Supporting Information

for

Terrylene on monolayer WS$_2$: coverage-dependent molecular re-orientation and interfacial electronic energy levels

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Note1: synthesis and transfer of ML-WS$_2$ films. The sapphire substrates were first annealing at higher temperature of 1000 °C. Then sapphire was cut into shape as needed and soaked in piranha solution (H$_2$O$_2$: sulfuric acid = 3:7) for 1 h, followed by ultra-sonic cleaning in DI water for 10 min by 3 cycles. The cleaned sapphire then was dried and spin coated with Na$_2$WO$_4$ solution (0.6 mg/mL in H$_2$O: IPA = 3:7) at a speed of 2.5 krpm. 30 mg of WO$_3$ powder is loaded in alumina crucible, covered with the spin coated sapphire with facing towards the precursor. Then it was loaded into a quartz tube, where a Sulphur crucible was placed in front. The quartz tube was evacuated by a rotary pump to a pressure of 10^{-2} mbar and vented with Ar gas which was used as gas carrier, with a flow rate of 6 L/h during reaction. The quartz tube is heated by a CVD oven at a reaction temperature of 850 °C for 15 min. Last, the CVD oven was cooled down naturally until room temperature. The as grown WS$_2$ films can then be spin coated with PMMA solution and dry for 30 min at 80 °C for transfer. After PMMA is cured, the WS$_2$ is cut into size as needed and soak into KOH (15M) for about 2h to allow its delamination from the substrate, when the excessive precursors and oxide are being etched. The WS2/PMMA film was picked up by a cleaned Si wafer and transfer to DI water and rinse three times, before lastly picked up by the target substrate. For WS$_2$/sapphire samples, the PMMA was removed by directly rinse the samples into acetone solution for 1h and isopropanol for 10 min. The samples then will be loaded into vacuum chamber (10E-9 mbar) and annealed at 350 °C for 5h to remove the residual PMMA. For WS$_2$/HOPG, due to the weak interaction, the samples were gently put in a saturated acetone vapor by heating the acetone solution at a hot plate

temperature of 110 °C for at least 10 min. Then, the WS$_2$/HOPG can be cleaned the same as sapphire. The WS$_2$/sapphire samples used in PES measurement were fixed on a sample holder by metallic screws to ensure electrical contact.

Note 2: estimation of molecular density of terrylene on ML-WS$_2$.

According to PES measurements, the first molecular monolayer is done by depositing a nominal thickness of 2.5 Å of terrylene, and 6 Å for the second layer. Therefore, the weight ratio of 2L to 1L is 6/2.5 = 2.4.

