

**Supporting information**

**Origin of layer-dependent SERS tunability in  
2D transition metal dichalcogenides**

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## **METHODS**

### **Samples synthesis.**

Large-scale continuous PtSe<sub>2</sub> thin films with different layers were synthesized on the sapphire substrate by chemical vapor deposition (CVD) via selenization of PtCl<sub>4</sub> pre-cursor as described previously<sup>1</sup>. Besides, a large area uniform ReS<sub>2</sub> film is synthesized by CVD method. ReO<sub>3</sub> and S are used as source and sapphires are utilized as collecting substrates in the growth<sup>2</sup>. The size of all the samples was approximately 10 mm × 10 mm. The optical microscope images demonstrate a flat and clean surface with only few randomly dispersed nanoparticles, suggesting the PtSe<sub>2</sub> and ReS<sub>2</sub> films are uniform and continuous. Furthermore, corresponding Raman spectroscopy and atomic force microscopy (AFM) characterizations reveal the high quality of all the as-grown films.

### **Raman Measurements.**

The ethanol solution of dye molecules (R6G and MeB) with different concentrations were obtained via sequential diluting processes. For each Raman measurement, 10 μL probe solution was dropped on the Raman-active material followed by a gentle dry process. The substrate was then rinsed in the absolute ethanol 3 times to remove the free molecules and was ready for Raman measurements. All the Raman measurements were taken with a HORIBA LabRAM HR Evolution system having a laser spot size of ~2 μm<sup>2</sup>. The excitation wavelength is 532 nm, and the laser power was set at 0.3 mW unless specified. The Raman spectra were obtained with 10 s acquisition time unless specified. For Raman measurements at low concentrations, we collected the average intensities among 20 single spectra taken on identical positions to minimize the signal noise. The spectra for comparison were acquired under identical measuring conditions and normalized by internal standard method.

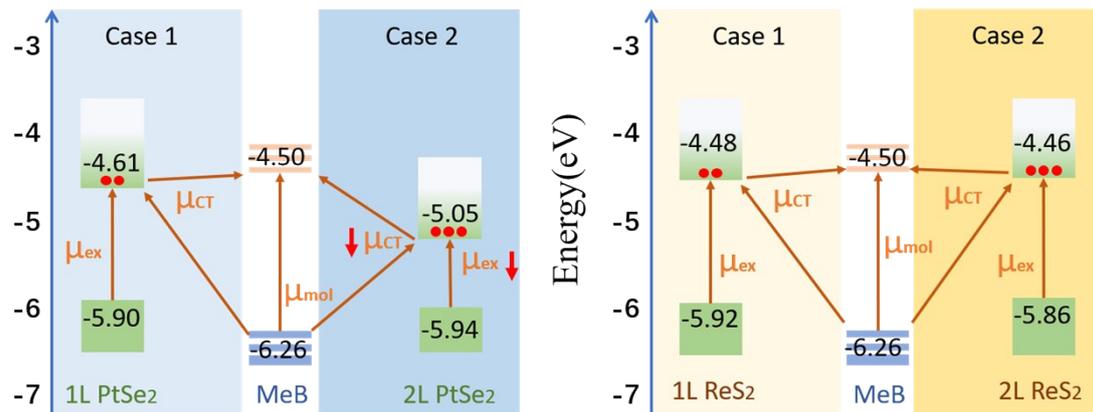
### **Density functional theory (DFT) calculations**

All first-principles calculations were performed using the plane-wave technique as implemented in the Vienna Ab Initio simulation package (VASP). The ion–electron interaction was described by the projector augmented wave (PAW) method, and the generalized gradient approximation (GGA) was expressed by the functional of Perdew,

