

Inkjet Printing of Single-Crystal Films of Organic Molecular Semiconductors for Flexible and Printed Electronics

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ABSTRACT

This paper summarizes our works on printed electronics based on organic semiconductors (OSCs) focusing on OSCs with high layered crystallinity. Through the development of unique inkjet printing technique and OSCs compatible with this technique, we have succeeded in fabrication of single-crystal films and dramatically improving the device performance.

1 Introduction

Printed electronics utilizing the solubility, processability in ambient condition, flexibility, and structural designability of organic semiconductors (OSCs) is expected to be an important trend in next-generation electronics. However, while excellent solution-processable OSCs have been developed in the last 20 years, processes to fabricate high-quality OSC films that can sufficiently exhibit their intrinsic electrical performance had not been established.

In 2011, we have succeeded in developing “double-shot inkjet printing (DS-IJP)” technique and fabricating single-crystal films of OSCs [1]. By introducing the concept of antisolvent crystallization into microfluidic inkjet process, controlled crystal growth and formation of exceptionally uniform films of OSCs can be achieved. Single-crystal films by DS-IJP afford high-performance organic thin-film transistors (OTFTs) whose mobility can be more than 100 times higher than previous polycrystalline OTFTs by conventional printing method and is comparable to that of oxide TFTs. This is the first report demonstrating fabrication of high-quality films of OSCs by industrially advantageous process such as inkjet printing, opening a promising perspective for printed and flexible electronics.

We found that the key feature to realize growth of single-crystal films in printing process, not just in DS-IJP, is high layered crystallinity of OSCs [2-5]. Meanwhile, OSCs have been strongly required to satisfy sufficient solubility, thermal and chemical stability, and semiconductor performance all together. Thus, we summarized how the layered crystallinity and these properties of OSCs are modulated by molecular design based on the systematic investigation of the substituent effects on these properties and crystal structures [6, 7].

In the following sections, we present the procedure and mechanism of DS-IJP and high performance OSCs with

high compatibility with printing, respectively.

2 DS-IJP of Single-Crystal Films of OSCs

In DS-IJP, an antisolvent for OSC (crystallization ink) and a solution of OSC (OSC ink) are deposited individually in sequence at the same position on the substrate using two inkjet nozzles. A schematic representation of the printing process is shown in Fig. 1(a). For DS-IJP of *di*-C₈-BTBT (2,7-dioctyl[1]benzothieno[3,2-*b*][1]benzothiophene) [1, 8], the crystallization ink is *N,N*-dimethylformamide, OSC ink is 1,2-dichlorobenzene solution (1 wt%), the substrate is doped p⁺-silicon wafers with 100 nm-thick SiO₂ layer and the substrate temperature is kept at 30°C. The OSC ink spreads over the surface of the droplet of crystallization ink to form a thin liquid layer, where two-dimensional self-organization of *di*-C₈-BTBT molecules and following single crystal growth ideally proceed [1, 3]. The resultant OSC film covering the droplet surface gradually falls off as the underlying solvent evaporates (Fig. 1(b)).

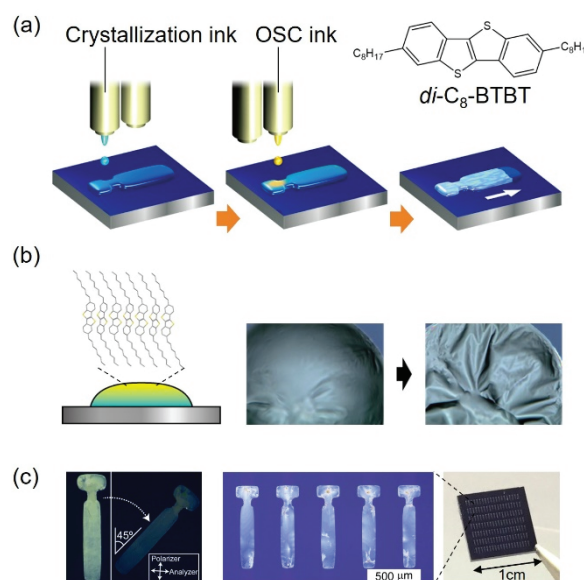


Fig. 1 (a) Schematics of DS-IJP process [1]. (b) Crystal growth at liquid-air interface. (c) Optical microscope images of printed films of *di*-C₈-BTBT.

