

## Sub-Molecular Structural Relaxation at a Physisorbed van der Waals Interface with Monolayer Organic Single-Crystal Semiconductors Revealed by X-Ray Reflectivity Measurements

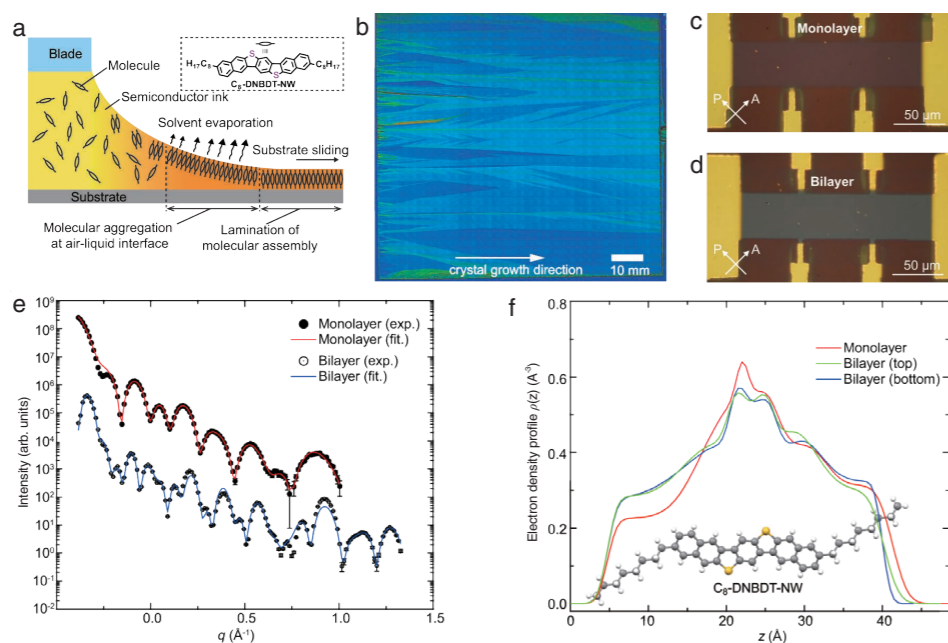
Arranging molecules into highly symmetric crystal structures is considered the best approach to functionalize electronic properties in molecular crystals, where the constituent molecules are assumed to be rigid in shape. In striking contrast, we present that the molecules in a monolayer organic crystal can undergo a significant deformation in proximity to the substrate. X-ray reflectivity measurements revealed that the highly planarized  $\pi$ -core is deformed into a bent shape. The molecular shape change was found to be perfectly suppressed in a bilayer single crystal, leading to a 40% increase in mobility in the bilayer crystal.

Quasi-2D single-crystal organic semiconductors (OSCs) with a thickness of a few monolayers offer great potential in the manufacturing of state-of-the-art organic field-effect transistors (OFETs) and integrated circuits [1, 2]. Charge transport in molecular semiconductors depends significantly on the molecular assembly [3], thus, structural studies of molecular crystals are essential for an in-depth understanding of the electronic properties [4, 5], where a single molecular shape aligned in a lattice has been assumed to be rigid. However, a molecular shape has a finite degree of freedom owing to the softness of organic compounds [6]. The effects of such molecular shape changes on electronic functionality are yet to be clarified, particularly at solid state interfaces between soft organic materials and substrates.

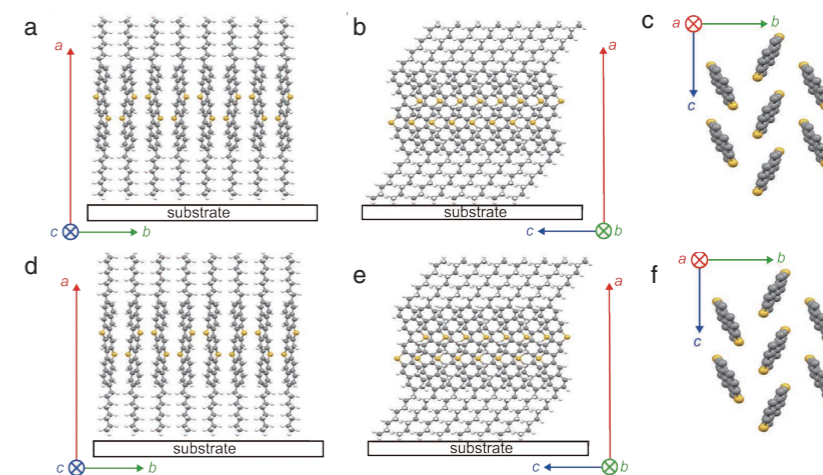
As an ideal platform to assess molecular structures at a buried interface, we use our benchmarked organic semiconductor  $C_8$ -DNBDT-NW [1-4, 6]. **Figure 1a** schematically illustrates the growth of an organic single crystal by the continuous edge-casting technique [1, 2, 7].