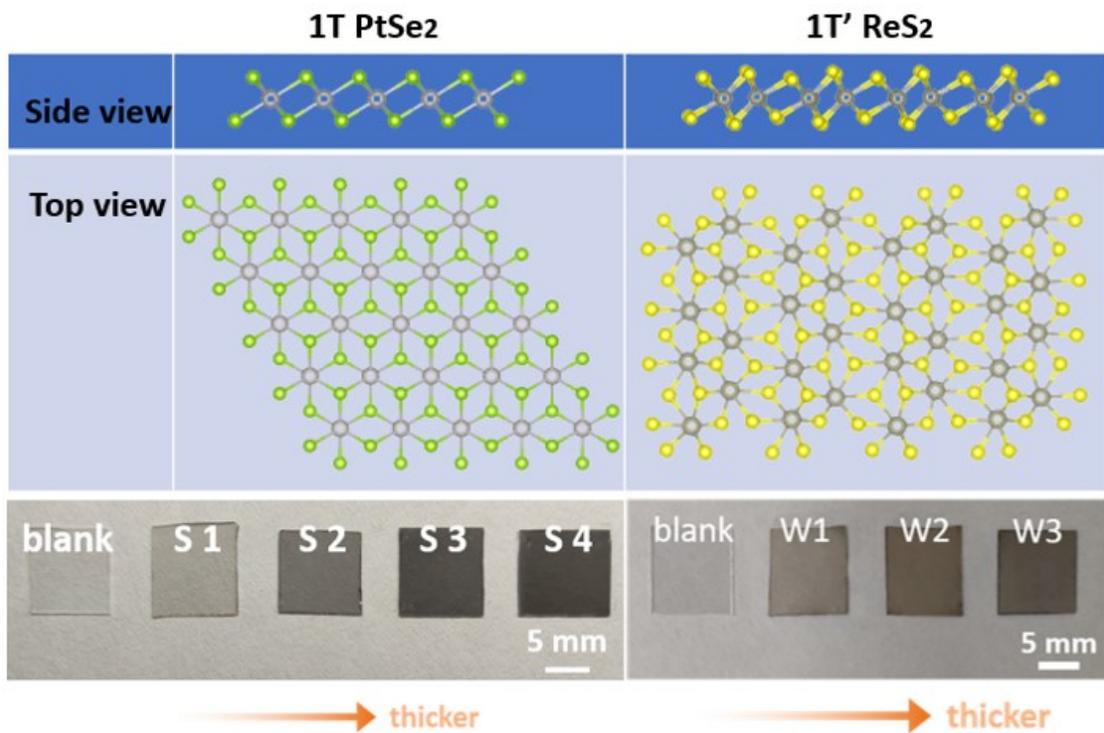
Burke, and Ernzerhof (PBE)<sup>3</sup>. The hybrid function of Heyd, Scuseria, and Ernzerhof (HSE) was also added. The Brillouin zone integration was sampled by a  $3 \times 3 \times 1$  k mesh. The systems were simulated with a periodic boundary condition by placing an MeB molecule on the surface of 72-atom monolayer PtSe<sub>2</sub> (Pt:24 and Se:48), 144-atom bilayer PtSe<sub>2</sub> (Pt : 48 and Se : 96), 96-atom monolayer ReS<sub>2</sub> (Re : 32 and S : 64) and 192-atom bilayer ReS<sub>2</sub> (Re : 64 and S : 128), respectively. The projector augmented wave (PAW) method was used to describe the wave function of the core region, while the valence wave function was extended to a linear combination of plane waves with 400 eV cut-off energy. The geometry was fully relaxed without any constraint until the force on each atom was less than 0.02 eV/Å. Grimme's DFT-D and BEEF correction were employed for dispersion interaction<sup>4</sup>. The adsorption energy for MeB adsorbed on 2D material (PtSe<sub>2</sub> and ReS<sub>2</sub>) was calculated using  $E_{abs} = E_{2d} + E_{MeB} - E_{all}$ , where  $E_{2d}$ ,  $E_{MeB}$ , and  $E_{all}$  is the energy of 2D material (PtSe<sub>2</sub> and ReS<sub>2</sub>), a MeB molecule, and the combined system of them, respectively.

