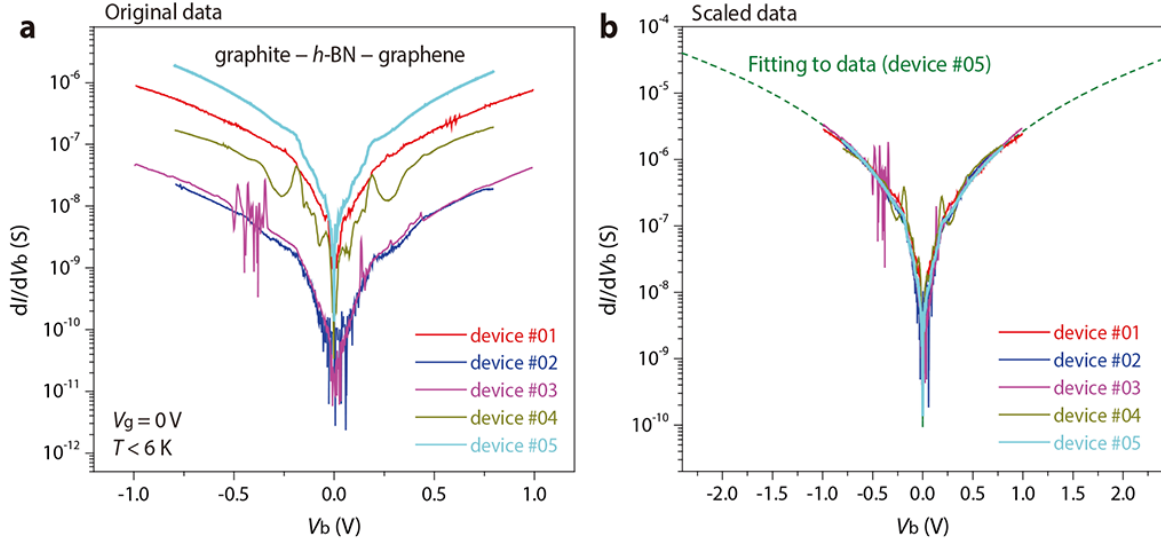


Supplementary Information

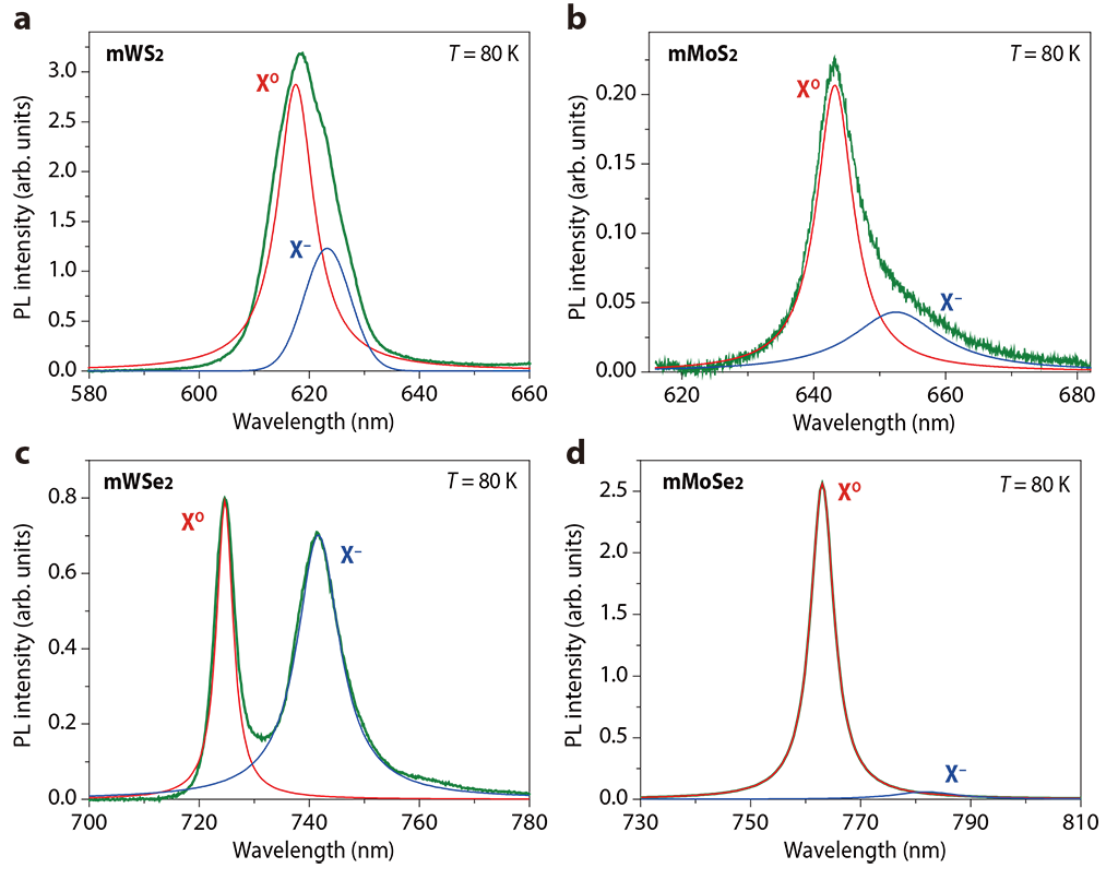
**Spectroscopic studies of atomic defects and bandgap renormalization in  
semiconducting monolayer transition metal dichalcogenides**

