS}_2/\text{tetracene}$ bilayer.

Tetracene. Figure 2(a) shows the evolution of the TA spectrum of tetracene upon 510 nm photoexcitation with an absorbed photon density of $2.1 \times 10^{12} \text{ cm}^{-2}$ at which exciton–exciton annihilation is insignificant.³⁷ The salient features at early delay times (1–2 ps) in Figure 2(a) are negative ΔA (bleach) around 530–545 nm (green arrow) and 580–600 nm (red arrow). These wavelengths correspond to the 0–0 and 0–1 photoluminescence peaks of tetracene,³⁴ and we, therefore, attribute these bleach features in the TA spectrum to stimulated emission from singlets. At 530–545 nm ground-state depletion will also contribute to bleach. As shown in Figure 2(b), both bleach features decay on a time scale of 100 ps due to singlet fission, in agreement with previous reports.^{34,38} The bleach at 580–600 nm has completely decayed after 1000 ps, which we attribute to the disappearance of SE. By contrast, the bleach at 530–545 nm persists, due to ground state depletion by triplets with a lifetime as long as ~ 100 ns.^{39,40}

The TA spectra exhibit broad PIA at wavelengths longer than 650 nm. The PIA at 650–665 nm due to singlets decays on a time scale of 100 ps (Figure S2, SI).³⁴ The PIA at 780–820 nm is due to both singlets and triplets being excited to higher-lying states of the same spin. The ratio of the oscillator strength of the PIA for singlets and triplet pairs is close to 1:2.³⁴ The increase of the PIA at 780–820 nm in Figure 2(b) reflects the dynamics of triplet formation via singlet fission (see also Figure S2, SI). In the region 720–765 nm, the PIA is virtually constant during the measurement time, which we attribute to the PIA by a singlet exciton being similar to that by a triplet pair.

$\text{ReS}_2/\text{Tetracene}$ Bilayer. We studied transfer photoexcited electronic states from ReS_2 to tetracene in a bilayer configuration. Please note that according to our recent study photoexcitation at 530 nm can lead to the formation of excitons and free charges in ReS_2 with an upper limit of the initial quantum yield of free charges near 20% and a lifetime before recombination to excitons or trapping of a few picoseconds.⁴¹ After photoexcitation of ReS_2 triplets can be

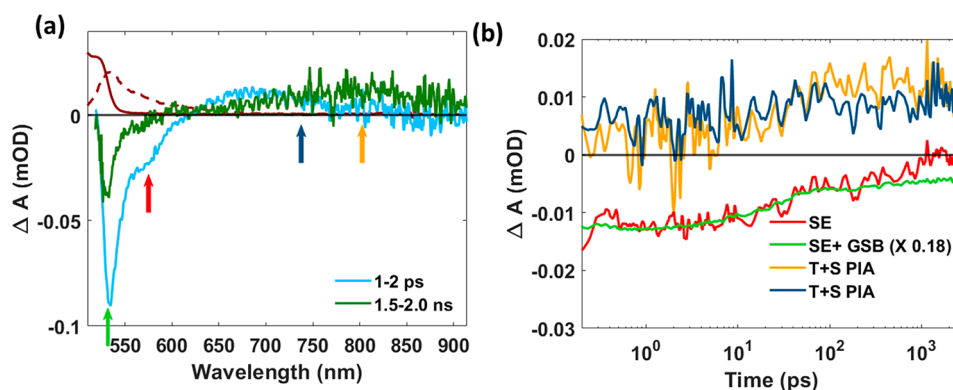


Figure 2. (a) TA spectra of tetracene at early (1–2 ps) and longer (1.5–2.0 ns) time delays after the 510 nm pump laser pulse. The steady-state absorption (dark red) and photoluminescence (dotted dark red) spectra are also shown. The colored arrows indicate the wavelength region where decay kinetics were monitored. (b) Normalized decay kinetics (on a log scale) for four different wavelength regions, i.e., stimulated emission (SE) and ground state bleach (GSB) at 530–545 nm, stimulated emission (SE) at 580–600 nm from singlets (S), and photoinduced absorption (PIA) at 720–765 nm and 780–820 nm by both singlets (S) and triplets (T). The TA kinetics has been averaged over the wavelength regions.