**Table S1.** The binding energy of different systems.

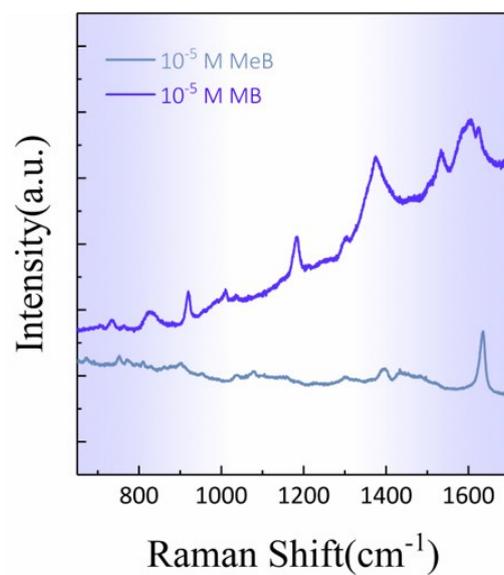
Type	MeB/1L-PtSe <sub>2</sub>	MeB/2L-PtSe <sub>2</sub>	MeB/Bulk-PtSe <sub>2</sub>	MeB/1L-ReS <sub>2</sub>	MeB/2L-ReS <sub>2</sub>
(Mats + Mols) Energy	-606.1116 eV	-979.9626 eV	-1705.0090 eV	-969.4368 eV	-1705.0832 eV
Mats Energy	-363.8300 eV	-738.2825 eV	-1464.3293 eV	-728.9565 eV	-1464.6949 eV
Mols Energy	-238.5248 eV	-238.5248 eV	-238.5259 eV	-238.5252 eV	-238.5264 eV
Adsorption Energy	-3.7568 eV	-3.1553 eV	-2.1538 eV	-1.9552 eV	-1.8618 eV
		<b>ENCUT</b>	<b>400 eV</b>		
		<b>VDW</b>	<b>DFT-D3(12)</b>		
		<b>VASPSol</b>	<b>Yes</b>		



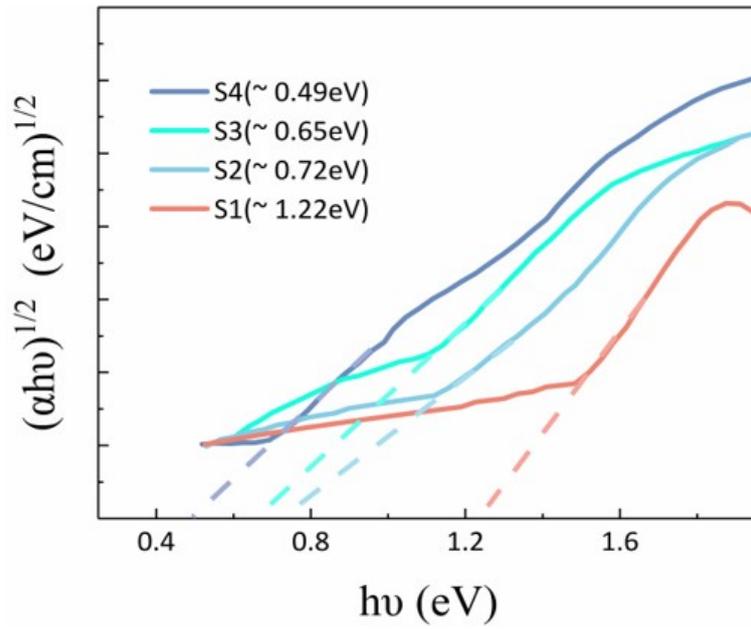
**Figure S1.** Schematic illustration of the PICT process of the PtSe<sub>2</sub>-MeB system and ReS<sub>2</sub>-MeB system while the number of layers increased.