The relative molecular densities of 1L and 2L can also be estimated from the reconstruction model as shown in Fig. 5b. For 1L, an overlayer of $(2\sqrt{3} \times 7\sqrt{3})$ unit cell is formed with respect to the ML-WS$_2$ lattice. For the 2L construction, it turns into an $(7\sqrt{3} \times 7\sqrt{3})$ overlayer. From Fig. 5a, each seven 1L overlayer units turns into four of 2L overlayer units after deposition the 2L and the reorientation occurs. As each unit cell of 1L and 2L contains one and four equivalent molecular respectively, the molecular density ratio of 2L:1L equals to (4×4)/(7×1) ≈ 2.3.
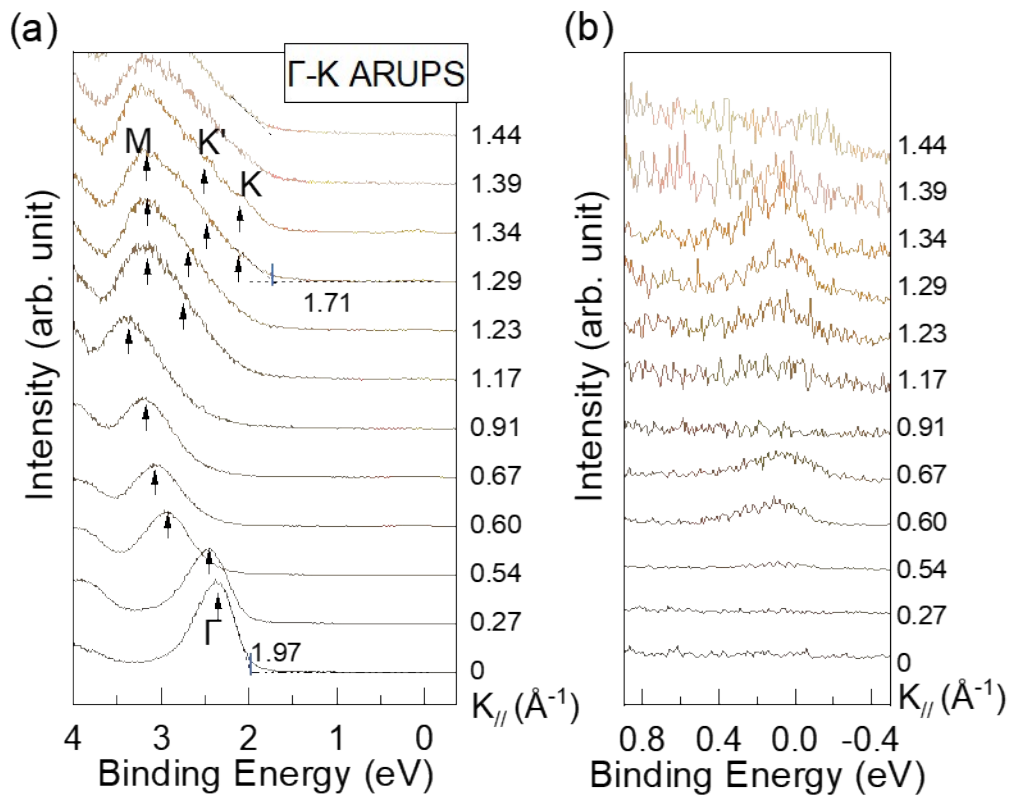

