

Single Molecular Bilayers of Organic Semiconductors Realized through Geometrical Frustration

We have developed a solution-based technology to form ultrathin organic-semiconductor layers with single-molecular-bilayer thickness. We used geometrical frustration to suppress multilayer crystallization, while maintaining intralayer molecular ordering, using an extended π -conjugated framework asymmetrically substituted by an alkyl chain (Ph-BTBT- C_n). Blade-coating with a solution containing two Ph-BTBT- C_n s with different alkyl-chain lengths yielded single-molecular bilayers (SMBs). Synchrotron X-ray diffraction and reflectivity measurements revealed that chain-length disorder did not perturb in-plane crystalline order, but effectively suppressed multilayer crystallization. The uniformity and size of fabricated SMBs were unprecedented compared to other self-assembly processes. This finding should pave the way for SMB-based super-flexible electronics.

Single-molecular bilayers (SMBs) are the basic components of cell membranes of living organisms and have been studied as they are fundamental for molecular nanostructures composed of biological lipids or synthetic amphiphiles. The uniqueness of SMBs is their nanometer-scale controlled thickness, which is well defined by the double length of constituent molecules. However, artificial SMBs produced thus far are unavoidably unstable and fragile under atmospheric conditions [1, 2], limiting their use in next-generation nanotechnology applications such as printed electronics [3]. Their features are closely associated with the fairly weak intermolecular interactions between constituent molecules.

We demonstrate an alternative approach to producing air-stable SMBs using molecules with an extended π -electron skeleton (π -Core). Recently, rod-shaped molecules composed of asymmetrically alkylated π -Cores were developed as high-performance organic semiconductors. These molecules have high-layered crystallinity associated with bilayer herringbone-type molecular packing, as exemplified by 2-phenyl-7-alkylated-[1]benzothieno[3,2-b][1]benzothiophene (Ph-BTBT- C_n) [4, 5] [see Fig. 1(a)]. The crystal structures of these molecules are characterized by molecular bilayers comprising antiparallely aligned polar monomolecular layers, resulting in head-to-head contact of π -Cores. The magnitude of intralayer interactions is much stronger than that of interbilayer interactions. The resulting high-layered crystallinity enables efficient two-dimensional carrier transport and the formation of smooth channel/gate-insulator interfaces, leading to the eventual realization of high-performance organic thin-film transistors (TFTs) [6]. To weaken interbilayer interactions, we introduced geometrical frustration to suppress multiple stacking of molecular bilayer units by taking advantage of the controllable nature of substituent alkyl-chain lengths while maintaining the strong intralayer interactions. Accordingly, two types of molecules with different alkyl-chain lengths (i.e. Ph-BTBT- C_6 and Ph-BTBT- C_{10})

were dissolved in chlorobenzene at various ratios while maintaining a constant concentration. We set the volume fraction of solutions with longer alkyl chain to 0.1. Note that the π -Cores of these molecules are identical, in contrast to the substituted alkyl chains shown in Fig. 1(a). Thus, the introduction of fewer longer alkyl-chain molecules results in a protuberance that geometrically frustrates the stacking of molecular bilayers, whereas the intralayer packing motif is unaffected by the residual part of longer alkyl chains, as schematically shown in Fig. 1(b). The mixed solutions were blade-coated on a Si-wafer covered with a 100-nm thermally grown silica layer. This methodology enabled the fabrication of a mono-colored ultrathin film of constant thickness with no obvious cracks over nearly the entire wafer area, as presented in Fig. 1(c). Note that the film thickness measured by atomic force microscope corresponds to the c-axis lattice constant (or bilayer thickness) of Ph-BTBT- C_6 .

Through synchrotron X-ray diffraction (XRD) and reflectivity measurements, we demonstrated that the obtained mono-colored films are composed of highly uniform and self-organized SMBs, as shown in Fig. 2. Figure 2(a) shows thin-film XRDs associated with the in-plane crystalline order. A single peak was clearly observed at scattering vector $q = 1.61 \text{ \AA}^{-1}$, which can be attributed to the (020) Bragg reflection of Ph-BTBT- C_6 . Evidence of a Bragg rod is also observed in the image shown in the upper panel of Fig. 2(a). Figure 2(b) presents the X-ray reflectivity (XRR) spectrum of the obtained film, which was simulated based on the assumed structure of SMBs, as schematically shown in Fig. 1(c) (i.e., the SMB is composed of antiparallely aligned polar monomolecular layers with head-to-head contact of π -Cores). Notably, the head-to-head molecular alignment in the SMB is consistent with our hypothesis that the introduction of chain-length disorder prevents multiple stacking of molecular bilayer units through geometrical frustration while minimizing the influence on intralayer crystallization.

