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An asymmetric oligomer based on thienoacene for solution processed crystal organic thin-film transistors[†]

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A novel thienoacene-based conjugated oligomer, *i.e.* BTTT-T-C12, was designed and synthesized. Its highly asymmetric structural feature enables the preparation of two-dimensional single-crystalline thin films in millimetre size and ~100 nm thick by a solution processing method directly on the Si/SiO₂ substrate. Single crystal organic thin film transistors exhibit a mobility of 0.70 cm² V⁻¹ s⁻¹ and an on/off ratio of 5.7 × 10⁴.

High mobility organic semiconductors are of great interest for their applications in electronics, such as organic thin film transistors (OTFTs).¹⁻⁴ It is well known that the performance of OTFTs was noticeably affected by the quality of the thin films besides the chemical and crystalline structures of the semiconductors. For example, grain boundaries usually function as traps which limited the transport of charge carriers between crystal domains. Therefore, the preparation of highly ordered organic semiconductor thin films with large domain size is crucial for making high performance OTFTs.⁵

Single-crystal OTFTs (SCOTFTs) have been developed as an ideal tool for exploring the intrinsic charge transport properties of organic semiconductors due to the absence of extrinsic effects of grain boundaries and molecular disorders which are usually present in the polycrystalline films.^{6–8} Traditionally, SCOTFTs were fabricated by laminating the single crystals, which are grown either by physical vapor transport or solution crystallization method, on the substrate.⁹ Recently, directly growing the single crystals on the substrates for fabrication of SCOTFTs was also reported.¹⁰ However, most of the single crystals in these reports are microribbons or two-dimensional (2D) crystals in the micrometre size or even nanometre size, which makes the fabrication procedure fairly complicated and the SCOTFTs lack practical usefulness.

For the fabrication of high performance OTFTs, an ideal case is to make 2D single crystal thin films in large areas directly on the substrate.¹¹ However, making these films with ≤ 100 nm thickness directly on the substrate, especially *via* the

solution processing method, is very challenging since the single crystal growth of organic semiconductors was governed by many factors, such as weak intermolecular interactions and interface property.⁷ Obviously, the preparation of large area 2D single crystal thin films not only needs the control of the crystallization process, but also requires semiconductors with appropriate chemical and crystalline structures. It was reported that the asymmetric conjugated oligomers could form crystalline films with much larger grains than their symmetric counterparts,¹² and thienoacene-based semiconductors exhibit high field-effect mobility.¹ Moreover, one can postulate that increasing the asymmetry of the molecules should be able to suppress the crystal growth along the substrate surface normal and therefore is beneficial for growing 2D thin crystals. In the current paper, by combining the features of asymmetric conjugated oligomers and thienoacene-based semiconductors, we designed and synthesized a highly asymmetric conjugated oligomer which shows 2D crystallization behavior. Single crystal thin films with a thickness of ~ 100 nm and lateral dimensions of several millimetres can be prepared directly on the Si/SiO₂ substrates by dip coating. SCOTFTs were fabricated with typical bottom-gate and top contact device geometry, which exhibited a mobility of $\sim 0.70 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an on/off ratio of 5.7×10^4 .

Fig. 1a shows the structure of the conjugated oligomer **BTTT-T-C12**. Its synthesis is summarized in ESI.[†] The molecule comprises three parts, thienoacene **BTTT**, thiophene and dodecyl.



Fig. 1 Chemical structure (a) and the molecular packing diagrams projected along the molecular long axis (b) and the b axis (c) of conjugated oligomer **BTTT-T-C12**.

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The introduction of a dodecyl chain not only improves the solubility, but also increases the asymmetry of the molecules. The plate-like single crystals can be grown through slow evaporation of the mixture solution of toluene and chlorobenzene for single crystal X-ray analysis. As shown in Fig. 1b, BTTT-T-C12 molecules adopt a herringbone packing motif in the ab plane with an intermolecular packing angle of approximately 51°, reminiscent of high performance organic semiconductors such as pentacene,¹³ C12-BTBT,¹⁴ and DNTT.¹⁵ In addition, a 2D network of intermolecular interactions exists through short S...C contact (3.36 Å) between the edge-to-face molecules and S...S contact (3.46 Å) between the parallel molecules, which are shorter than the van der Waals sum of S and C (3.56 Å) and S and S (3.68 Å), respectively. These short contacts were also observed in the single crystals of C12-BTBT¹⁴ and may be the main driving force for the formation of plate-like single crystals. Along the *c* axis, the molecules form a layer-by-layer structure consisting of antiparallel alignment of molecules in the unit cell (Fig. 1c). The plane of a conjugated backbone is nearly perpendicular to the *ab* plane with a dihedral angle of approximately 87° .

Dip coating, which has been proved to be an effective method for controlling growth of highly crystalline films of organic semiconductors,^{16,17} was employed to prepare the single crystal films of BTTT-T-C12 on Si/SiO₂ substrates modified by phenyltrichlorosilane (PTS). Solution concentration, solvent composition and withdrawal speed were optimized. As shown in Fig. 2a, with a withdrawal speed of 0.01 mm min⁻¹, a mixed solvent of toluene and chlorobenzene (6/1 v/v) and a concentration of 2 mg ml⁻¹ of BTTT-T-C12, 2D single crystalline films with lateral dimensions of 3-6 mm and a thickness of ~ 100 nm could be prepared at room temperature as measured by optical microscopy and AFM (Fig. S2, ESI[†]). Fig. 2a and b show micrographs of the single crystal film without and with a polarizer. The variation of the colors in different areas is attributed to the thickness difference.¹⁸ The films have anisotropic characteristic as indicated by the reflected-light-intensity minima when the films were rotated $\pm 45^{\circ}$ to the polarizer (inset of Fig. 2b). The AFM image of the fringe of the film showed the terrace morphology and the steps are approximately 5.7 nm (Fig. 2c and Fig. S3, ESI[†]). In addition, over the range of micrometre-scale terraces, the surface is molecularly flat. The terrace-and-step structure is typical of representative organic single crystals such as rubrene and pentacene.¹⁹ In order to confirm the single crystal nature of the film, thin-film X-ray diffraction (XRD) and electron diffraction were conducted. As shown in Fig. 3a, the thin-film XRD pattern shows sharp and strong diffractive peaks up to 31st order. The primary diffraction was observed at $2\theta = 1.58^{\circ}$ corresponding to the *d*-spacing of



