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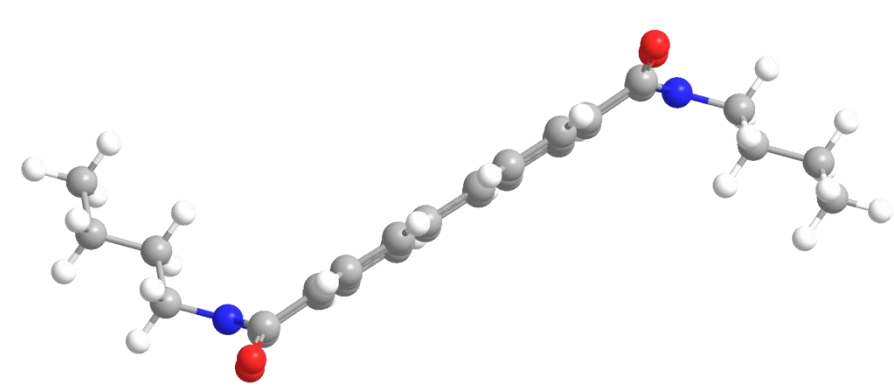
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Abstract

Two-dimensional layered semiconductors have proven to be versatile examples in the exploration of their unique layer-number dependent electronic and optical properties. Recent progress on altering the physical properties of transition metal dichalcogenides (TMDCs) using surface molecular doping effect has much interest.[1-2] In this study, we investigate the molecular alignment and the ultrafast charge transfer dynamics of N,N'-Dibutyl-3,4,9,10-perylenedicarboximide (PTCDI-C4) molecules at different molecular thicknesses on molybdenum disulphide (MoS₂) substrates using near edge X-ray absorption fine structure spectroscopy (NEXAFS) and Resonant Photoemission (RPES), respectively. The average tilt angle analysis revealed a strong anisotropy in the π* symmetry transition (284-288 eV range) across the absorption threshold. The non-planar molecular configuration was extracted from the carbon K-edge of the perylene spectrum.[3] Core hole clock spectroscopies at the few monolayer sample displayed a resonant enhancement of the occupied state level which indicates the existence of a moderate interfacial electronic coupling between the adsorbed molecules and substrate. These findings provide a deeper understanding of the interfacial interaction of organic semiconductors on transition metal dichalcogenide surfaces, which is essential for the development of non-planar geometry-based organic devices.

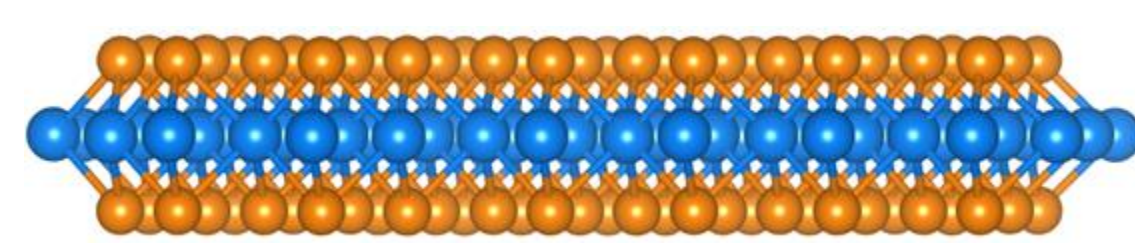
Background



The perylene derivative family is one of the most extensively studied organic semiconductor in the field of organic electronics

