

Supplementary Materials for **Highly mobile charge-transfer excitons in two-dimensional WS₂/tetracene heterostructures**

Tong Zhu, Long Yuan, Yan Zhao, Mingwei Zhou, Yan Wan, Jianguo Mei, Libai Huang

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Supplementary Notes

section S1. Physical vapor deposition of tetracene

Tetracene thin film was deposited by thermal evaporation in the glove box at a deposition rate of 2 nm/s under high vacuum ($< 7 \times 10^{-4}$ Pa). The substrate temperature was kept at 290 K.

section S2. AFM

AFM measurements were performed under ambient conditions using a Veeco Dimension 3100 AFM instrument in the tapping mode.

section S3. Microreflection microscopy

In the micro-reflection spectroscopy, the white light from a stabilized tungsten-halogen light source (Thorlabs) was focused on a pinhole with 10 μ m diameter. It was then collimated and focused on the sample with a $50\times$ /NA = 0.95 objective. The beam size of white light is about 3 μ m. The reflected light was collected with the same objective, dispersed with a monochromator (Andor Technology) and detected by a TE cooled charge-coupled device (CCD) (Andor Technology). The differential reflectance is defined as

$$\delta R(\lambda) = \frac{R_{sample} - R_{substrate}}{R_{substrate}} \quad (S1)$$

where R_{sample} is the reflectance intensity of sample with substrate and $R_{substrate}$ is the reflectance intensity of bare substrate.

The absorption coefficient of 1L-WS₂ is determined from the differential reflection spectra. For ultrathin film on transparent substrate, the differential reflection is directly related to the absorption by the following Ref. 30

$$\delta R(\lambda) = \frac{4}{n_{sub}^2 - 1} A(\lambda) \quad (S2)$$

section S4. Factors that limits the spatial precision of TAM imaging

In the TAM imaging of exciton transport, the measured carrier distribution is convoluted with profiles of pump and probe beams, so that the measured carrier distribution could be written as

$$\sigma_{(measurement)}^2 = \sigma_{(exciton)}^2 + \sigma_{(pump)}^2 + \sigma_{(probe)}^2 \quad (S3)$$

The diffusion length of hot carrier propagation is written as

$$L^2 = \sigma_{(t)}^2 - \sigma_{(0)}^2 \quad (S4)$$

Since $\sigma_{(pump)}^2$ and $\sigma_{(probe)}^2$ don't change during pump-probe delay, the diffusion length is only determined by the change of exciton density profiles.

Here we performed a sensitivity analysis by differentiating equation S4 and obtain the error of measured diffusion length written as

$$\Delta L = \sqrt{\frac{\sigma_{(t)}^2}{\sigma_{(t)}^2 - \sigma_{(0)}^2} (\Delta \sigma_{(t)}^2)^2 + \frac{\sigma_{(0)}^2}{\sigma_{(t)}^2 - \sigma_{(0)}^2} (\Delta \sigma_{(0)}^2)^2} = \sqrt{\Delta \sigma_{(t)}^2 + \left(\frac{\sigma_{(0)}}{L}\right)^2 (\Delta \sigma_{(0)}^2 - \Delta \sigma_{(t)}^2)} \quad (S5)$$

From equation (S5), we can clearly see the error mainly comes from the uncertainty of Gaussian profiles obtained at different time delays, which is determined by the signal-to-noise of the TAM system.

section S5. Thickness-dependent energy transfer from Tc to WS₂

We applied a simplified expression from Ref. 39 to fit thickness dependent energy transfer rate from Tc to WS₂. The energy transfer rate Γ_{ET} as a function of the number of layers of WS₂ d is written as

$$\Gamma_{ET} \approx A\eta'' \frac{1+|\eta|^2 e^{-2Cd}}{1-2\text{Re}|\eta|^2 |e^{-2Cd} + |\eta|^4 e^{-4Cd}} \quad (\text{S6})$$

where A and C are constants and are obtained from fitting, η , η' and η'' are related to dielectric constant of WS₂ ε , and are given as, $\eta = \eta' + i\eta''$, $\eta = \frac{|\varepsilon|^2 - 1 + 2i\varepsilon''}{|\varepsilon|^2 + 2\varepsilon' + 1}$, and $\varepsilon = \varepsilon' + i\varepsilon''$.

By using values of the real part ($\varepsilon' = 16.2$) and the imaginary part ($\varepsilon'' = 6.4$) of WS₂ dielectric constant⁴⁰, the dependence of energy transfer rate on WS₂ thickness from 2L to 7L was fitted to extrapolate energy transfer rate from Tc to 1L-WS₂ as described in the main text.