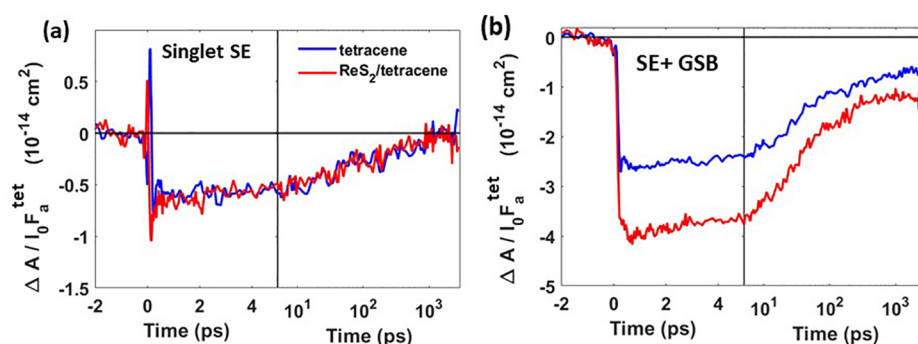


Figure 3. $\Delta A/I_0 F_a^{\text{tet}}$ after 510 nm photoexcitation of the tetracene film (blue) and the ReS_2 /tetracene bilayer (red), due to (a) SE from singlets in tetracene (580–600 nm) and (b) SE and GSB (530–545 nm) due to singlets and triplets in tetracene.

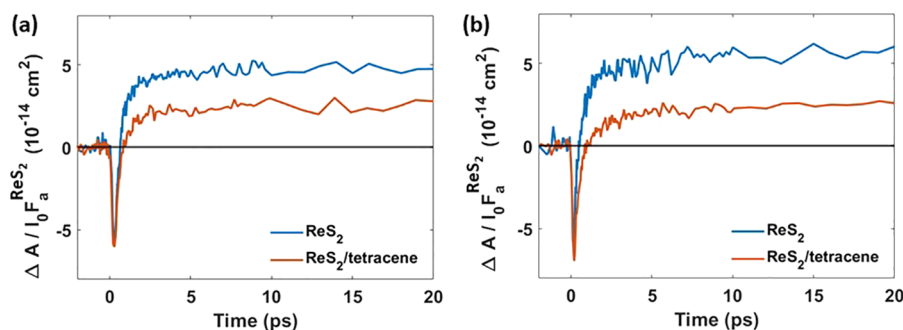


Figure 4. $\Delta A/I_0 F_a^{\text{ReS}_2}$ at the ReS_2 ground state bleach position (830–840 nm) for ReS_2 and ReS_2 /tetracene after (a) 510 nm and (b) 700 nm photoexcitation.

produced in tetracene both due to transfer of excitons and to sequential transfer of electrons and holes from ReS_2 to tetracene. In this work, we do not distinguish these two processes and henceforth refer to them as transfer of photoexcited states to tetracene. The ReS_2 /tetracene bilayer was photoexcited at 510 nm (above the band gap of tetracene) and at 700 nm (below the band gap of tetracene). The pump laser entered the ReS_2 /tetracene bilayer from the side of tetracene. We first discuss the data obtained at 510 nm from which we infer transfer of photoexcited states from ReS_2 to triplet states in tetracene. The 700 nm photoexcitation data corroborate this mechanism of triplet generation in tetracene after photoexcitation of ReS_2 .

Since pump laser light of 510 nm is absorbed both by tetracene and ReS_2 , it leads to the initial formation of both singlets in tetracene and photoexcited states in ReS_2 . Using the data in Figure 1, we calculated the number of photons absorbed per unit area in tetracene ($I_0 F_a^{\text{tet}}$) and ReS_2 ($I_0 F_a^{\text{ReS}_2}$) separately and determined the corresponding $\Delta A/I_0 F_a$, which is directly proportional to the quantum yield, ϕ , of excitons probed at a particular wavelength, see eq 1. Details of the calculations can be found in Section S7 of the SI. Figure 3(a) shows that the SE bleach (580–600 nm) due to singlets in tetracene is identical in both tetracene and the bilayer. This indicates that initially hot photoexcited states at 510 nm in ReS_2 (well-above the exciton energy of 1.5 eV) relax quickly to lower energies in ReS_2 , preventing the significant transfer of hot electron–hole pairs to singlet states in tetracene. It can be seen in Figure S3, SI, that the time-resolved PIA at 495–500 nm due to singlet excitons (we can ascribe the fast decay to singlets in tetracene)⁴² in tetracene is similar for tetracene and the ReS_2 /tetracene bilayer. This corroborates the absence of