Goal

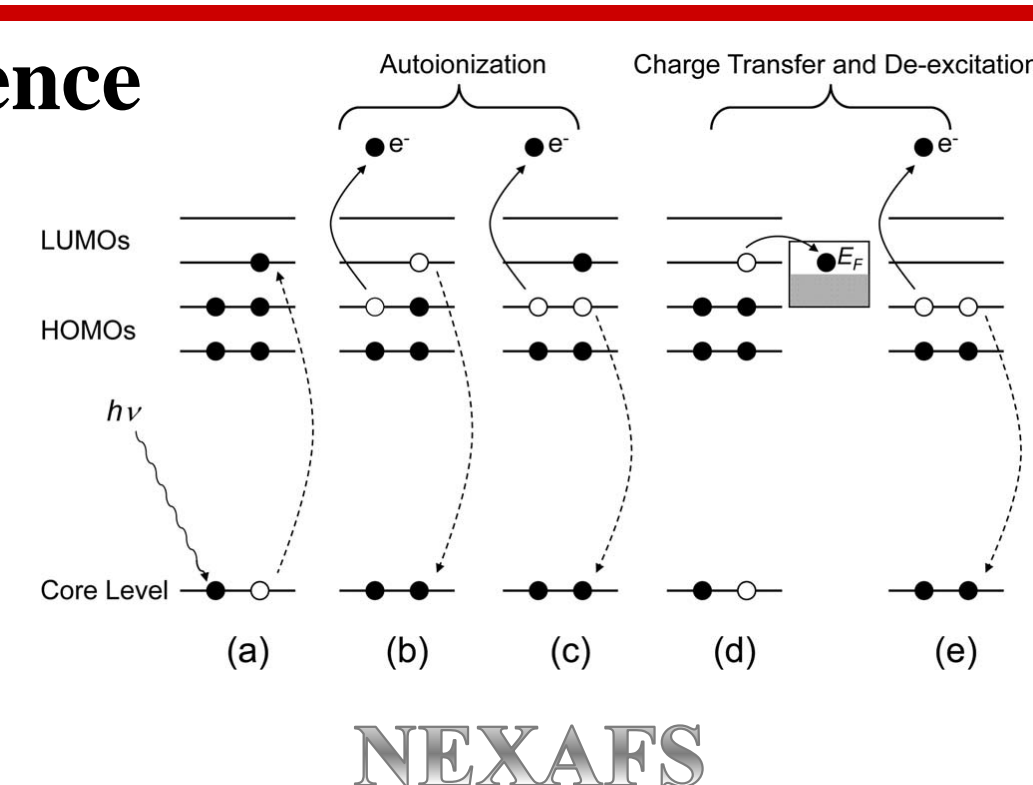
To investigate the molecular orientation and the charge transfer dynamics of the hybrid organic/inorganic heterostructures.



TMDCs are exotic materials of current interest especially in 2D van der Waal heterostructures due to their band gap tunable properties