**Jeong et al.**

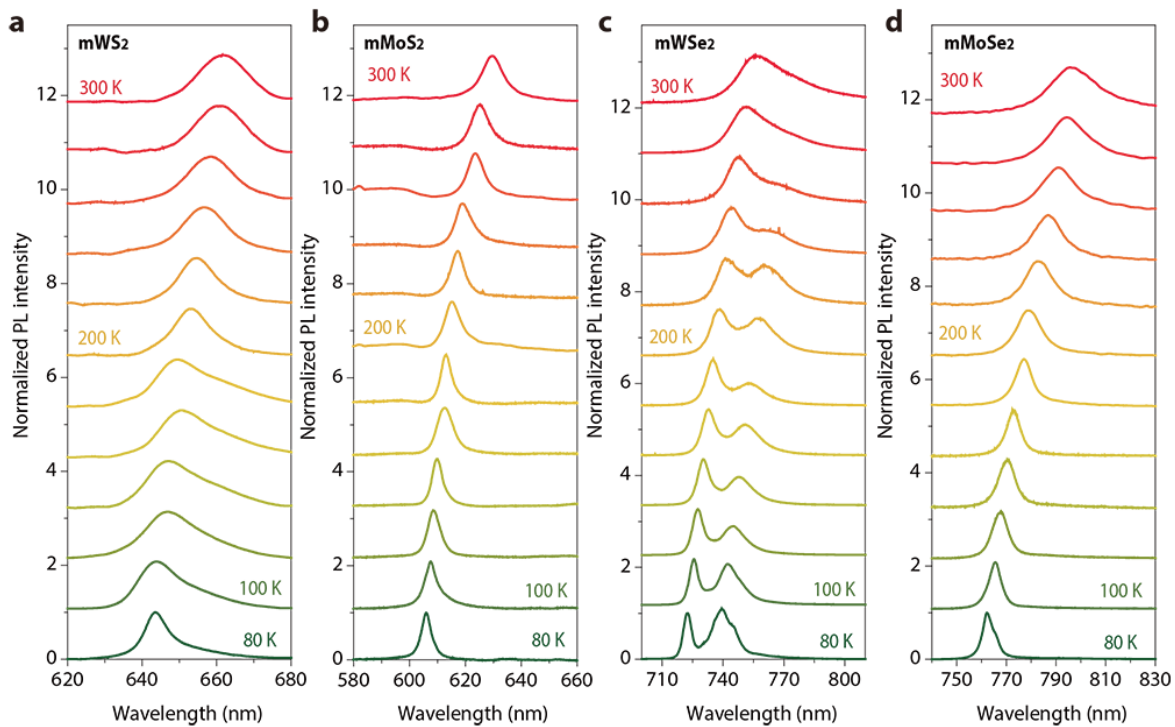
## Supplementary Figures



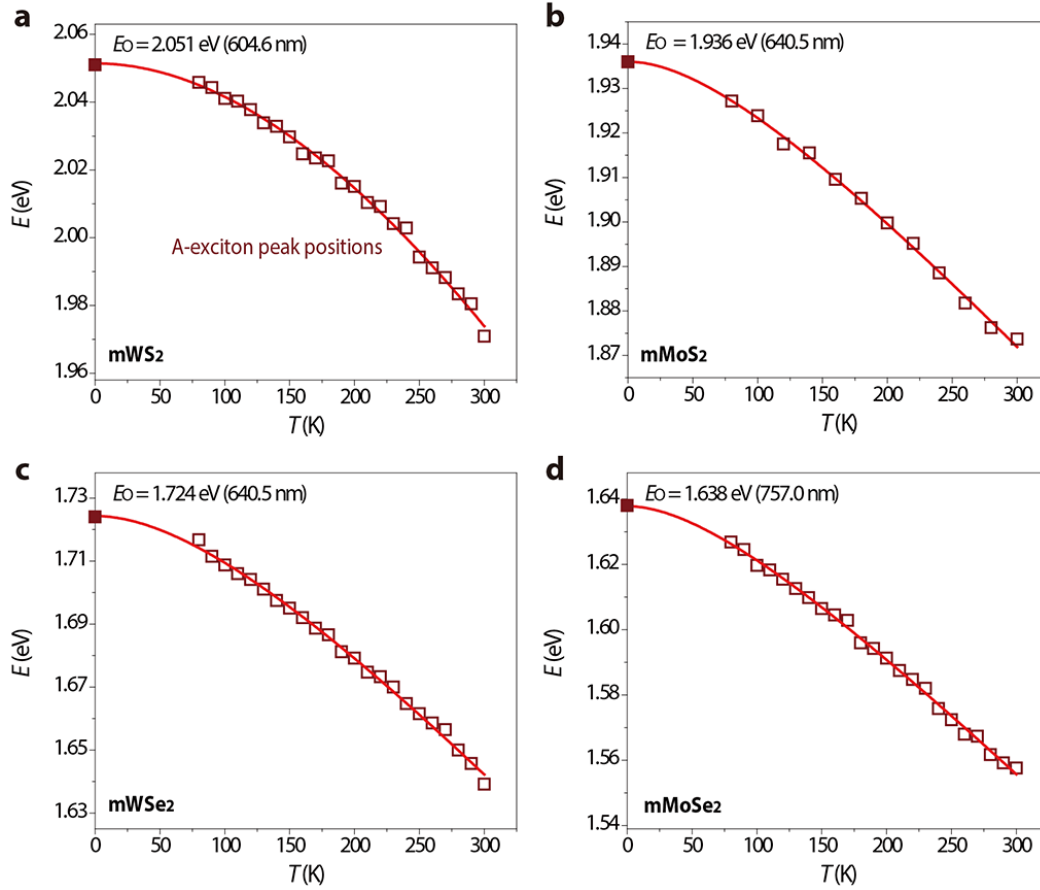
**Supplementary Figure 1. Electron tunneling spectra of graphite-*h*-BN-graphene tunnel junctions.** **a**, Series of  $dI/dV_b$  spectra from multiple planar tunnel junctions of single-layer graphene with graphite as a probe and thin *h*-BN as a tunnel barrier. Dirac points for all graphene tunnel junctions are close to the Fermi level ( $V_b = 0$  mV) at  $V_g = 0$  V.  $V_b$  is applied to the graphite probe and tunnel current is monitored through the graphene layer, in an identical setup as the measurements in the main text. Differences in  $dI/dV_b$  values are ascribed to tunnel *h*-BN layers and tunnel junction area. **b**, Scaled tunneling spectra adjusted with  $dI/dV_b$  multiplication constants to overlay with the  $dI/dV_b$  of device #05 (solid cyan line). Dotted green lines represent numerical fittings to the experimental data of device #05, requiring different fitting parameters for positive and negative  $V_b$  regions, which exhibit the electron-hole asymmetric electronic structures of the graphite-*h*-BN-graphene planar tunnel junctions. This fitting data, referred to as the graphene baseline, is used to analyze the electron tunneling spectra of the SC-mTMD-based planar junctions in the main text.



