

Molecular Orientation of a π -Conjugated Polymer Monolayer

The face-on orientation dominates the surface-segregated monolayer, as revealed by NEXAFS and GIWAXS spectra.

A synthetic-polymer thin film plays a crucial role in the modern economy. Although many artificial-polymer-based technologies have been successfully integrated into industrial processes, electronic applications based on a conjugated polymer are still in a dawn. Many believe that π -conjugated polymers have the potential to revolutionize electronic technologies, as their peculiar properties can be engineered with a highly developed synthesis toolbox from polymer science. The charge-transport property of a π -conjugated polymer is governed by not only the chemical composition of the polymeric macromolecules but also their conformation inside the membrane. Intensive effort has consequently been devoted to manipulate the crystallinity and molecular orientation of the membrane. Among various approaches, the packing structure and molecular orientation of a surface-segregated monolayer are susceptible to molecular design, allowing its properties to be tailored from the bottom up.

In this report, Yaw-Wen Yang (NSRRC), Chain-Shu Hsu (National Chiao Tung University) and Keisuke Tajima (RIKEN Center, Japan) and their coworkers take advantage of the surface-segregated monolayers (SSM) forming mechanism to set up a monolayer of π -conjugated polymer. By replacing the alkyl side chain of N2200 with a semifluoroalkyl chain, the surface energy of the product, named FNDIT2, is decreased (see Fig. 1(a) for the monomer structures). The difference in surface energy inside the spin-coated blended

FNDIT2/N2200 film drives a phase separation, resulting in an enhanced surface concentration of FNDIT2 over that of N2200. Depth profiling of fluorine with X-ray photoelectron spectroscopy (XPS) etching experiment concluded that the thickness of the surface layer is about 1.8 nm. This condition indicates a single-layer thickness for the FNDIT2 overlayer, as illustrated in Fig. 1(b).

The literature shows that the SSM mechanism can induce an ordered single-layer polymer with its π -conjugated plane oriented to the substrate surface in either face-on or edge-on or end-on manner, as illustrated in Fig. 2(a). For electronic applications, this orientation is of the utmost importance, as it strongly influences the anisotropic charge-transport properties. In this work, the π -plane orientation about the surface region was characterized with near-edge X-ray absorption fine structure (NEXAFS) spectra. Quantum mechanics indicates that the X-ray absorbance depends on how well the electric-field vector overlaps with the participating molecular orbitals. As the initial state is a symmetrical C 1s orbital in this case, only the final state, the carbon π^* orbital, accounts for the degree of such overlap. As the carbon π^* orbital is perpendicular to the molecular π plane, a dependency between the electric-field vector and the molecular π -plane is established, formulated in this equation: $I = A [P \cos^2 \theta (1 - \frac{3}{2} \sin^2 \gamma) + \frac{1}{2} \sin^2 \gamma]$, in which I is absorbance, P is degree of polarization, which is 0.9 for the bending magnet used in the present experiment, θ is

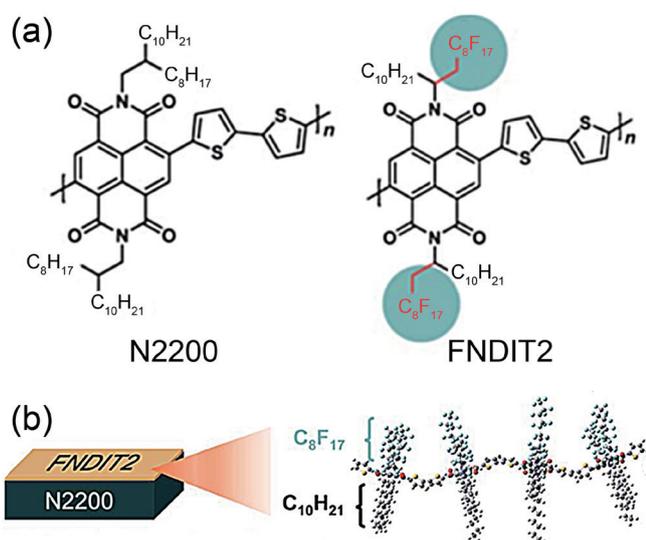


Fig. 1: (a) Molecular structure of the monomer unit of N2200 and FNDIT2. (b) A FNDIT2/N2200 surface-segregated monolayer. [Reproduced from Ref. 1]