Synchrotron radiation technique

SINS : Surface, Interface and Nanostructure Science

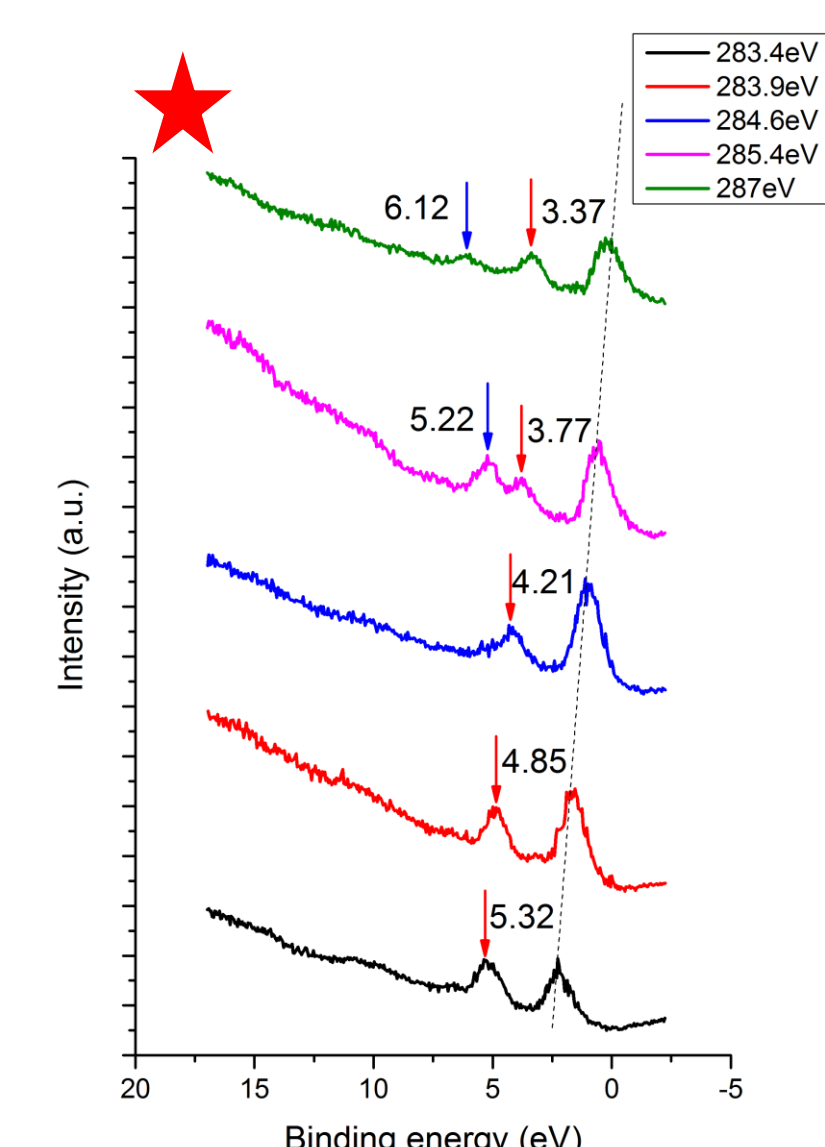
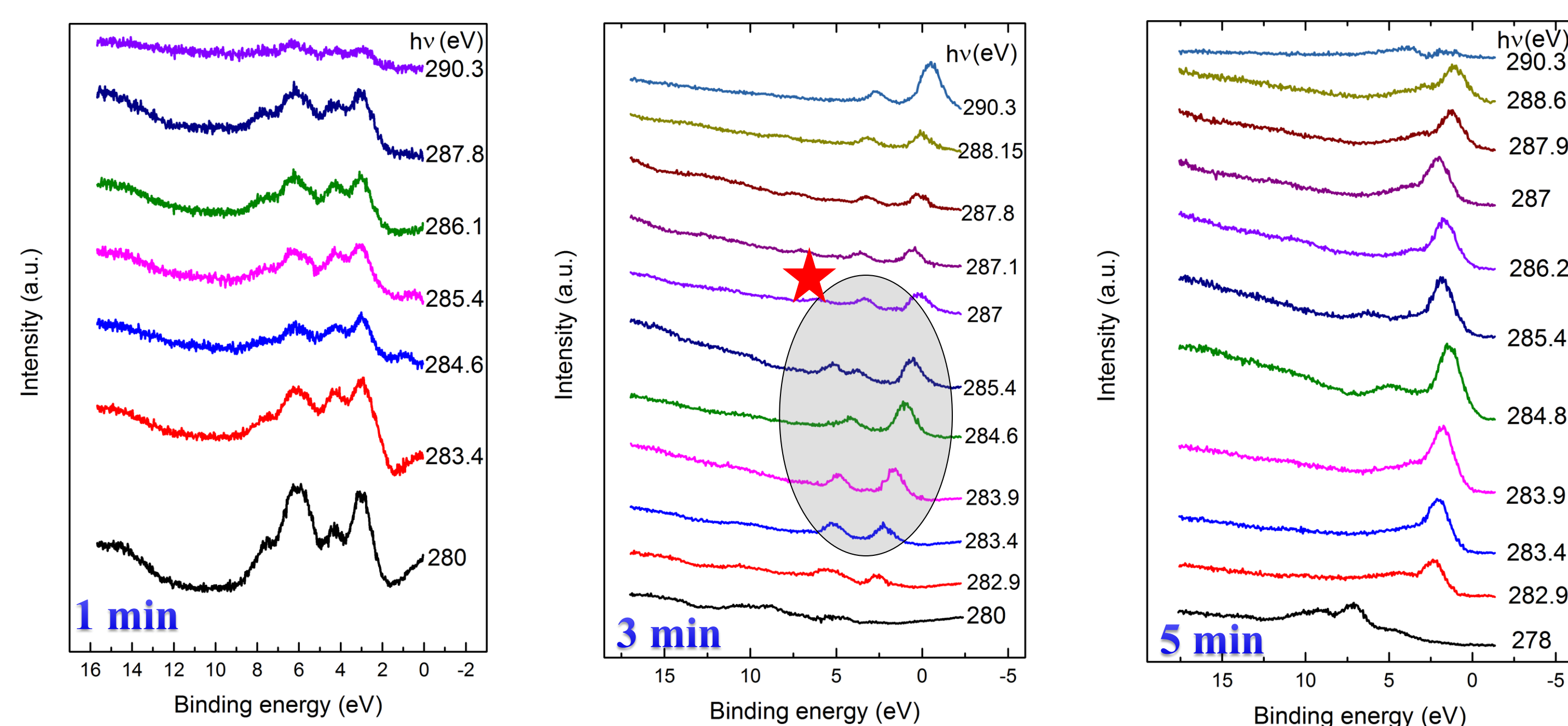