**Supplementary Figure 2. Photoluminescence (PL) measurements of the SC-mTMD films.** PL spectra displaying A-exciton peaks of the mWS<sub>2</sub> (a), mMoS<sub>2</sub> (b), mWSe<sub>2</sub> (c), and mMoSe<sub>2</sub> (d) films at  $T = 80$  K. PL signals are collected right at the junction where the respective films are encapsulated by *h*-BN, graphite, and graphene layers in the planar tunnel junction platform. Pump light, CW Nd:YAG laser centered at 532 nm, is vertically shone onto the flakes through a  $\times 50$  objective lens, and PL signals are collected through the same objective lens and analyzed with a liquid-nitrogen cooled Si CCD detector with 550 nm long pass filter. The positions of the A-exciton ( $X^0$ ) peaks are determined by Lorentzian fittings with consideration of nearby charged excitons ( $X^-$ ).



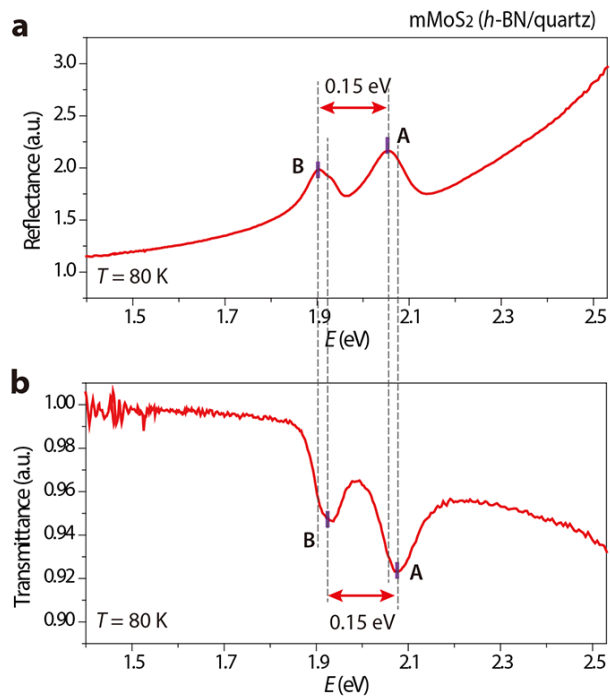
**Supplementary Figure 3. Temperature-dependent PL measurements of the SC-mTMD films.** Normalized PL spectra of mWS<sub>2</sub> (a), mMoS<sub>2</sub> (b), mWSe<sub>2</sub> (c), and mMoSe<sub>2</sub> (d) measured in the temperature range  $80 \text{ K} \leq T \leq 300 \text{ K}$ . Each spectrum is normalized to the maximum PL intensity. Moderate blue-shifts of the A-exciton peaks are universal in all four films.



**Supplementary Figure 4. Extracting the optical energy gaps of the SC-mTMD films.** a–d Series of A-exciton peaks of the respective SC-mTMD films measured in the temperature range  $80 \text{ K} \leq T \leq 300 \text{ K}$ . Continuous blue-shift of the A-exciton peaks with decreasing temperature allows for the extraction of the intrinsic optical energy gaps of the films by following the peak positions to  $T = 0 \text{ K}$ , utilizing the Varshni relation that explains the temperature dependence of semiconductor energy gaps:

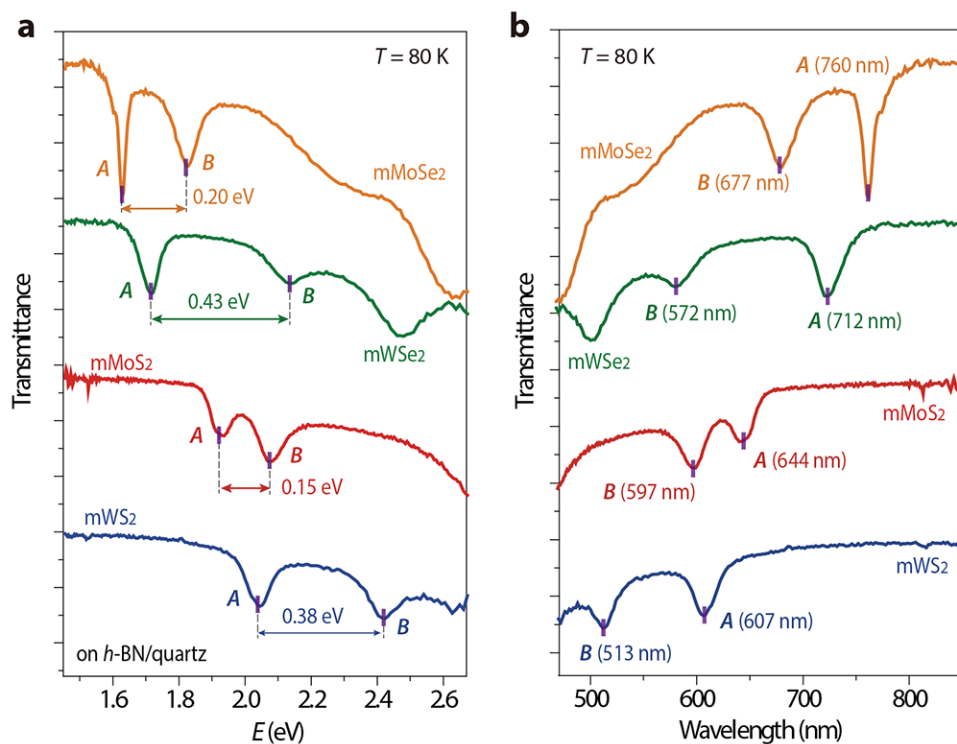
$$E_g(T) = E_o - \frac{\alpha T^2}{T + \beta},$$

where  $E_o$  is the energy gap at  $T = 0 \text{ K}$  and  $\alpha$  and  $\beta$  are material-dependent fitting parameters.