Figure S1. (a) angle dependent UPS data of ML-WS$_2$/sapphire sample. Arrows show the highly symmetric points. (b) the region in the filled bands near fermi level.
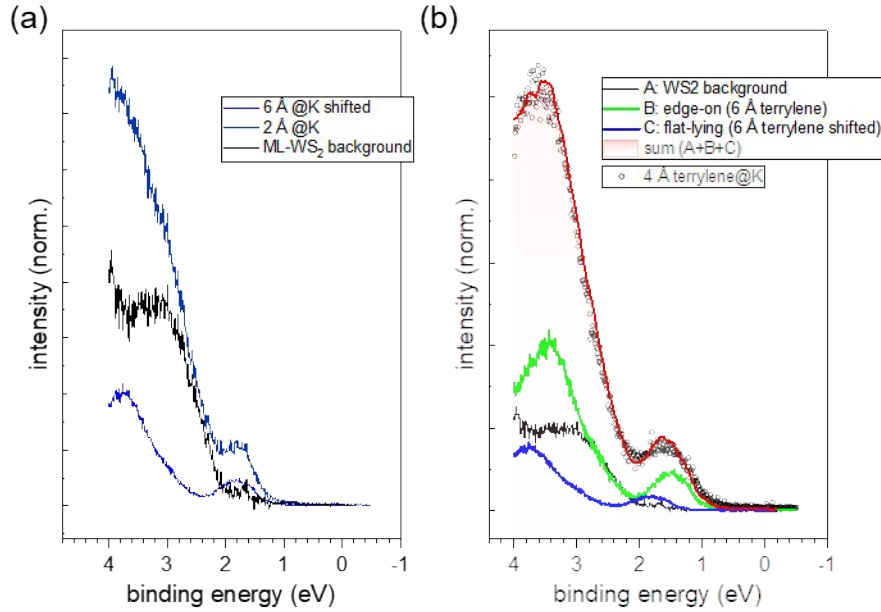
Figure S2. (a) the numerical difference UPS spectra of 2 Å terrylene/ML-WS$_2$/sapphire to that of 6 Å at K point shifted to the same onset position. The difference results the signal contribution of the ML-WS$_2$. (b) The numerical sum of the spectra of ML-WS$_2$ background in a), 6 Å at K point, and shifted 6 Å at K point. The resulting spectra fits the curve of 4 Å terrylene/ML-WS$_2$/sapphire at K point, indicating there're two components assign to flat-lying and edge-on molecules, then turning into one component as the molecules rearrange into edge-on configuration for thicker films.
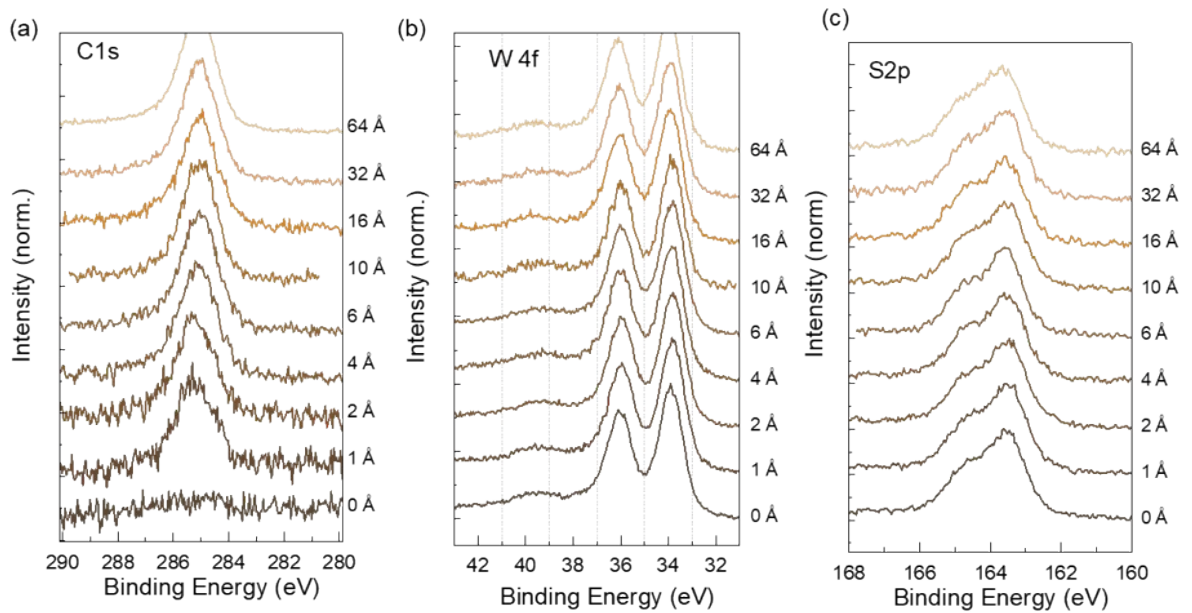
Figure S3. (a) C1s, (b)W4f and (c) S2p XPS spectra of terrylene/ML-WS$_2$/sapphire sample.
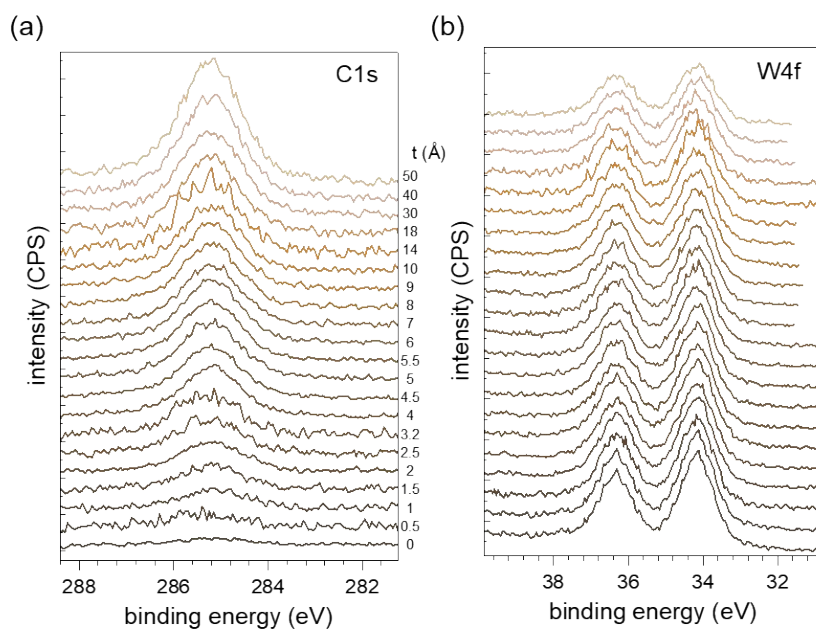
Figure S4. Thickness dependent XPS data of (a) C1s and (b) W4f of terrylene/ML-WS$_2$/sapphire sample used for relative intensities analysis (Fig.2b).
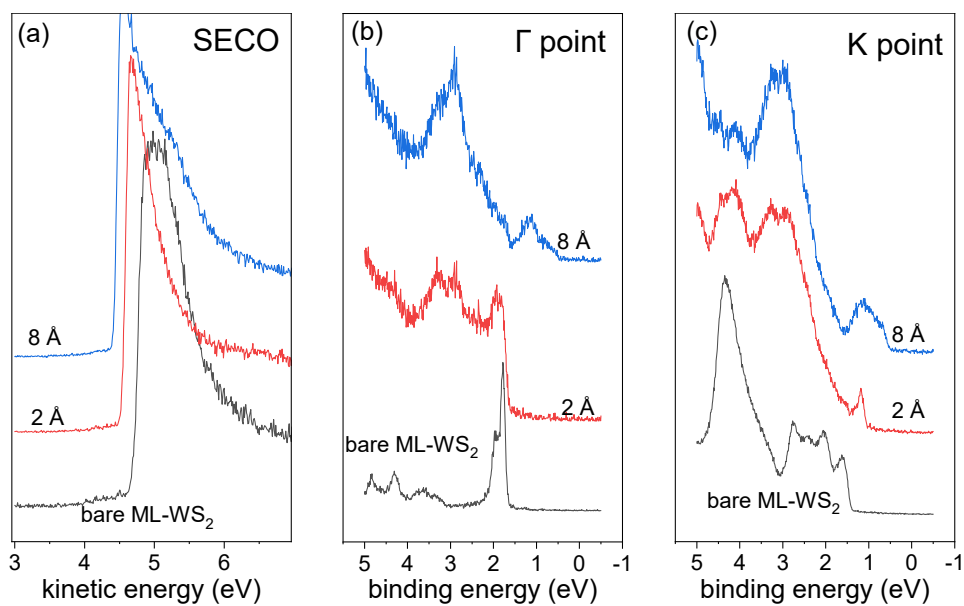