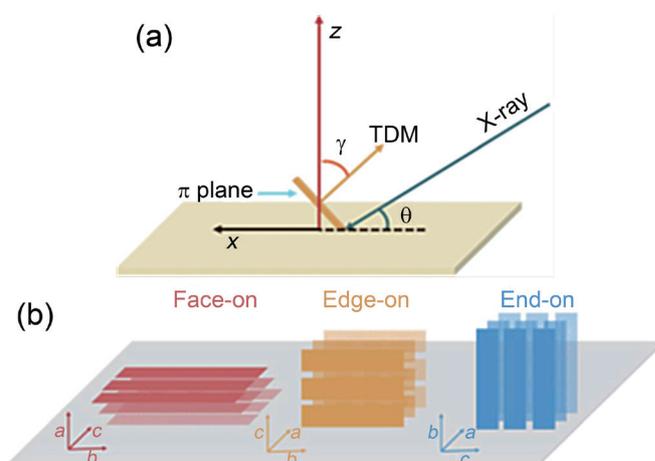


Fig. 2: (a) Schematic diagram of the NEXAFS experiment geometry. (b) Schematic diagram of molecular π -plane orientations. [Reproduced from Ref. 1]

incident angle of the X-ray beam, γ is the tilt angle of the molecular π -plane; A is an arbitrary proportional parameter. The set-up is illustrated in Fig. 2(b). Figure 3 depicts the dependency of the C 1s- π^* absorbance on the angle of incidence of the X-rays. The fitting outcome for tilt angle γ in the π -plane is 44° , which corresponds to a distorted face-on orientation. Thermal annealing at 260°C further flattens γ to 42° . In contrast, γ from the pure N2200 sample is 52° , which indicates an edge-on configuration; it turns 5° more upright upon the same thermal annealing. Even though the annealing treatment further rectifies the orien-

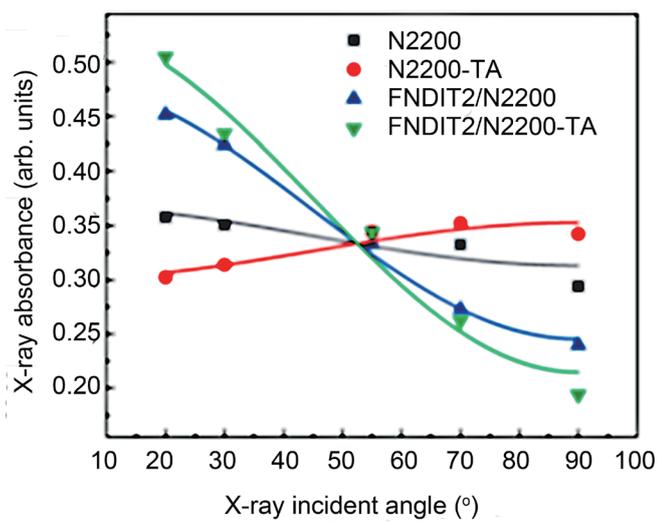


Fig. 3: Angularly dependent C 1s- π^* absorbance of N2200 and FNDIT2/N2200 SSM. TA stands for “thermal annealing”. [Reproduced from Ref. 1]

tations, the fact that it does not disturb the film integrity also demonstrates the thermostability. As a complement to NEXAFS spectra, grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements showed that the π -plane of the FNDITN2/N2200 SSM has a ratio 1:2 of edge-on to face-on. This result is derived from the crystalline part of the specimen, as only the crystallites contribute to the diffraction signal.

“The interface is the device,” pointed out by Herbert Kroemer, the 2000 Nobel laureate in physics. For decades, interface engineering has been a major task for the development of science and technology. The work presented here demonstrates a synthetic route for a π -conjugated polymer monolayer with a characteristic π -plane orientation. The combination of NEXAFS and GIWAXS spectra also effectively determines such an orientation. It carves a path for forging functional organic/metal or organic/organic interfaces to build layered composite structures used in organic electronic devices. (Reported by Dr. Bo-Hong Liu)

This report features the work of Yaw-Wen Yang, Chain-Shu Hsu, Keisuke Tajima and their collaborators published in J. Mater. Chem. A 8, 6268 (2020).

TLS 24A1 BM – (WR-SGM) XPS, UPS, XAS, APXPS

- XPS
- Soft Materials, Chemistry, Conjugated Polymers

Reference

1. W. C. Wang, S. Y. Chen, Y. W. Yang, C. S. Hsu, K. Tajima, J. Mater. Chem. A 8, 6268 (2020).