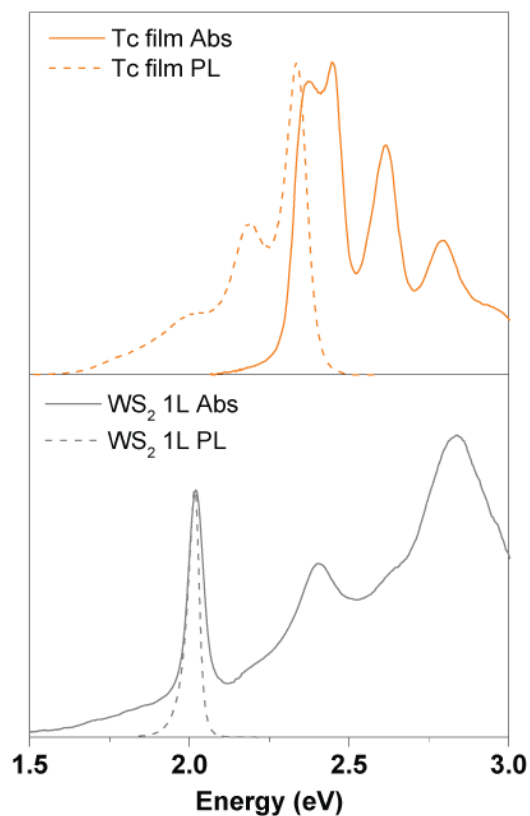


fig. S1. Absorption and PL spectrum of Tc film and 1L-WS₂. From the absorption spectrum, excitation energy at or below 2.1 eV allows for selectively pumping WS₂ without exciting Tc layer. Excitation energy at 3.1 eV allows for exciting both components of the heterstructure. The spectral overlap between Tc emission and WS₂ absorption indicates possibility of energy transfer from Tc to WS₂.

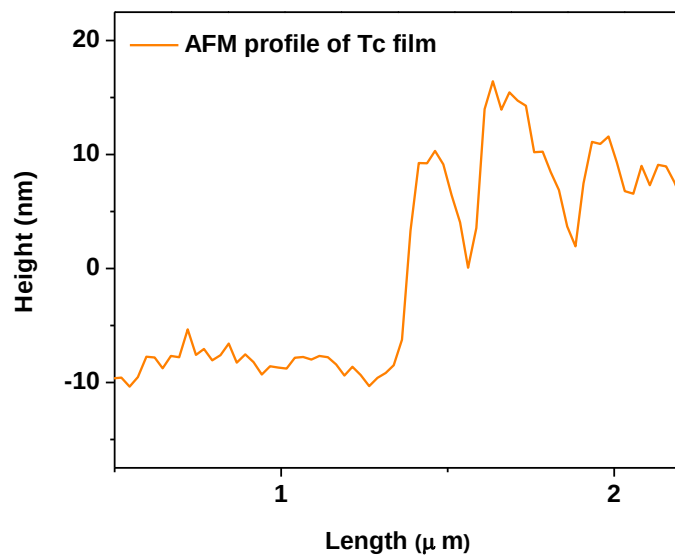


fig. S2. AFM line profile of the Tc film thickness.

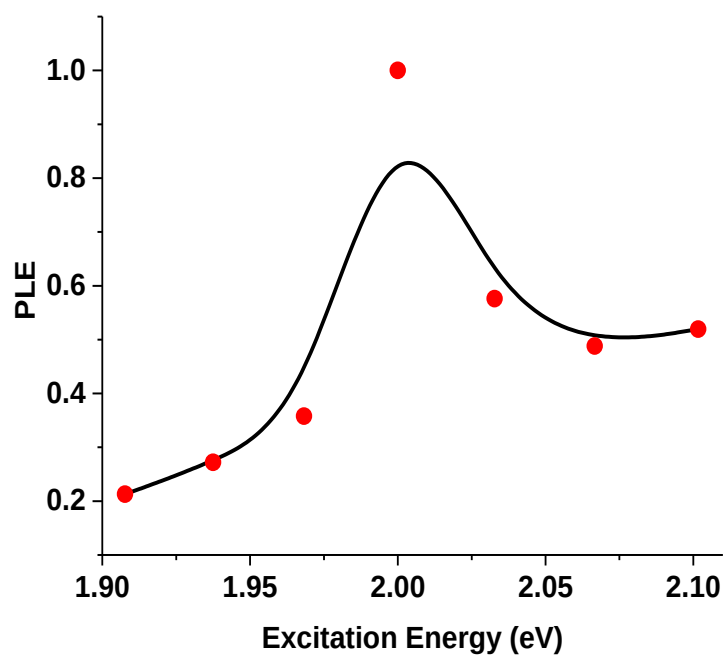


fig. S3. PLE measurements. Photoluminescence excitation (PLE) measurements monitoring CT exciton emission at 1.7 eV.