Figure S5. PES spectra of subsequent deposition of terrylene/WS$_2$ heterostructure on HOPG (a) secondary cut-off spectra. (b) thickness-dependent UPS curves in the valence region at Γ and K points.
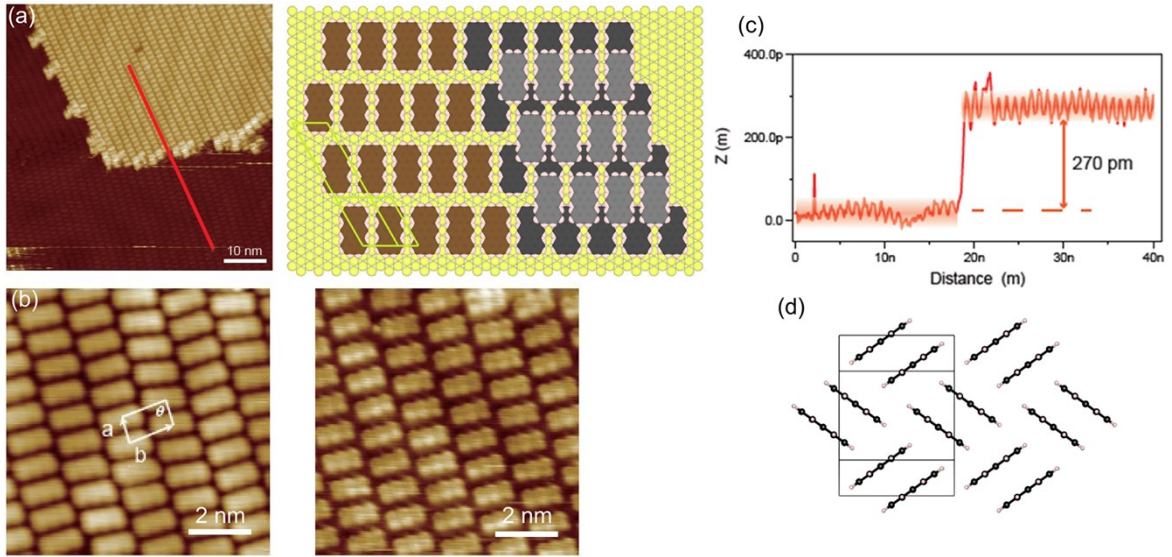
Figure S6. (a) Large-scale STM images of terrylene/Au (111) sample with deposition time of 15 min at room temperature. top view and side view of the reconstructed model showing a superlattice unit cell of $(2\sqrt{3} \times 8\sqrt{3})$. （b）High resolution STM images of the first layer of terrylene molecules over Au (111), with lattice dimensions of a = 1.61± 0.1 nm, b = 1.08 ± 0.1 nm and θ = 77 ± 2 °. (c) The line profile in (a) shows the relative height in STM images of flat-lying terrylene monolayer is 270 pm, with 50 pm in-plane corrugations. Set point: (a) 1 V, 10 pA; (b) -200 mV, 10 pA; and (c) 100 mV, 10 pA. (d) the single crystal structure of terrylene from literature[1].
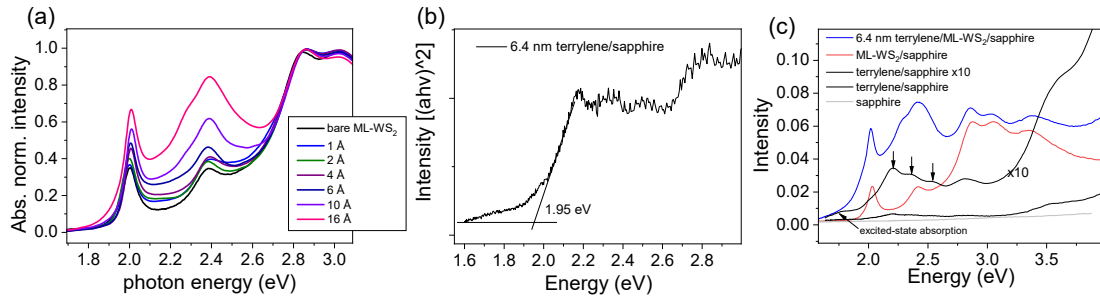