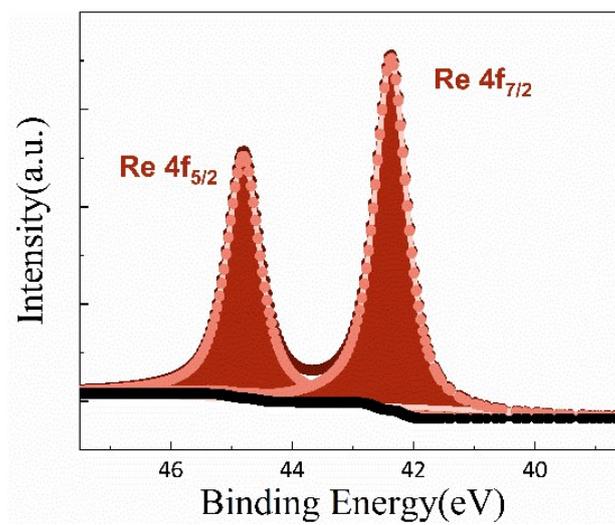
**Figure S2.** Basic character of 1T PtSe<sub>2</sub> and 1T' ReS<sub>2</sub>. Crystal structure of 1T PtSe<sub>2</sub> and 1T' ReS<sub>2</sub> from top and side views (top part). The photos of PtSe<sub>2</sub> and ReS<sub>2</sub> with different thickness, which marked as S1 to S4 and W1 to W3.



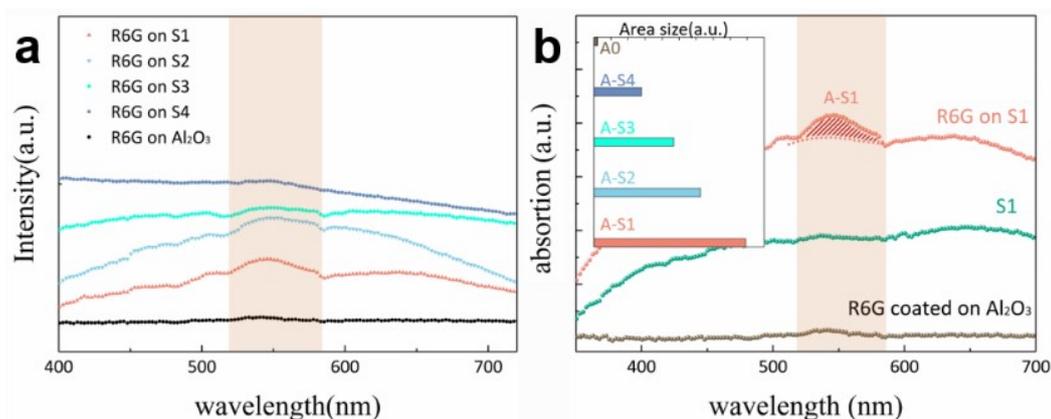
**Figure S3.** The enhanced Raman spectra of 10<sup>-5</sup> M MB and MeB on S1.



**Figure S4.** The optical absorption of PtSe<sub>2</sub> with different thickness. The bandgap of each film obtained from Tauc plots. The bandgaps are approximately 1.22 eV (S1), 0.72 eV (S2), 0.65 eV (S3), and 0.49 eV (S4) respectively.

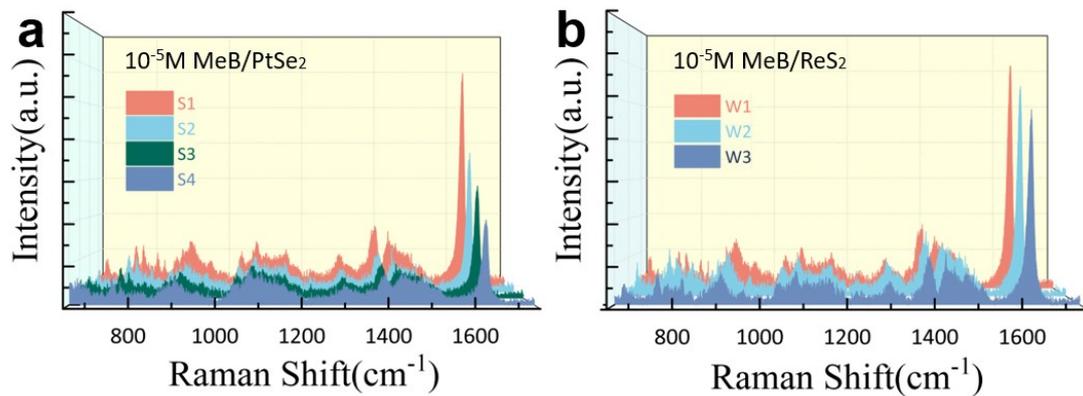


**Figure S5.** XPS spectrum for Re 4f of 2D ReS<sub>2</sub> film.



**Figure S6.** (a) The absorption contribution of R6G coated on S1, S2, S3, and S4. (b) Absorption spectra of S1 and R6G ( $10^{-5}$  M) coated S1 and Al<sub>2</sub>O<sub>3</sub>. The dashed box denotes the R6G absorption band, marked as A-S1.

