

## Supporting Information

### Generating Triplets in Organic Semiconductor Tetracene upon Photoexcitation of Transition Metal Dichalcogenide ReS<sub>2</sub>

Sourav Maiti<sup>§</sup>, Deepika Poonia<sup>§</sup>, Pieter Schiettecatte,<sup>†,‡</sup> Zeger Hens<sup>†,‡</sup>, Pieter Geiregat<sup>†,‡</sup> Sachin Kinge<sup>§,#</sup>, Laurens D.A. Siebbeles<sup>§</sup>

<sup>§</sup>*Optoelectronic Materials Section, Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, Delft, 2629 HZ, The Netherlands*

<sup>†</sup>*Physics and Chemistry of Nanostructures, Ghent University, Ghent, Belgium*

<sup>‡</sup>*Center for Nano and Biophotonics, Ghent University, Ghent, Belgium*

<sup>#</sup>*Toyota Motor Europe, Materials Research & Development, Hoge Wei 33, B-1913, Zaventem, Belgium*

Corresponding Authors: Sourav Maiti and Laurens D.A. Siebbeles

emails: [s.maiti@tudelft.nl](mailto:s.maiti@tudelft.nl), [l.d.a.siebbeles@tudelft.nl](mailto:l.d.a.siebbeles@tudelft.nl)

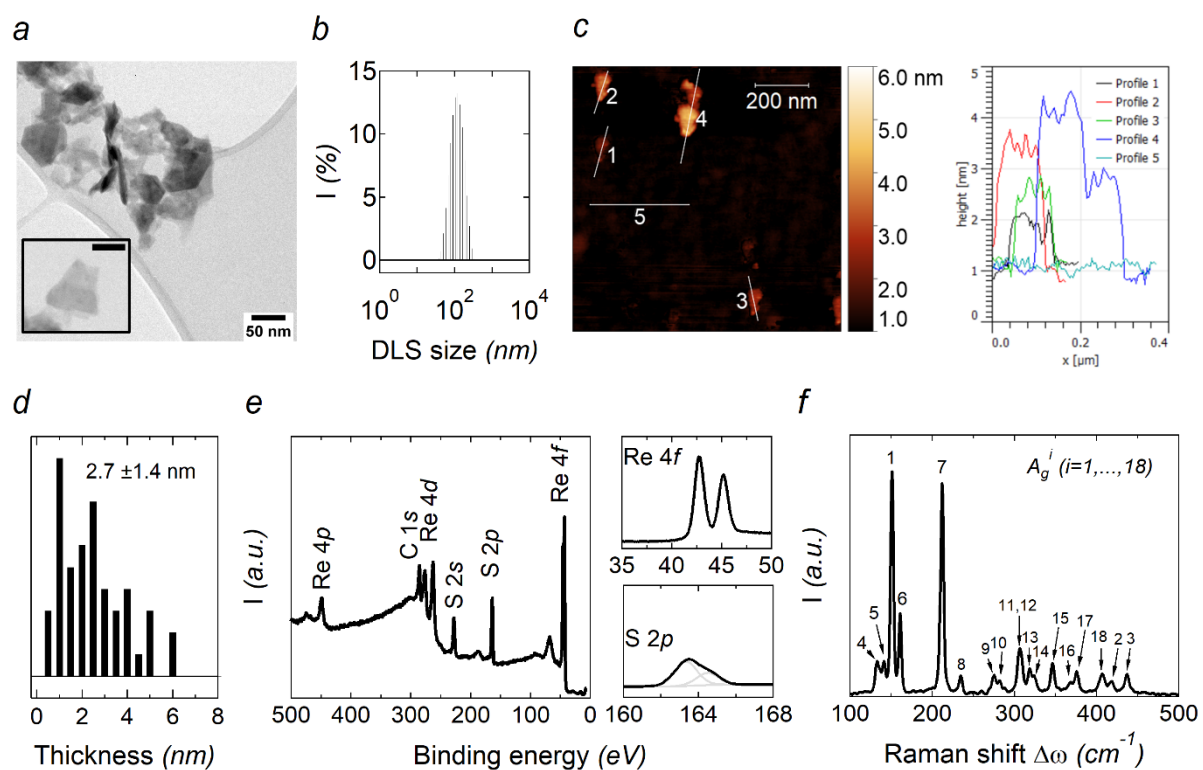


Figure S1. Overview of the material characteristics of liquid-phase exfoliated rhenium disulfide. (a) TEM image. (b) DLS size distribution. (c) AFM images together with extracted line profiles. (d) AFM histogram. (e) XPS survey spectrum together with high-resolution XPS spectra of the Re 4f and S 2p core levels. (f) Raman spectrum with the  $A_g^i$  ( $i=1, \dots, 18$ ) modes of  $\text{ReS}_2$  labeled according to the literature.<sup>1</sup>