Fig. 2 Optical micrographs without (a) and with (b) crossed polarizers and AFM image of the fringe (c) of the single crystal film. The inset of (b) indicates that the reflected-light-intensity minima were observed for films rotated $\pm 45^{\circ}$ to the polarizer.



Fig. 3 Thin-film XRD and proposed packing model of BTTT-T-C12.

5.58 nm, suggesting the edge-on alignment of molecules with respect to the substrate surface (Fig. 3b). The *d*-spacing is in consistence with the step height observed from AFM and little shorter than the length of the c axis (5.67 nm) in the single crystal. The difference of the interlayer distance between the thin film and single crystal may be ascribed to the transformation of the dihedral angle between the dodecyl chain and the planar skeleton or the less inclination of the molecular long axis with respect to the substrate normal. Typical selected area electron diffraction (SAED) patterns of single crystal films were observed as shown in Fig. 4. No change in the SAED pattern was observed at different sections of the same film, indicating that the whole film was uniform. The diffraction pattern corresponds to the herringbone structure, and implies a less tight packing in the *ab* plane than in the single crystals (for details see ESI[†]). All the above results strongly indicate that the whole film is a single crystal. The formation of such 2D large-area single-crystal films can be attributed to the low nucleation density at a low withdrawal speed and 2D crystal growth mode of the molecules due to the strong 2D intermolecular interaction network as revealed by the single crystal structure analysis and the highly asymmetric molecular structure. The asymmetry of the molecules may be helpful for lowering the growth rate along the substrate surface



Fig. 4 Selected area electron diffraction patterns (1–5) of the single crystal films in the different area.



Fig. 5 The top-contact device geometries (a). (b) The photographic image of an OTFT device. The width and length of the channel are 1500 and 50 μ m, respectively. Typical output (c) and transfer (d) curves of the OTFTs.

normal, allowing the preparation of ~100 nm thick single crystal films. In contrast, **DTBDT-C9**¹⁷ and condensed benzo-thiophene derivative²⁰ adopt a 1D π - π stacking motif in the crystals and the thin film prepared by dip-coating shows a rod or dendritic-like morphology.

Top-contact SCOTFTs with a configuration as shown in Fig. 5a were fabricated on the entrained single crystal films by vacuum deposition of a hexadecafluorophthalocyanine/copper phthalocyanine (F₁₆CuPc (3 nm)/CuPc (3 nm)) buffer layer and Au source and drain electrodes (40 nm) in succession through a shadow mask. The resulting devices have a channel width (W) of 1500 μ m and a channel length (L) of 50 μ m (Fig 5b). Since BTTT-T-C12 exhibits a deep highest occupied molecular orbital (HOMO) energy level at -5.57 eV as estimated by cyclic voltammogram measurement (Fig. S4, ESI[†]), the F₁₆CuPc/CuPc buffer laver²¹was used in order to reduce the contact resistance. At least 6 devices were fabricated for confirming the reliability. Device performance measurements were done in an ambient atmosphere. The typical output and transfer curves of the devices are shown in Fig. 5c and d, and the mobility was calculated from the saturation regime. For the devices with the channel length along the dip-coating direction, a mobility of 0.6–0.7 cm² V⁻¹ s⁻¹ with a threshold voltage of -10 to -15 V and a current on/off ratio of 10^5 was achieved. The mobility perpendicular to the dip-coating direction was $0.2-0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, one third of that along the dip-coating direction. It is found that a non-linear drain current increases at a low-drain voltage even with the F₁₆CuPc/CuPc buffer layer. A similar phenomenon was also observed in other SCOFETs.^{10a,b,22} This should be ascribed to the injection barrier at the metal/organic-semiconductors interface^{10a,b} or the high resistance of the films itself from the metal to the conductive channel.22

In conclusion, we have shown that the single crystal film with lateral dimensions of several millimetres can be prepared from a highly asymmetric conjugated oligomer by a dip-coating method. A high mobility of 0.7 cm² V⁻¹ s⁻¹ along with the high current on/off ratio has been realized with a device structure generally used in solution processed OTFTs. These results provide a

conceptual idea for designing solution processed organic semiconductors capable of forming highly ordered thin films in large areas.

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Notes and references

‡ Crystal data: C₂₈H₃₂S₄, M = 496.76, triclinic, space group $P\overline{I}$, a = 5.8660(7) Å, b = 7.5451(9) Å, c = 56.721(7) Å, $\alpha = 91.309(2)^{\circ}$, $\beta = 91.191(2)^{\circ}$, $\gamma = 90.093(2)^{\circ}$, V = 2509.2(5) Å³, T = 185(2) K, Z = 4, 12 251 reflections measured, 8584 unique ($R_{int} = 0.0261$). $R_1 = 0.1367$, w $R_2 = 0.3014$. CCDC 863201.

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