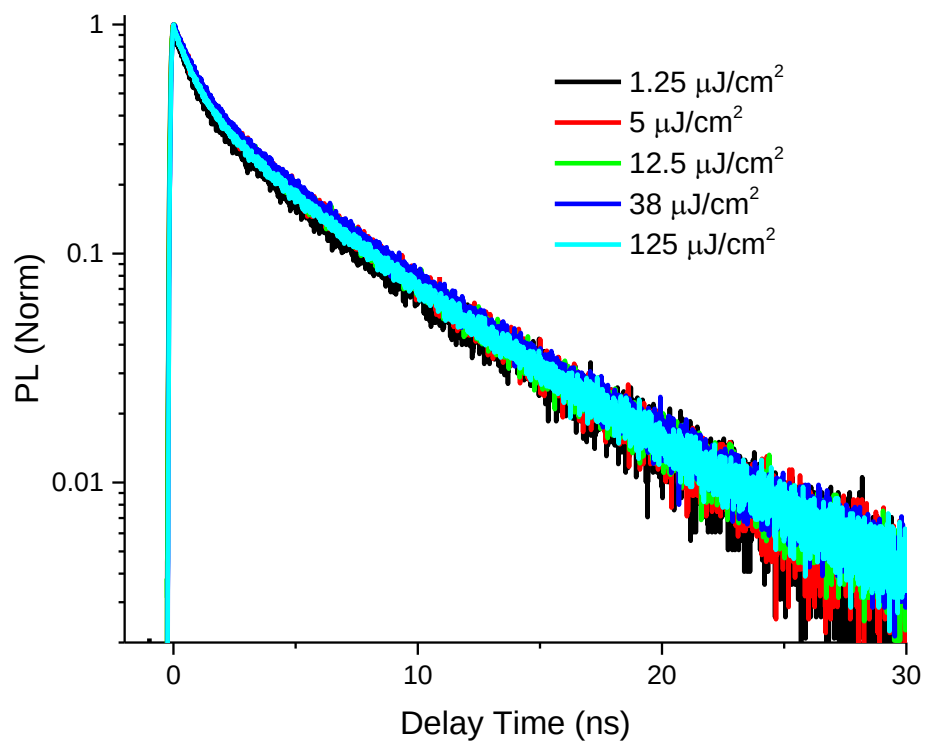


fig. S4. Excitation intensity–dependent measurements of PL dynamics of CT exciton emission. Excitation photon energy: 2.1 eV.

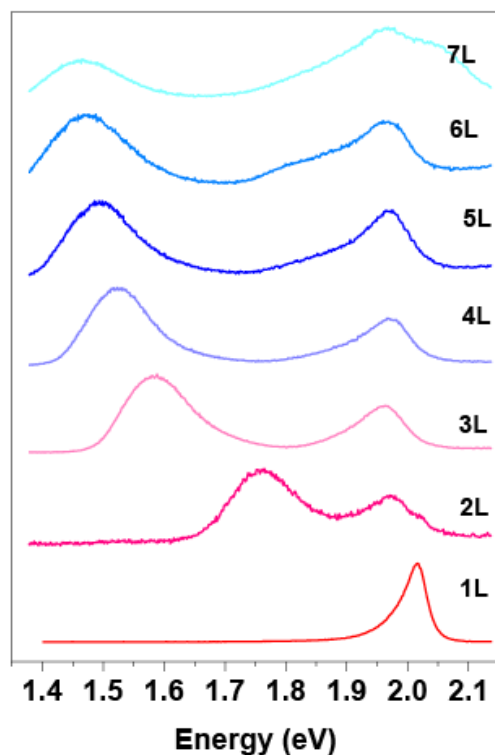


fig. S5. Identification of numbers of WS₂ layers using PL spectroscopy. PL spectrum of WS₂ from 1L to 7L are shown from bottom to top.