Characterization of liquid-phase exfoliated rhenium disulfide. We exfoliated  $\text{ReS}_2$  in *N*-methyl-2-pyrrolidone (NMP) following a procedure detailed in our previous work.<sup>2</sup> Transmission electron microscopy (TEM, Figure S1a) reveals thin  $\text{ReS}_2$  flakes with lateral dimensions of a few tens to a hundred nanometer. Dynamic light scattering (DLS, Figure S1b) corroborates this result by showing a monomodal particle size distribution centered around 106 nm, a value corresponding to an estimated lateral size of  $\approx 75$  nm according to the DLS sizing curves for two-dimensional materials proposed by the Coleman group.<sup>3</sup> Thickness measurements by atomic force microscopy (AFM, Figure S1c) indicate that the flakes are

typically a few nanometers thick, corresponding to a layer number of  $\approx 4 \pm 2$  ReS<sub>2</sub> layers (see AFM histogram, Figure S1d). X-ray photoelectron spectroscopy (XPS, Figure S1f) emphasizes that the flakes are stoichiometric and oxide-free. This result is supported by Raman spectroscopy (Figure S1g) that only shows the 18 characteristic vibrations of ReS<sub>2</sub><sup>1</sup>. We refer the reader to our previous work for a more elaborate description.<sup>2</sup>

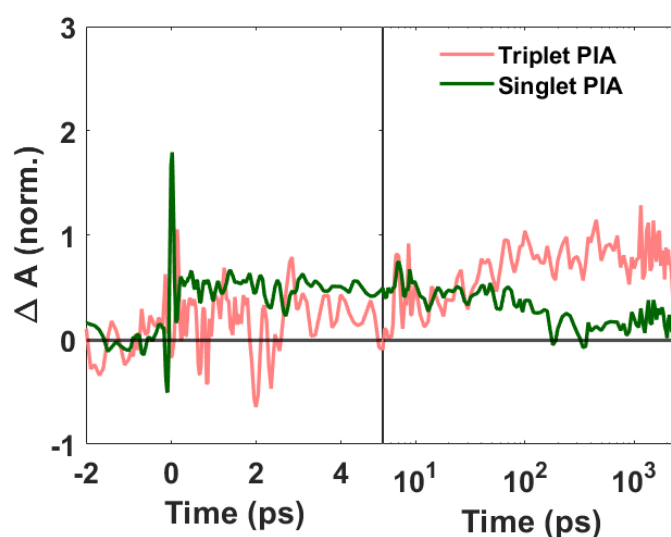


Figure S2. Tetracene photoinduced absorption (PIA) kinetics (normalized to maxima at a short time) in the range 650-665 nm (singlet PIA) and 780-820 nm (triplet PIA, also shown in Figure 2(b) of main text).

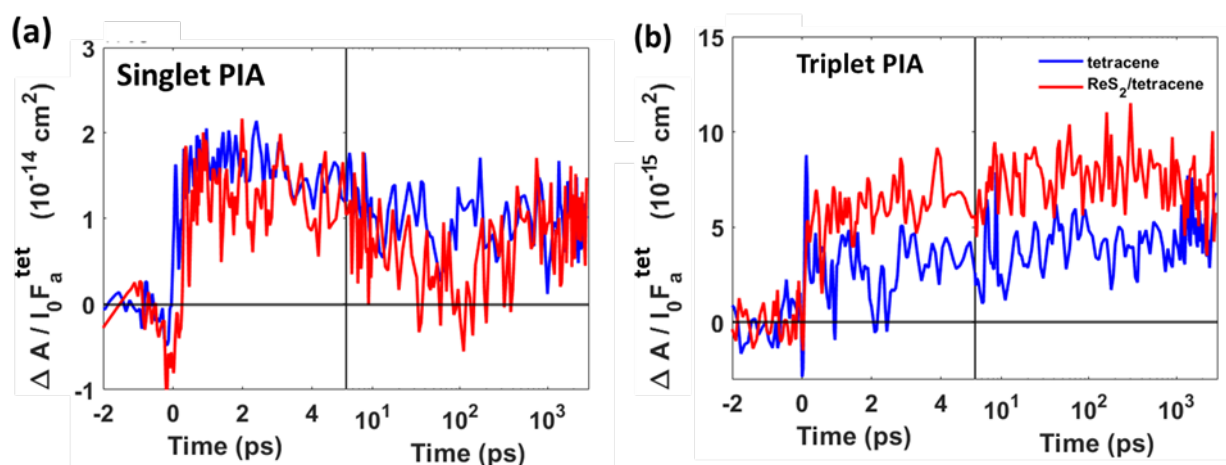


Figure S3. Comparison of time-dependent TA for the tetracene film and the ReS<sub>2</sub>/tetracene bilayer due to (a) absorption by singlets in tetracene (495-500 nm) and (b) triplets in tetracene (720-765 nm).