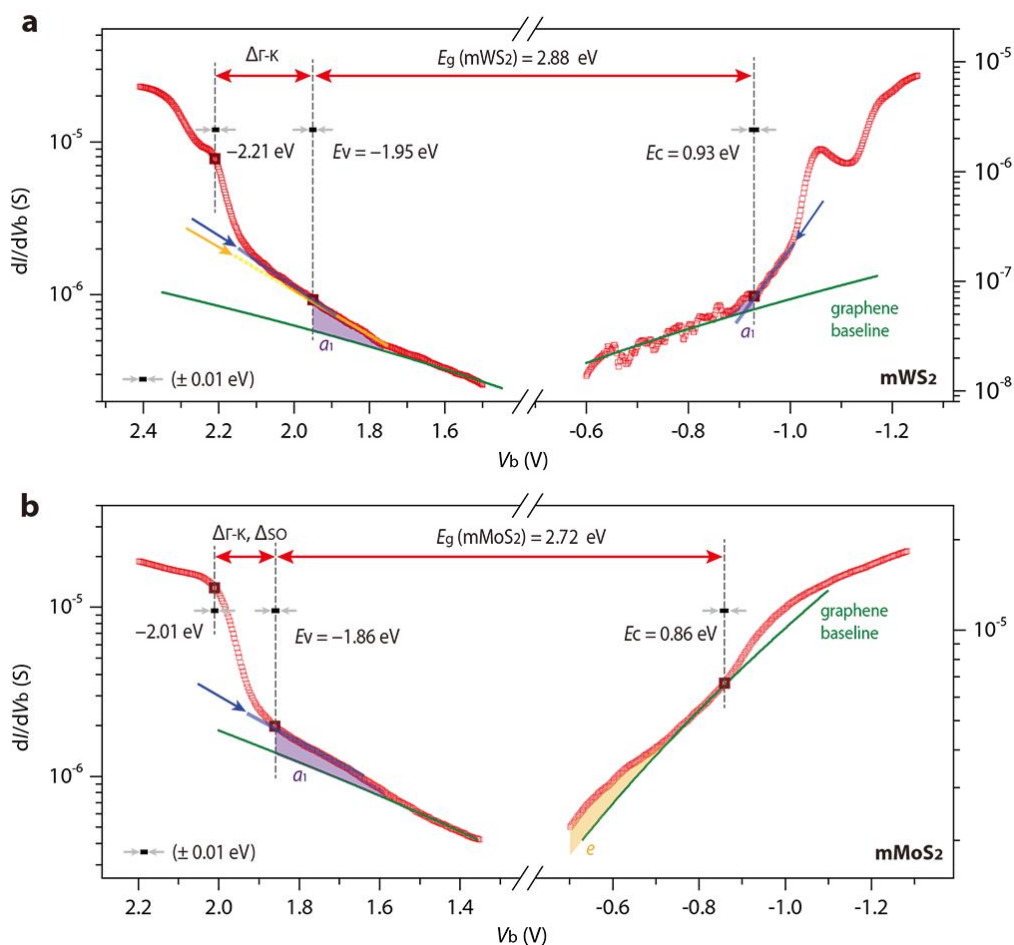


**Supplementary Figure 5. Optical reflectance and transmittance measurements of mMoS<sub>2</sub>.**

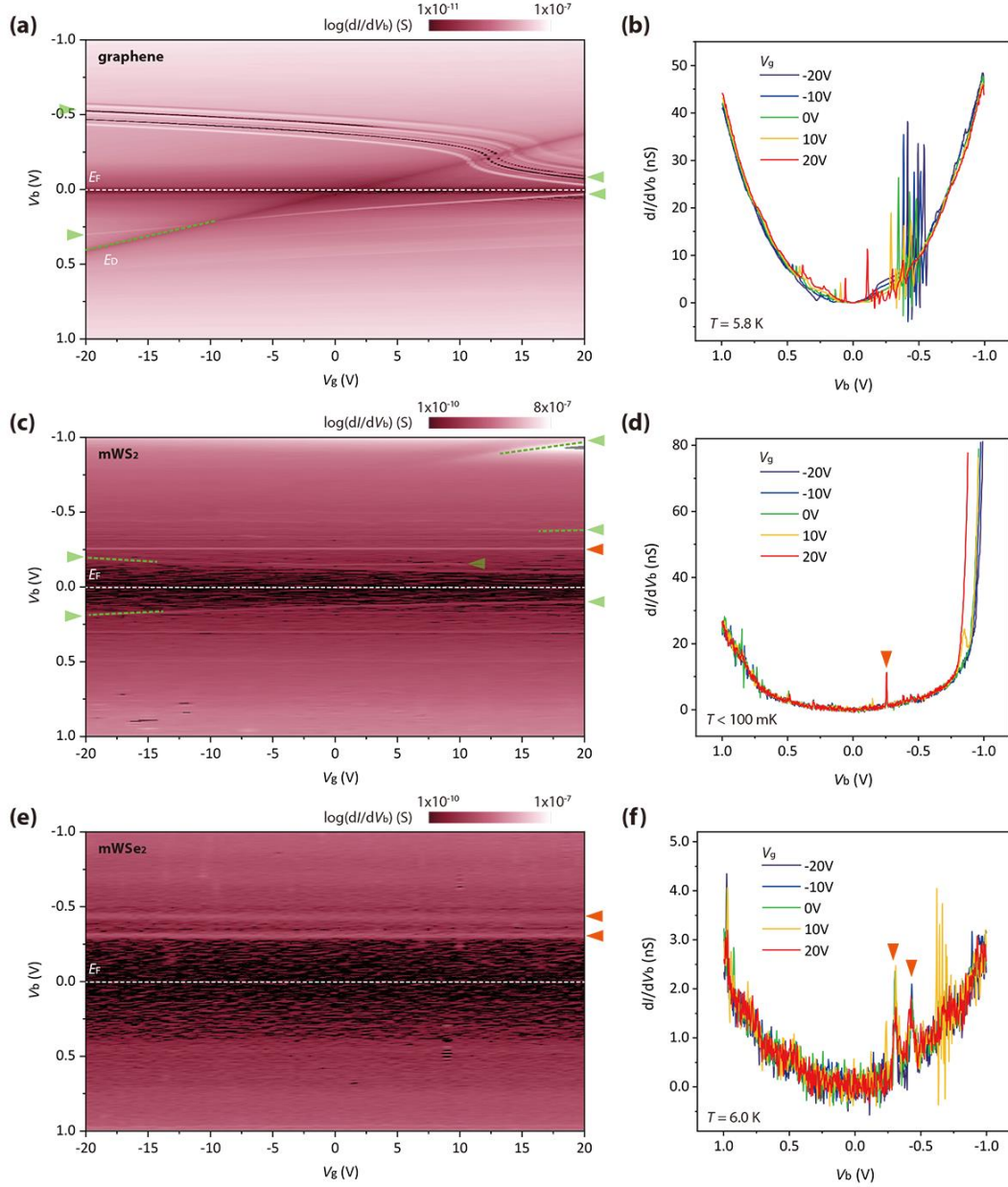
Optical reflectance (a) and transmittance (b) spectra of mMoS<sub>2</sub> film at  $T = 80$  K. The film is transferred onto thick *h*-BN layers and then placed on a transparent quartz substrate. For reflectance and transmittance measurements, supercontinuum white source (NKT SuperK COMPACT supercontinuum lasers) is vertically shone onto the mMoS<sub>2</sub> film, mounted in a liquid nitrogen-cooled cryostat. Both optical measurements clearly show signals relating to the A and B excitons of the mMoS<sub>2</sub> film. The A–B exciton spacing, thereby spin-orbit coupling (SOC) induced valence band splitting of the mMoS<sub>2</sub>, is estimated to be  $\Delta_{\text{SO}}(\text{mMoS}_2) = 0.15 \pm 0.01$  eV. Note that individual exciton peak (a) and dip (b) positions in the reflectance and transmittance optical spectra are slightly off, attributed to different physical mechanisms in optical measurements.