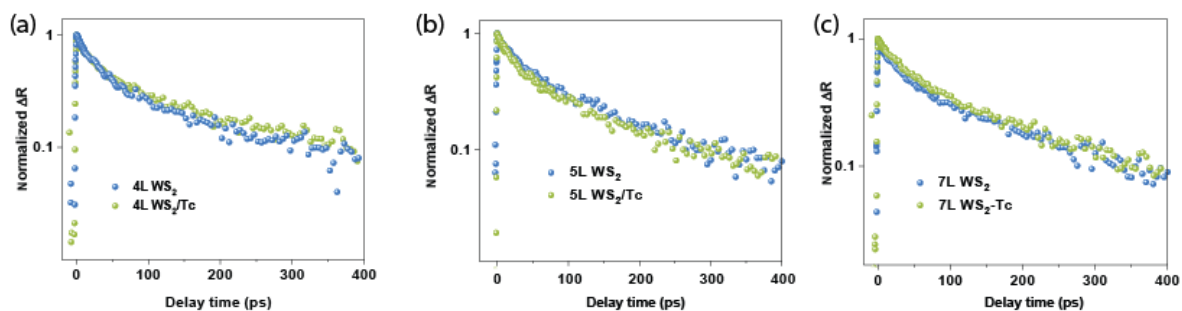


fig. S6. TAM dynamics of 4L to 7L WS₂ before and after Tc deposition. TAM dynamics of 4L (a), 5L (b) and 7L WS₂ (c) before (blue) and after (green) Tc deposition showing no hole transfer in the heterostructures built by thick WS₂ flakes and Tc film. (2.1 eV pump and 2.0 eV probe)

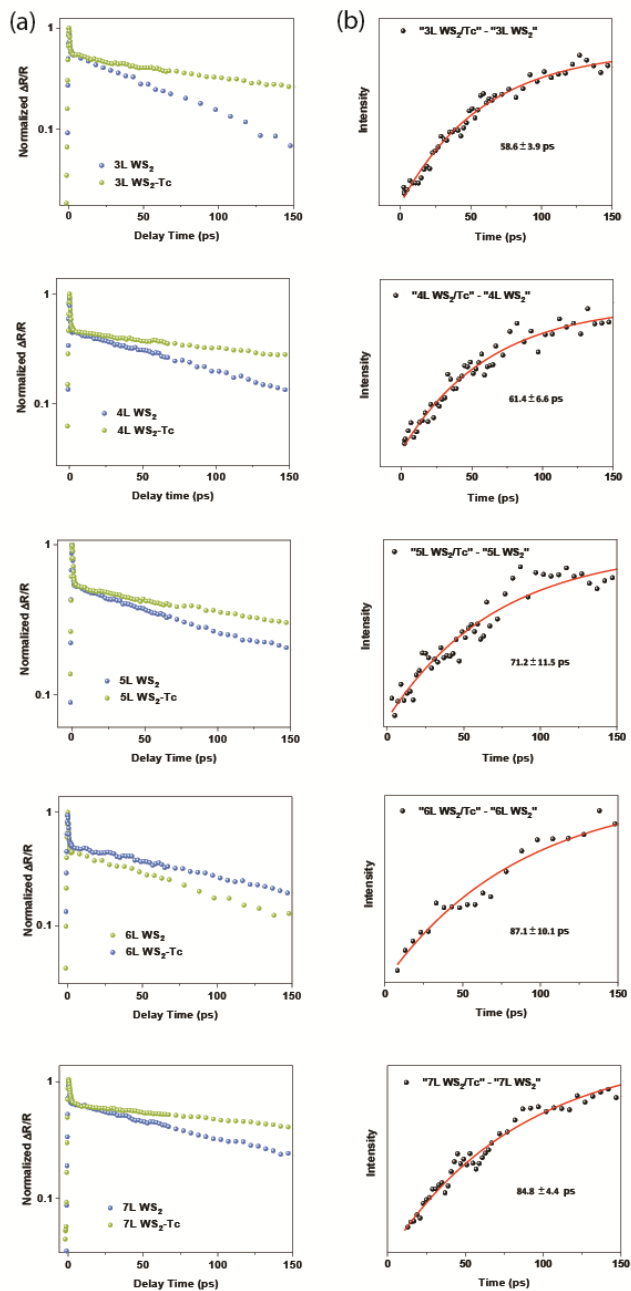


fig. S7. Energy transfer from Tc to WS_2 measured with TAM (3.1-eV pump and 2.0-eV probe). (a) Transient dynamics of 3L-7L WS_2 before (blue) and after (green) Tc deposition. (b) Subtraction of WS_2 dynamics from WS_2/Tc dynamics yielding rising curves fitted with exponential function for each WS_2 thickness, indicating energy transfer time constants.