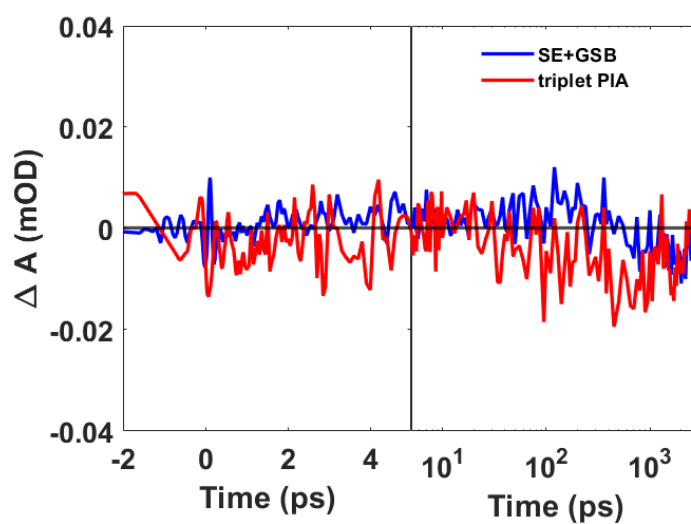


Figure S4.  $\Delta A$  for the ReS<sub>2</sub> film at wavelengths where tetracene exhibits ground state bleach and stimulated emission (530-545 nm) or triplet photoinduced absorption (PIA at 720-765 nm) after 510 nm photoexcitation.

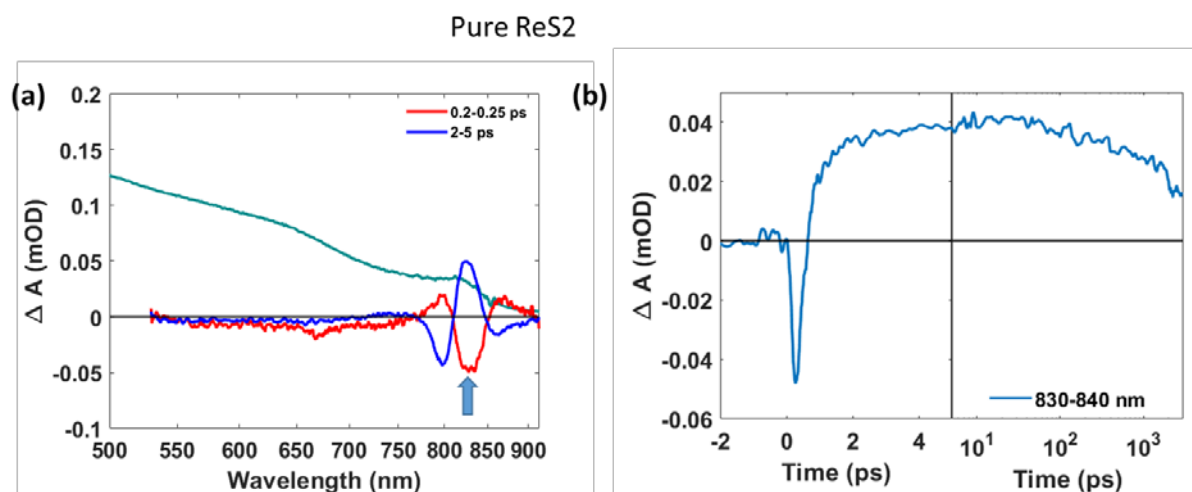


Figure S5. (a) TA spectra (after 510 nm photoexcitation) of the ReS<sub>2</sub> film at 0.20-0.25 ps and 2-5 ps delay time, together with the ground state absorption in dark cyan. (b) Kinetics in the probe region 830-840 nm. At longer delay times (> 2 ps) the TA spectra have a pronounced PIA near 820 nm along with bleach features at shorter and longer wavelengths, which has been attributed to pump-induced shifts and broadening of the optical absorption spectrum.<sup>4</sup>