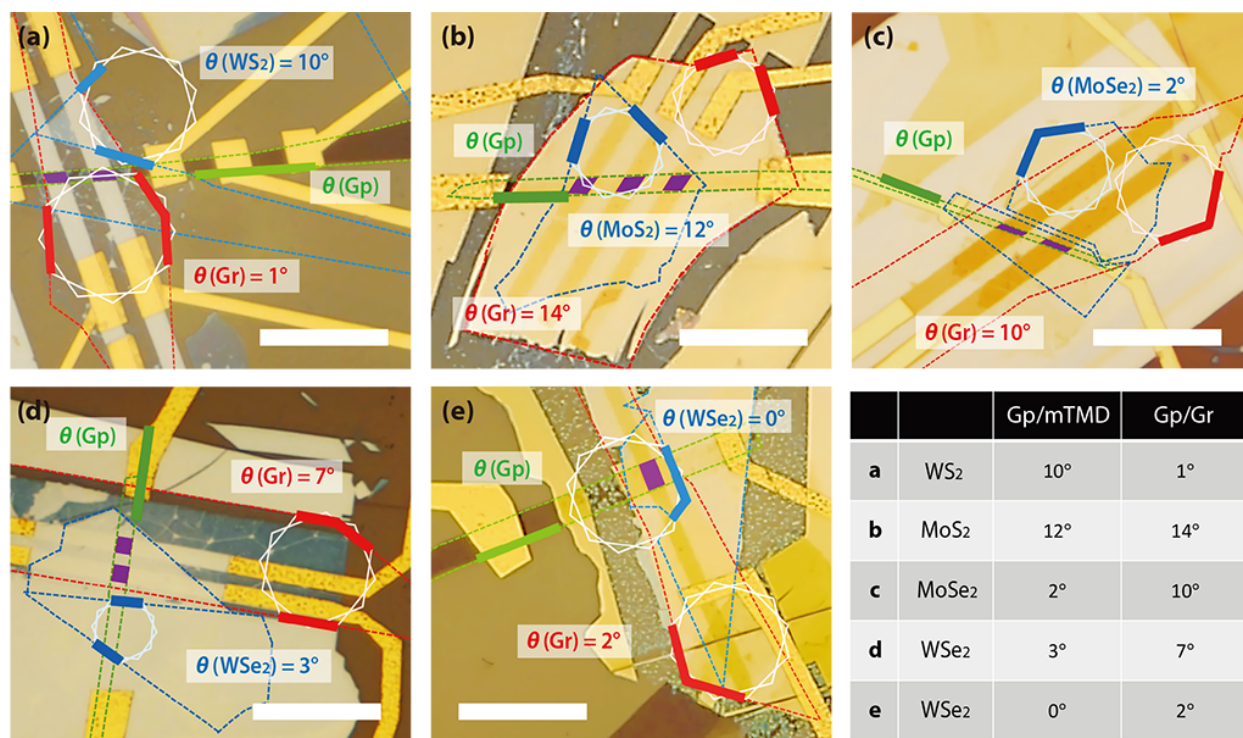
**Supplementary Figure 6. A–B exciton spacing in SC-mTMD films.** Series of optical transmittance spectra of the four respective films at  $T = 80$  K, fabricated onto  $h$ -BN layers and a transparent quartz substrate at varying energy (a) and wavelength (b). The clearly resolved A–B excitonic peak spacings allow us to determine the SOC-induced valence-band splittings in all four films at high accuracy with an uncertainty level of less than  $\pm 0.01$  eV. Individual peak positions are extracted from numerical fittings to Lorentzian functions with baseline subtractions.



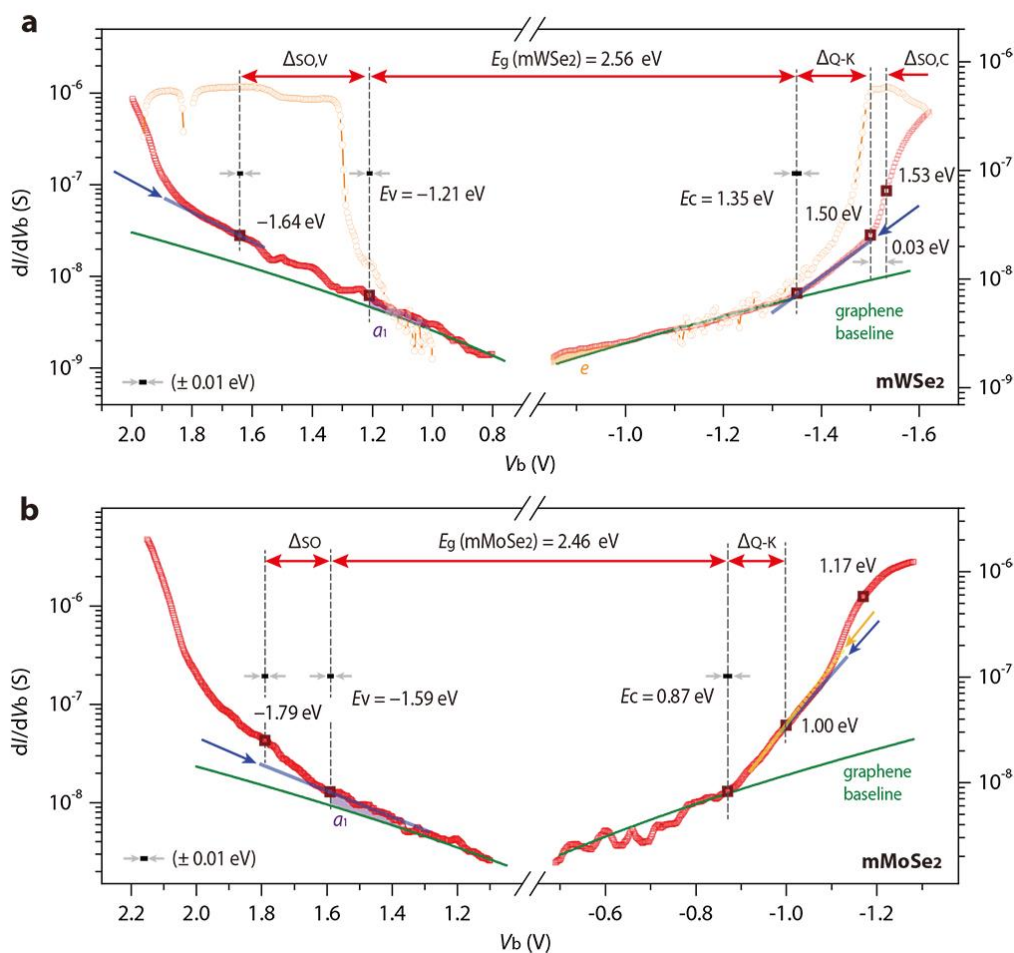
**Supplementary Figure 7. Detailed electronic structure analyses of mWS<sub>2</sub> and mMoS<sub>2</sub> films.**  $dI/dV_b$  tunneling spectra focused around the valence- and conduction-band edges of S-based mTMD films mWS<sub>2</sub> (a) and mMoS<sub>2</sub> (b). Valence band edges (the higher SOC-split band edge at the K point) are located based on the optically addressed *A–B* exciton spacings (Supplementary Figure 6) and eminent  $dI/dV_b$  features as marked with open brown squares. Conduction band edges are similarly located where the graphene baseline (green lines) and  $dI/dV_b$  spectra start deviating.