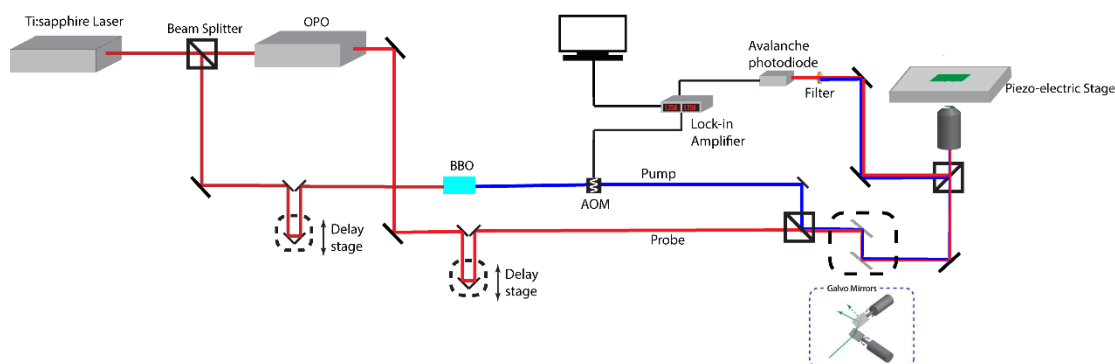
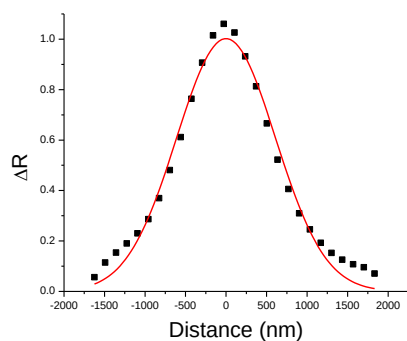


fig. S8. Schematics of the TAM setup. BS: beam splitter; OPO: optical parametric oscillator; AOM: acoustic optical modulator; APD: avalanche photodiode.

a



b

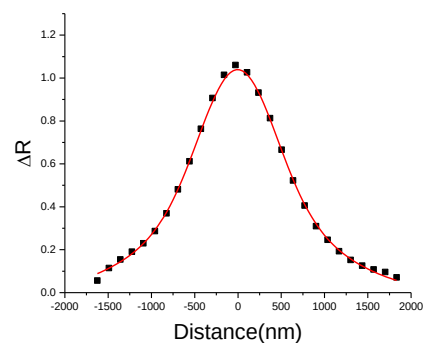


fig. S9. CT exciton population profile fitted with a single Gaussian function and a sum of two Gaussian functions. Exciton population profile at 1 ns delay fitted with a single Gaussian function (a) and a sum of two Gaussian functions (b) as described in the main text for the 1L-WS₂/Tc heterostructure. The pump photon energy is 3.1 eV (pump fluence: 4.4 μJ/cm²) and the probe energy is 2.0 eV

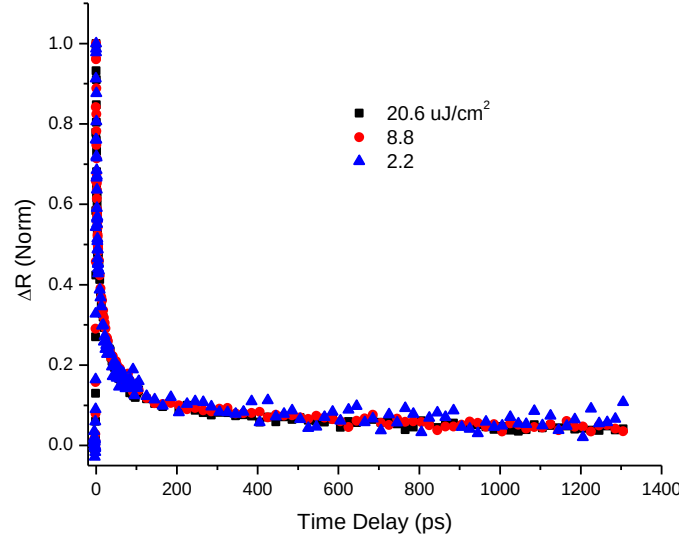


fig. S10. Transient absorption dynamics of a 1L-WS₂/Tc heterostructure measured at different pump fluences.