production of singlets in tetracene from hot photoexcited states in ReS_2 .

Interestingly, Figure 3b shows that $\Delta A/I_0 F_a^{\text{tet}}$ at 530–545 nm due to both SE and GSB from singlets and triplets in tetracene is higher for the ReS_2 /tetracene bilayer than for tetracene only. We attribute this difference to the transfer of photoexcited states from ReS_2 to triplets in tetracene. Note that pure ReS_2 does not have any significant signal in this wavelength region, as shown in Figure S4, SI. Using the magnitudes of $\Delta A/I_0 F_a^{\text{tet}}$ for tetracene and the bilayer, the efficiency of photoexcited state transfer from ReS_2 to triplets in tetracene was calculated to be $38 \pm 13\%$, assuming a triplet yield of 1.5⁴³ (for details see Section S7 in the SI). We also monitored the time-dependent population of triplets in tetracene via the PIA at 720–765 nm (see Figure S3, SI). The magnitude of $\Delta A/I_0 F_a^{\text{tet}}$ is higher (with a rise until 5 ps) for the bilayer than for tetracene, which further substantiates photoexcited state transfer from ReS_2 to triplets in tetracene. The absence of decay of the PIA on the 2 ns time scale in Figure S3, SI, agrees with the much longer triplet lifetime of ~ 100 ns.^{39,40}

The TA kinetics at the ReS_2 ground state bleach position (830–840 nm) further corroborates the transfer of photoexcited states from ReS_2 to triplets in tetracene. The TA spectrum of pure ReS_2 (Figure S5, SI) upon 510 nm photoexcitation exhibits bleach (negative ΔA) around 835 nm at early time delays, due to ground state bleach. The bleach signal recovers fast and changes into PIA due to charge carriers in ReS_2 .⁴⁴ As shown in Figure 4a, the $\Delta A/I_0 F_a^{\text{ReS}_2}$ at a short time (< 1 ps) (see Figure S5, SI), due to photoexcited states in ReS_2 , is similar for the ReS_2 film and the ReS_2 /tetracene bilayer. Interestingly, the PIA on longer times due to photoexcited states in ReS_2 (see Figure 4a) is lowest for the bilayer (by $57 \pm 13\%$). This is an additional indication of

transfer of photoexcited states from ReS₂ to long-lived triplets in tetracene.

Now we consider selective photoexcitation of ReS₂ at 700 nm. Figure 4b shows that PIA at 830–840 nm due to photoexcited states in ReS₂ is reduced in the bilayer by $51 \pm 15\%$, which we attribute to transfer of photoexcited states from ReS₂ to tetracene, in agreement with the results for 510 nm photoexcitation in Figure 4a. Moreover, Figure S6 shows that the PIA at 720–765 nm due to triplets in tetracene increases during the first 5 ps and persists longer than 2 ns, in agreement with the much longer triplet lifetime of ~ 100 ns.^{39,40}

In conclusion, we have shown transfer of photoexcited states from a solution-processed ReS₂ layer to tetracene on a time scale of 5 ps. This is orders of magnitude faster than triplet transfer from semiconductor nanocrystals or perovskite to organic molecules. This opens up the possibility of triplet–triplet annihilation upconversion in organic materials upon light absorption in inorganic TMDCs. Future research is needed to increase the efficiency of the transfer of photoexcited states by improving the electronic coupling between the TMDC layer and the organic material.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpclett.1c01411>.

Characterization of ReS₂, additional TA data, and transfer efficiency calculations (PDF)

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Notes

The authors declare no competing financial interest.

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