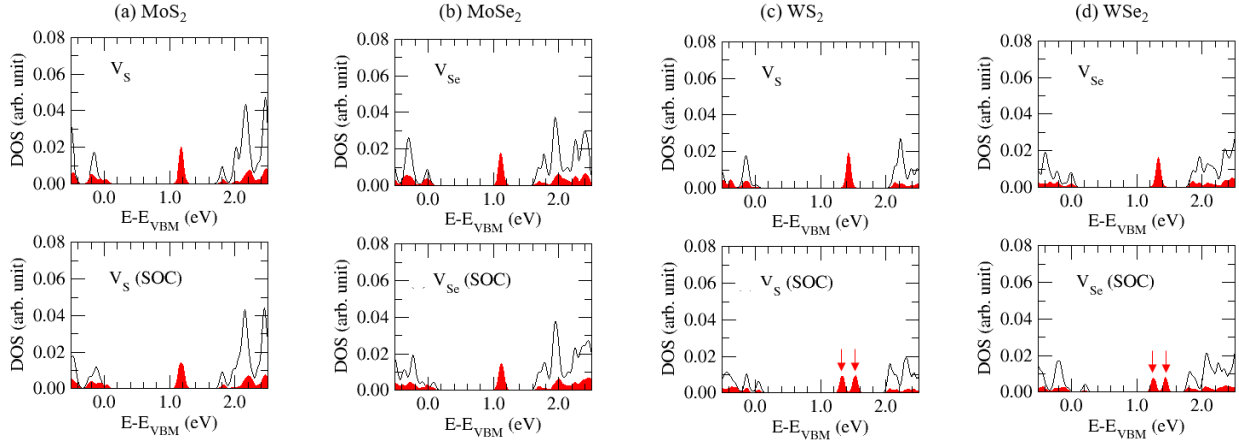
**Supplementary Figure 8. Gate mappings and individual tunnel spectra for different tunnel junctions.** Two-dimensional display of  $dI/dV_b$  curves at varying  $V_b$  and  $V_g$  for graphene (a), mWS<sub>2</sub> (c), mWSe<sub>2</sub> (e) based planar heterojunctions with a graphite as a tunnel probe and a thin *h*-BN as a tunnel insulator. The collections of individual  $dI/dV_b$  spectra at varying  $V_g$  are shown in (b) for the graphene, (d) for the mWS<sub>2</sub>, and (f) for the mWSe<sub>2</sub> planar junctions.



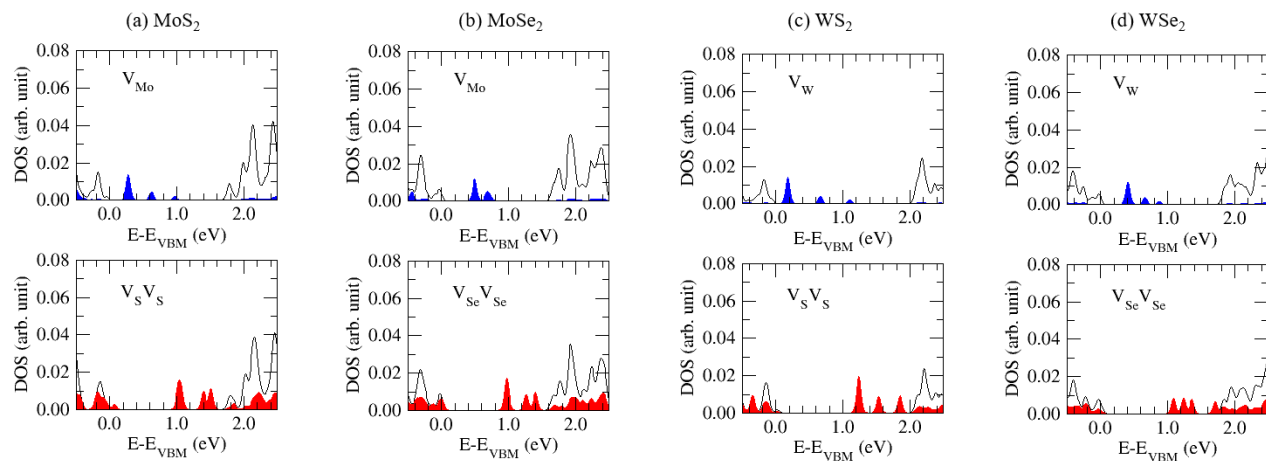
**Supplementary Figure 9. Optical viewgraphs of SC-mTMD-based planar tunnel junctions.** Optical images and the twist angle of SC-mTMD films and underlying graphene with respect to the top graphite for (a) mWS<sub>2</sub>, (b) mMoS<sub>2</sub>, (c) mMoSe<sub>2</sub>, and mWSe<sub>2</sub> devices without (d) and with (e) angles aligned. Scale bars are 20 μm.