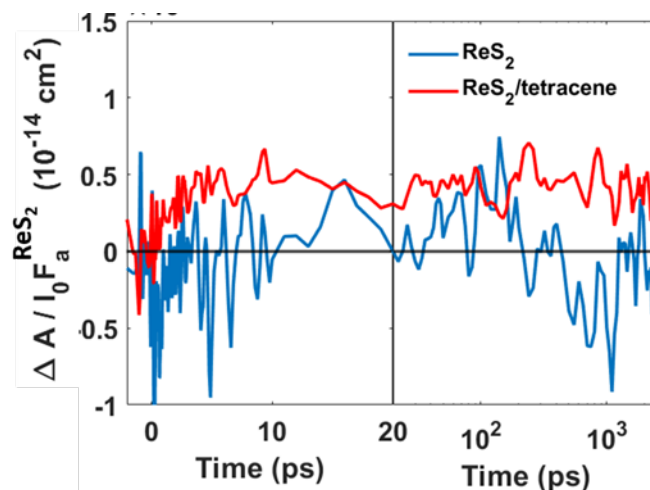


Figure S6.  $\Delta A/I_0 F_a^{ReS_2}$  after 700 nm photoexcitation at tetracene triplet photoinduced absorption (720-765 nm) of the ReS<sub>2</sub> film (blue) and the ReS<sub>2</sub>/tetracene bilayer (red).

### S7: Calculation of exciton transfer efficiency:

**510 nm pump excitation**

For the tetracene/ReS<sub>2</sub> bilayer: photoexcitation through tetracene side

$$I_0 = 1.7 \times 10^{13} \text{ cm}^{-2}$$

In the bilayer,

$$F_a^{tet} = F_a^{total} - F_a^{ReS_2} = 0.31 - 0.14 = 0.17$$

$$I_0 F_a^{tet} = (1.7 \times 10^{13}) \times 0.17 = 2.9 \times 10^{12} \text{ cm}^{-2}$$

$$I_0 F_a^{ReS_2} = (I_0 - I_0 F_a^{tet}) \times F_a^{ReS_2} = (1.4 \times 10^{13}) \times 0.14 = 2 \times 10^{12} \text{ cm}^{-2}$$

**At triplet GSB positon (530-545 nm) position**

For pure tetracene, the GSB between 530-545 nm from 500 ps-3 ns (when all the singlets are converted to triplets)

Using equation 1:  $\frac{|\Delta A|}{I_0 F_a} = \varphi \frac{\sigma_B}{\ln 10}$

$\varphi = 1.5$  for singlet fission.

$\sigma_{GSB}$  is calculated considering the pure tetracene TA data for 510 nm excitation.

$$\sigma_{GSB} = \frac{|\Delta A| \times \ln 10}{\varphi \times I_0 F_a^{tet, pure}}; (\Delta A = 26.9 \pm 2.8 \mu OD)$$

In the bilayer,

$$\Delta A^{Bi} = \Delta A^{tet} + \Delta A^{tr} = \frac{\varphi \sigma_{GSB} I_0 F_a^{tet} + \varphi_{tr} \sigma_{GSB} I_0 F_a^{ReS_2}}{\ln 10}$$

$$\Delta A^{Bi} = 58.5 \pm 4.2 \mu OD$$

$$\varphi_{tr} = 0.38 \pm .13$$

**References:**

- (1) McCreary, A.; Simpson, J. R.; Wang, Y.; Rhodes, D.; Fujisawa, K.; Balicas, L.; Dubey, M.; Crespi, V. H.; Terrones, M.; Hight Walker, A. R. Intricate Resonant Raman Response in Anisotropic Res2. *Nano Lett.* **2017**, *17* (10), 5897-5907.
- (2) Schiettecatte, P.; Rousaki, A.; Vandenabeele, P.; Geiregat, P.; Hens, Z. Liquid-Phase Exfoliation of Rhenium Disulfide by Solubility Parameter Matching. *Langmuir* **2020**, *36* (51), 15493-15500.
- (3) Lotya, M.; Rakovich, A.; Donegan, J. F.; Coleman, J. N. Measuring the Lateral Size of Liquid-Exfoliated Nanosheets with Dynamic Light Scattering. *Nanotechnology* **2013**, *24* (26), 265703.
- (4) Sim, S.; Shin, H.-S.; Lee, D.; Lee, J.; Cha, M.; Lee, K.; Choi, H. Opposite Behavior of Ultrafast Dynamics of Exciton Shift and Linewidth Broadening in Bilayer Res2. *Phys. Rev. B* **2021**, *103* (1), 014309.