Here, solvent evaporation occurs predominantly at the vapor–liquid interface, resulting in solute supersaturation. This leads to an initial molecular aggregation at the surface of the solution and subsequent crystallization on the substrate. A self-assembled molecular nanosheet grows at the vapor–liquid interface, and is then laminated onto the substrate. We successfully manufactured a 4-inch ( $\sim 100$  mm) organic single-crystal wafer (**Fig. 1b**), and prepared monolayer and bilayer single crystals selectively by adjusting the substrate temperature (**Figs. 1c and d**).

The molecular structure at the buried interface is characterized by assessing the electron density profile along the depth direction by X-ray reflectivity (XRR) measurements. Electron density profiles with sub-molecular resolution are derived from the reflectivity measurements by an analysis based on a slab model. In the model, each  $C_8$ -DNBDT-NW molecule is divided into seven slabs. Each slab is characterized by the three parameters of electron density, thickness, and



**Figure 1:** a Schematic image of the continuous edge-casting method. Solvent evaporation at the air–liquid interface induces a pre-aggregation of solute molecules, forming crystal nucleation. b Confocal microscopy image of a  $90 \times 90$  mm  $C_8$ -DNBDT-NW crystal on a silicon wafer substrate. Cross-polarized optical microscopy images of c monolayer, and d bilayer crystals. e Measured XRR intensities from monolayer and bilayer samples. The solid curves show the corresponding fitting results based on a slab model. f Electron density profiles of monolayer and bilayer  $C_8$ -DNBDT-NW crystals. The molecule in the monolayer exhibits noticeable molecular distortion on the substrate side.



**Figure 2:** Structural relaxation in  $C_8$ -DNBDT-NW monolayer crystals. Packing model of a–c bulk crystal and d–f monolayer structure. The structural optimization was performed by a density-functional theory calculation.

roughness. **Figure 1e** shows the measured XRR intensities from monolayer and bilayer crystals, together with the fitting results. **Figure 1f** shows the electron density profiles extracted by the slab-model analysis, displaying the profiles for the monolayer, and top and bottom layers of the bilayer. The electron density profile of the monolayer film clearly differs from the bilayer profiles, exhibiting an asymmetric profile, while those for the top and bottom layers of the bilayer are identical and agree with the bulk structure of  $C_8$ -DNBDT-NW. A possible molecular packing arrangement in a monolayer crystal is illustrated in **Fig. 2**. This suggests that the monolayer  $C_8$ -DNBDT-NW experiences intramolecular distortion, resulting in the alkyl chain standing upright and the  $\pi$ -conjugated core to be bent, particularly in proximity to the substrate. The upper-half of the  $\pi$ -conjugated core remains intact despite the molecular distortion, indicating that the change in molecular shape at the physisorbed interface is limited to a sub-molecular-layer thickness. Remarkably, the molecular deformation is drastically reduced in the bottom layer of the bilayer crystal, suggesting that the presence of the top layer suppresses the conformational change of the bottom layer [8].

The intrinsic carrier transport properties of monolayer and bilayer crystals at the buried interface were evaluated by fabricating bottom-gate top-contact transistors. The four-terminal mobility of the bilayer transistors is 40% higher than that of the monolayer transistors, where the maximum value reaches about  $14 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , which indicates an inherent difference in carrier transport properties. The bilayer single crystal does not experience any molecular deformation at the buried interface, resulting in a 40% improvement of the intrinsic carrier mobility [8].

We demonstrated that intramolecular deformation occurs particularly for a monolayer single crystal at a physisorbed van der Waals interface, using highly-sensitive XRR analyses. The physisorption-induced struc-

tural transformation is screened perfectly by a bilaminar formation of  $C_8$ -DNBDT-NW, which improves the carrier mobility by 40%. The overall results indicate that due to the intrinsically soft nature of organic crystals, nano-scale proximity can be used to tune not only the molecular shape, but also the molecular assembly, resulting in fine control of electronic functionality. Our finding of a unique molecular transformation in monolayer single crystals offers a new perspective on the relationship between structure and properties in molecular crystals.

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### BEAMLINE

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A. Yamamura<sup>1,2</sup>, H. Fujii<sup>3,4</sup>, Y. Wakabayashi<sup>4</sup>, S. Watanabe<sup>1,2</sup> and J. Takeya<sup>1,2,5</sup> (The Univ. of Tokyo, <sup>2</sup>OPRANDO-OIL, AIST, <sup>3</sup>Osaka Univ., <sup>4</sup>Tohoku Univ., <sup>5</sup>WPI-MANA, NIMS)