Figure S7 (a) UV-vis absorption spectra of bare ML-WS$_2$/sapphire and terrylene/ML-WS$_2$/samples. (b) the optical bandgap pf terrylene film on sapphire is determined using Tauc Plot. (c) Comparison of the UV-vis spectra of ML-WS$_2$/sapphire without and with 6.4 nm terrylene film, intensity of given in arbitrary units. The terrylene film have excited-state absorption at low energy range. The characteristic peaks at 2.2 eV, 2.36 eV and 2.54 eV are not in the range of Rydberg exciton discussed in this paper.
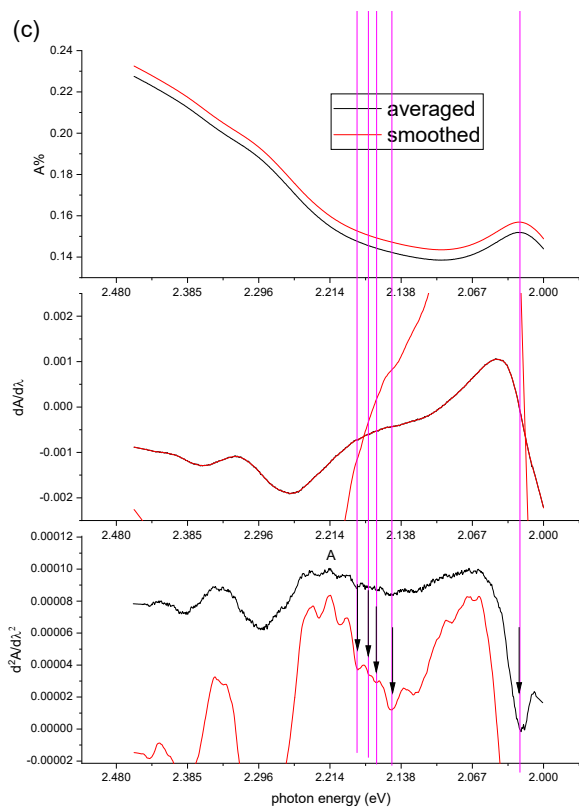
(a)