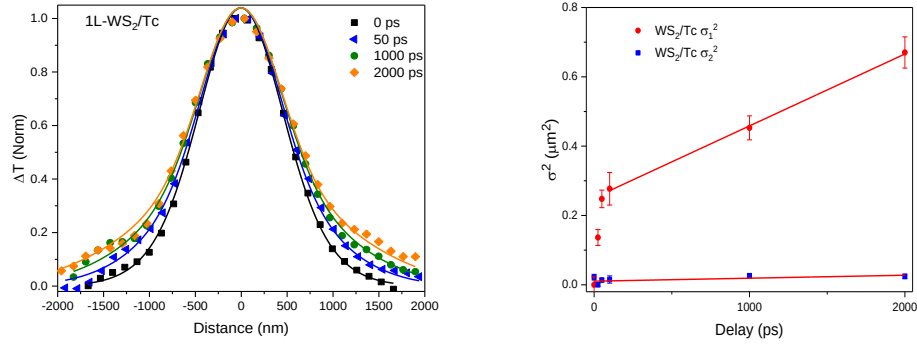


fig. S11. TAM of CT exciton diffusion measured at $10.0 \mu\text{J cm}^{-2}$. TAM exciton population profiles fitted with a sum of two Gaussian functions as described in the main text at different delay times with the maximum ΔR signal normalized to unity for the same 1L-WS₂/Tc heterostructure as shown in Fig.4. The pump photon energy is 3.1 eV (pump fluence: $10.0 \mu\text{J/cm}^2$) and the probe energy is 2.0 eV. $\sigma_{1,t}^2 - \sigma_0^2$ and $\sigma_{2,t}^2 - \sigma_0^2$ as a function of pump-probe delay time, with a linear fit to equation 3 (line) for the 1L-WS₂/Tc heterostructure. $D_1 = 1.0 \pm 0.1 \text{ cm}^2\text{s}^{-1}$ and $D_2 = 0.04 \pm 0.01 \text{ cm}^2\text{s}^{-1}$.

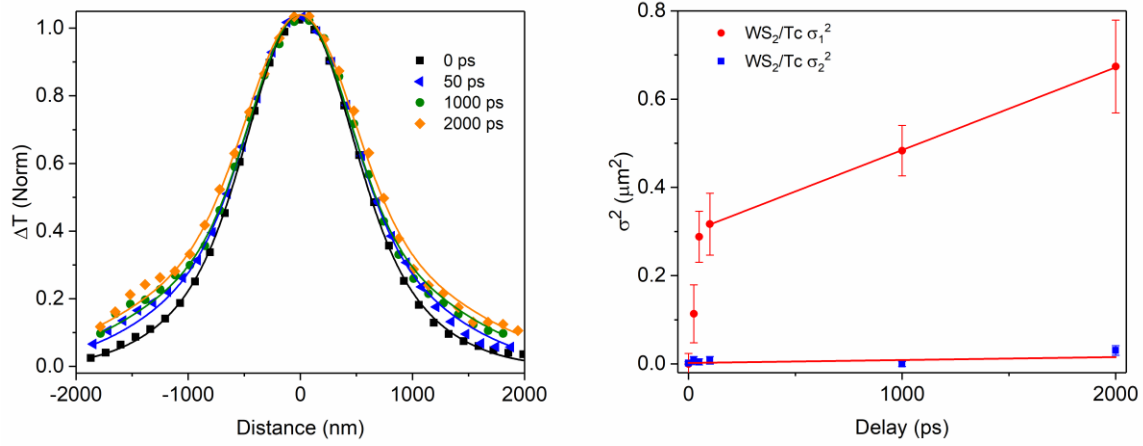


fig. S12. TAM of CT exciton diffusion measured at $20.6 \mu\text{J cm}^{-2}$. TAM exciton population profiles fitted with a sum of two Gaussian functions as described in the main text at different delay times with the maximum ΔR signal normalized to unity for the same 1L- WS_2/Tc heterostructure as shown in Fig.4. The pump photon energy is 3.1 eV (pump fluence: $20.6 \mu\text{J}/\text{cm}^2$) and the probe energy is 2.0 eV. $\sigma_{1,t}^2 - \sigma_0^2$ and $\sigma_{2,t}^2 - \sigma_0^2$ as a function of pump-probe delay time, with a linear fit to equation 3 (line) for the 1L- WS_2/Tc heterostructure. $D_1 = 0.9 \pm 0.1 \text{ cm}^2\text{s}^{-1}$ and $D_2 = 0.03 \pm 0.02 \text{ cm}^2\text{s}^{-1}$.