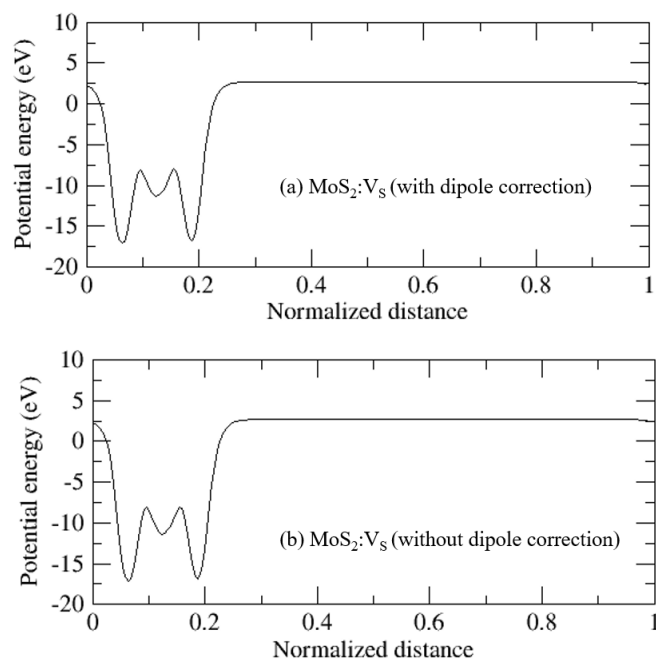
**Supplementary Figure 10. Detailed electronic structure analyses of mWSe<sub>2</sub> and mMoSe<sub>2</sub> films.**  $dI/dV_b$  tunneling spectra focused around the valence- and conduction-band edges of Se-based mTMD films mWSe<sub>2</sub> (**a**) and mMoSe<sub>2</sub> (**b**). Valence band edges and conduction band edges are found in the same manner as in Supplementary Figure 7.



**Supplementary Figure 11. DFT results on single chalcogen-atom vacancies.** **a–d**, Calculated defect density of states induced from single chalcogen-atom vacancies ( $V_S$  or  $V_{Se}$ ) in four SC-mTMD films of **(a)** MoS<sub>2</sub>, **(b)** MoSe<sub>2</sub>, **(c)** WS<sub>2</sub>, and **(d)** WSe<sub>2</sub> without (upper row) and with (lower row) consideration of SOC effects. The splits of the doublet  $e$  defect states in WS<sub>2</sub> and WSe<sub>2</sub> with the SOC are marked with red arrows.



**Supplementary Figure 12. DFT results on single transition metal-atom and double chalcogen-atom vacancies.** a–d, Calculated defect DOS for four SC-mTMD films of (a) MoS<sub>2</sub>, (b) MoSe<sub>2</sub>, (c) WS<sub>2</sub>, and (d) WSe<sub>2</sub> from the missing of single transition-metal atoms (upper row, V<sub>Mo</sub> or V<sub>W</sub>) and double chalcogen-atom vacancies (lower row, V<sub>S</sub>V<sub>S</sub> or V<sub>Se</sub>V<sub>Se</sub>).



**Supplementary Figure 13. DFT results on dipole correction.** Plane-averaged local Hartree potentials for single sulfur vacancies in mMoS<sub>2</sub> films with (a) and without (b) dipole corrections.

## Supplementary Table

|                    |                 |       | A (eV) | A (nm) | B (eV) | B (nm) | A-B (meV) |
|--------------------|-----------------|-------|--------|--------|--------|--------|-----------|
| mMoSe <sub>2</sub> | On quartz       | 80 K  | 1.632  | 759.6  | 1.841  | 673.7  | 209       |
|                    | On quartz       | 300 K | 1.574  | 787.8  | 1.773  | 699.3  | 199       |
|                    | On <i>h</i> -BN | 80 K  | 1.628  | 761.6  | 1.823  | 680.2  | 195       |
|                    | Sandwiched      | 80 K  | 1.631  | 760.3  | 1.832  | 677.0  | 201       |
|                    | Sandwiched      | 300 K | 1.570  | 789.9  | 1.769  | 701.1  | 199       |
| mWSe <sub>2</sub>  | On quartz       | 80 K  | 1.675  | 740.4  | 2.111  | 587.3  | 436       |
|                    | On quartz       | 300 K | 1.623  | 764.1  | 2.035  | 609.2  | 412       |
|                    | On <i>h</i> -BN | 80 K  | 1.712  | 724.2  | 2.128  | 582.7  | 416       |
|                    | Sandwiched      | 80 K  | 1.742  | 712.0  | 2.169  | 571.8  | 427       |
|                    | Sandwiched      | 300 K | 1.681  | 737.8  | 2.094  | 592.2  | 413       |
| mMoS <sub>2</sub>  | On <i>h</i> -BN | 80 K  | 1.927  | 643.5  | 2.078  | 596.8  | 151       |
| mWS <sub>2</sub>   | On <i>h</i> -BN | 80 K  | 2.041  | 607.4  | 2.417  | 513.1  | 376       |

**Supplementary Table 1. Exciton peaks of SC-mTMD films from optical transmittance measurements.** A- and B-exciton peak positions of mMoSe<sub>2</sub>, mWSe<sub>2</sub>, mMoS<sub>2</sub>, and mWS<sub>2</sub> from transmittance spectra in different dielectric environments: monolayer films on quartz substrates (on quartz), monolayers on *h*-BN and quartz (on *h*-BN), and encapsulated monolayers with *h*-BN flakes and placed on quartz substrate (sandwiched). Both A- and B-exciton peaks are more susceptible to nearby dielectric environments and temperature variations than the rather unresponsive A–B exciton spacings, whose values are estimated to be  $200.6 \pm 5.2$  meV for mMoSe<sub>2</sub> and  $420.8 \pm 10.4$  meV for mWSe<sub>2</sub> films. Uncertainty levels are further improved to  $198.3 \pm 3.1$  meV for mMoSe<sub>2</sub> and  $418.7 \pm 7.4$  meV for mWSe<sub>2</sub> when considering the case with high-quality non-interacting *h*-BN layers. We are thus able to assign with full confidence the SOC-induced valence band splittings of the four SC-mTMD films in the graphite–*h*-BN–graphene planar tunnel devices with an uncertainty level of  $\pm 0.01$  eV (Supplementary Figure 6), and later utilize them for analyzing the electronic structures of the semiconducting films with data from electron tunneling spectroscopy measurements.