(b)
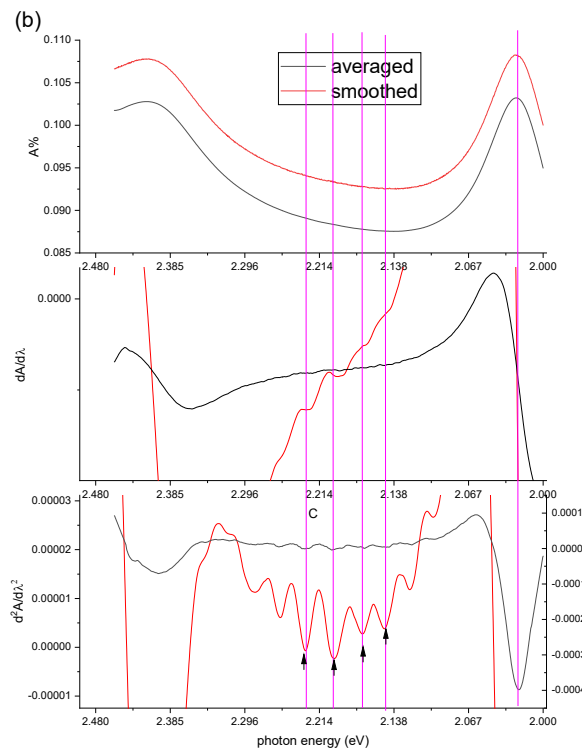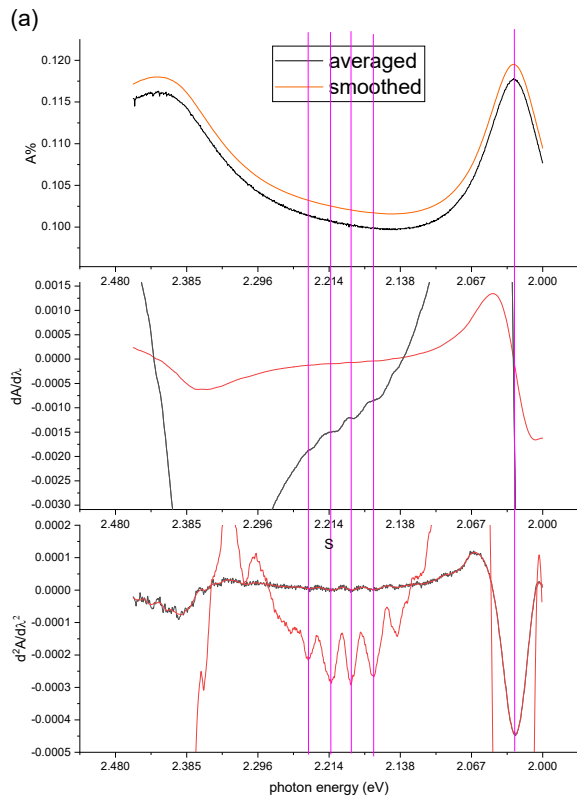
Fig. S8 UV-vis spectra and the first and second derivatives are taken to enhance the spectral features of (a) ML-WS$_2$/sapphire, (b) 2 Å terrylene/ML-WS$_2$/sapphire, and (c) 6.4 nm terrylene/ML-WS$_2$/sapphire. The sample was annealed in vacuum and then test in ambient condition. A Savitzky-Golay smoothing is used for more pronounced peaks.

Reference:

1.   C. L. Hall, I. Andrusenko, J. Potticary, S. Gao, X. Liu, W. Schmidt, N. Marom, E. Mugnaioli, M. Gemmi and S. R. Hall, *ChemPhysChem*, 2021, **22**, 1631-1637.