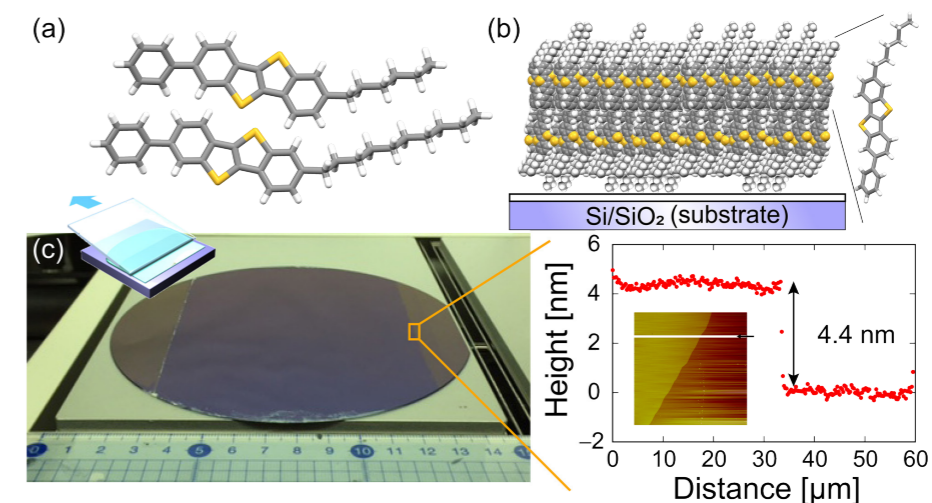


Figure 1: Production of a single-molecular bilayer. (a) Chemical structure of Ph-BTBT- C_n . (b) Schematic representation of geometrical frustration produced by alkyl-chain-length disorder. (c) (left) Photograph of a wafer-scale SMB produced using a mixed solution of Ph-BTBT- C_6 and Ph-BTBT- C_{10} . (right) Height profile of the SMB.

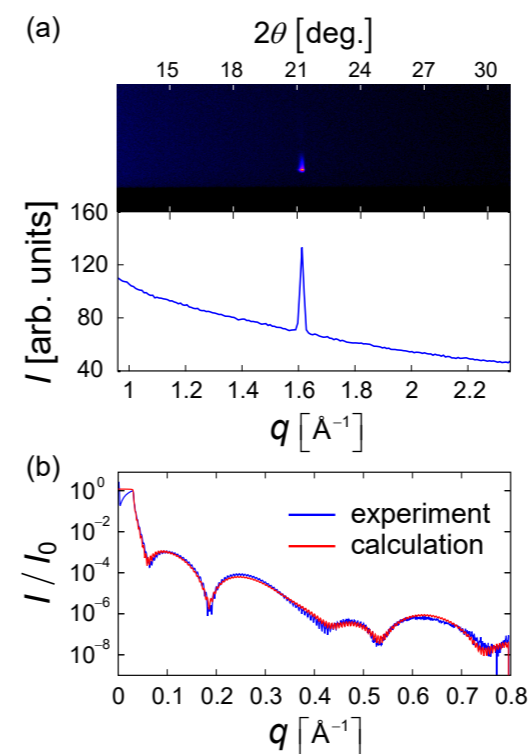


Figure 2: Characterization of fabricated SMB using synchrotron XRD and XRR measurements. (a) In-plane thin-film XRD image and profile of the fabricated SMB. (b) Thin-film XRR spectrum of the fabricated SMB. The incident X-ray photon energy is 9.0 keV.

To investigate the semiconducting properties of SMBs, we fabricated bottom-gate top-contact TFTs based on the fabricated SMBs. Typical mobility was estimated as $6.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the saturation regime [7]. The obtained SMBs exhibited excellent device characteristics, exceeding those of amorphous Si TFTs.

In summary, we successfully developed a technique of manufacturing self-assembled SMBs that have uniformity of both molecular-level thickness and in-plane crystalline order. These SMBs were reproducibly created by a simple blade-coating technique in which geometrical frustration produced by chain-length disorder was introduced. We believe the technique is applicable to a wide variety of molecules composed of π -Cores substituted by alkyl chains. The obtained SMBs also afford high-performance TFTs exceeding those of amorphous Si TFTs. These findings should open a new route to SMB-based ultrathin super-flexible electronics.

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BEAMLINES

BL-7C, BL-8A and BL-8B

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