NEXAFS

Thermally-sublimated samples were probed using synchrotron based resonant photoemission spectroscopy (RPES) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy.

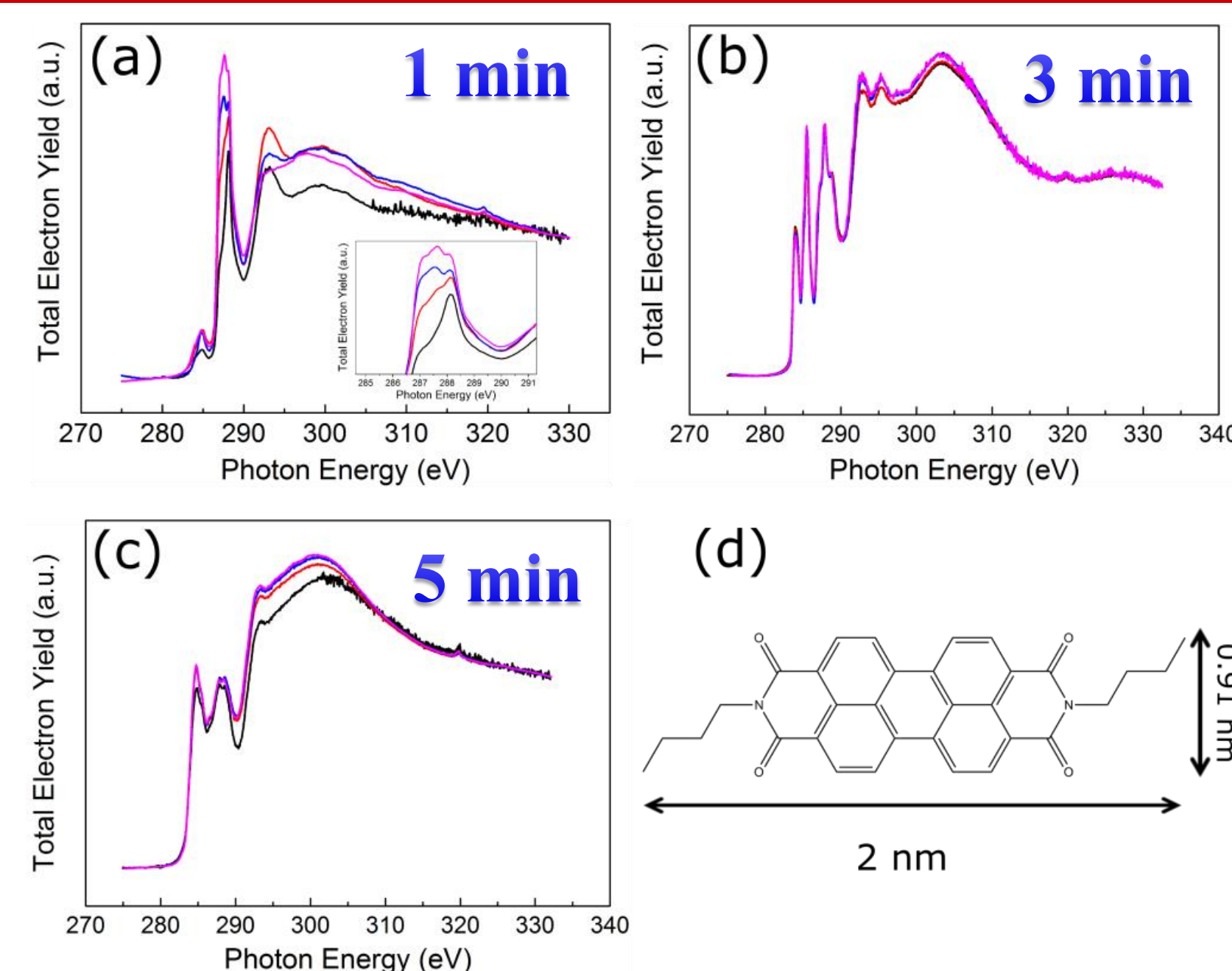
RPES

RPES results



- Two weak-resonant enhancements of photoemission signals are visible across the C K-edge absorption edge for 1 & 3 min sample.
- The RPES signals were quenched in the multilayer thick sample (5 min).
- The enlargement peak profile (left graph) indicates that a slight HOMO peak enhancement is still persistent.

NEXAFS results



Carbon K-edge NEXAFS spectra of PTCDI-C4 film as a function of deposition time.

- peak spectrum below 285.4 eV π* resonances transitions from the initial states into the unoccupied π* molecular orbitals (LUMOs).
- 292.4 eV feature is attributed to the σ* resonances transition into LUMOs.

Average tilt angle

$$I \propto A \cdot \left\{ \frac{P}{3} \left[1 + \frac{1}{2} (3 \cos^2 \theta - 1)(3 \cos^2 \alpha - 1) \right] + \frac{(1-P)}{2} \sin^2 \alpha \right\}$$

Linear plots of I versus $\cos^2 \theta$ were used to extract the slope and intercept $\rightarrow \alpha$

Sample	average tilt angle (α)
1 min	$62.3^\circ \pm 0.1^\circ$
3 min	$55.0^\circ \pm 0.9^\circ$
5 min	$55.8^\circ \pm 0.3^\circ$

For 1 min sample, we can deduce that the molecule has a stronger tendency to stand upright with respect to the MoS₂ surface. The extracted tilt angles for the other two thicker samples are close to the magic angle (54.7°), implying that a random PTCDI-C4 molecular orientation exists in the multilayer samples.

Summaries

1. A polarization dependence is clearly resolved in the case of submonolayer coverage (1 min). In contrast, the degree of polarization of the other two cases (3 min and 5 min) showed negligible changes in both π* and σ* electronic transition as a function of incident photon angle.
2. Thickness-dependent of RPES profile suggested that a weak electronic coupling was established at the PTCDI-C4/MoS₂ interface.

References

- [1] Mak, K. F. et al., Atomically thin MoS₂: a new direct-gap semiconductor. Phys. Rev. Lett. 105, 136805 (2010).
- [2] Chhowalla, M. et al., The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. Nature Chem. 5, 263-275 (2013).
- [3] Arramel et.al., *submitted*, (2016).