The interaction between the analyte and the S1 to S4 was examined by UV–Vis measurements. An additional absorption band around 520–585 nm (named as A-S1) was observed in the absorption spectrum (red curve) of R6G dye ( $10^{-5}$  M) coated on S1 with respect to the case of pristine S1 (green curve), which can be assigned to the contribution of R6G absorption. It is noteworthy that the enhancement of dye absorption on the surface reflects the efficient charge transition between the dye molecule and the substrate. What's more, the inset in Figure S6b indicates that the molecule absorption is more powerful on thinner PtSe<sub>2</sub> than that of the relatively thicker one after the same treatment, suggesting that the charge transfer in R6G–S1 is the strongest in all the control groups. The corresponding original absorption spectra was presented in Figure S6a.



**Figure S7.** Enhanced Raman spectra of  $10^{-5}$  M MeB on the (a) PtSe<sub>2</sub> films (S1 to S4) and (b) ReS<sub>2</sub> films (W1 to W3).

### Calculation of the enhancement factor.

The enhancement factor (EF) was calculated according to the formula:

$$EF = (I_{\text{SERS}}/N_{\text{SERS}})/(I_{\text{bulk}}/N_{\text{bulk}}) \quad (1)$$

$$N_{\text{SERS}} = CVN_{\text{A}}A_{\text{Raman}}/A_{\text{Sub}} \quad (2)$$

$$N_{\text{bulk}} = M\rho hA_{\text{Raman}}N_{\text{A}} \quad (3)$$

$I_{\text{SERS}}$  and  $I_{\text{bulk}}$  are the intensities of the selected Raman peak in the SERS and non-SERS spectra, and  $N_{\text{SERS}}$  and  $N_{\text{bulk}}$  are the average number of molecules in scattering area for SERS and non-SERS measurement.  $C$  is the molar concentration of the analyte solution,  $V$  is the volume of the droplet,  $N_{\text{A}}$  is Avogadro constant.  $A_{\text{Raman}}$  is the laser spot area (1  $\mu\text{m}$  in diameter) of Raman scanning.  $A_{\text{Sub}}$  is the effective area of the substrate, which obtained from 20 mL of the droplet on the substrate was spread into a circle of about 3 mm in diameter after solvent evaporation. The confocal depth ( $h$ ) of the laser beam is 21  $\mu\text{m}$ . Besides, both the molecular weight ( $M$ ) and density ( $\rho$ ) of bulk R6G (1.15  $\text{g}/\text{cm}^3$ ) are easily available.

The data for R6G ( $10^{-2}$  M) on bare  $\text{SiO}_2/\text{Si}$  substrate were used as non-SERS-active reference. Specifically, the intensity was obtained by taking average from measurements of 15 spots, and the number of analyte molecules was estimated by Supplementary equation 2 on the assumption that the analyte molecules were distributed uniformly on the substrates. The  $N_{\text{bulk}}$  is calculated by Supplementary equation 3.

Here, we calculate the enhancement factors (EFs) of 612  $\text{cm}^{-1}$  peak of R6G on different substrates as an example for comparison.

PtSe <sub>2</sub>		ReS <sub>2</sub>	
S1	$3.04 \times 10^4$	W1	$5.86 \times 10^5$
S2	$1.61 \times 10^4$	W2	$5.56 \times 10^5$
S3	$1.20 \times 10^4$	W3	$5.22 \times 10^5$
S4	$1.01 \times 10^4$		

## Reference

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- (3) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Physical review letters* **1996**, *77* (18), 3865.
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