Defining a lyophilic area containing a protuberance part on the substrate surface was found to be effective to induce single crystal growth by causing local seeding in the protrusive area. After seeding, the growing front moves to the other end of the droplet to cover the entire surface of the droplet by single-domain film as shown in Fig. 1(a). Single-domain nature over few hundred micrometers was confirmed by polarized optical microscope observation (Fig. 1(c)) and X-ray diffraction measurement. Such high-quality films can be printed at desired positions reproducibly under the ambient condition (Fig. 1(c)). For top-gate top-contact devices, the mobility in the saturation regime was as high as $16 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ on average, on/off current ratio is 10^5 – 10^7 and V_{th} of about -10 V .

As presented above, high layered crystallinity of OSCs is quite compatible with not just the film formation mechanism of DS-IJP but other printing or coating technique and regarded as a key requirement for solution-processable OSCs, thus the next issue is how to design such OSCs.

3 Requirements for solution processable OSCs

Most of solution-processable OSCs are based on planar π -electron skeletons like acenes or thienoacenes introducing alkyl chains or bulky groups as substituents. The molecular packing structures for these π -electron skeletons in the crystal can be classified into some typical motifs. Among them, layered herringbone (LHB), where π -electron skeletons are arranged in face-to-edge fashion to form two-dimensional layers, is known to be most suitable for obtaining high-performance TFTs due to efficient carrier transport within the layers. However, such molecular packing in the crystal can be easily altered by slight change in molecular structure and the origin of layered crystallinity was not well understood.

We systematically investigated stabilization and modulation of layered-herringbone (LHB) packing based on systematic crystal structure analyses for alkyl-substituted BTBT derivatives shown in Fig. 2(a) [6, 7]. BTBT without substituents adopts LHB packing. By introducing relatively short alkyl chains, non-layered one-dimensional columnar arrangements arise for asymmetrically substituted BTBTs and π -stacking motifs for symmetrically substituted BTBTs. Longer alkyl chains induce LHB packing again (Fig. 2(b)) for all alkylated BTBTs ($n = 4$ – 6). The shapes of the crystals of these BTBTs prepared by recrystallization from solution correspond their respective packing motifs, e.g., needles for columnar motif and thin flakes for LHB.

All three series of BTBTs show similar alkyl chain length dependence in solubility and thermal property. As shown in Fig. 2(c) for *mono*- C_n -BTBTs, the rapid increase and decrease at relatively short alkyl chain length regions correspond to the variation of molecular packing, while the subsequent gradual decrease at longer n can be ascribed

to the increased intermolecular interaction energies between the neighboring alkyl chains in the crystals. Melting points and phase transition temperatures, which relate to the thermal durability of OTFTs, are also affected by intermolecular interactions in the crystals. These trends as well as stabilization of LHB can be explained by intermolecular attractive forces between the neighboring alkyl chains evaluated by DFT calculations based on the single crystal structures (Fig. 2(b)). All results clearly demonstrate how and why the alkyl chains play crucial roles in the formation of LHB packing and the modulation of the material properties. It would be useful to mention that introducing phenyl group increases thermal stability in Ph-BTBT- C_n derivatives. This indicates the advantage of asymmetrical molecular design by introducing different substituents, where the alkyl chain induces the formation of LHB and the other substituent control the material properties. We confirmed that the BTBT derivatives with LHB synthesized in this study gave single-crystal films by DS-IJP or other printing techniques as well as high performance OTFTs, as expected [9].

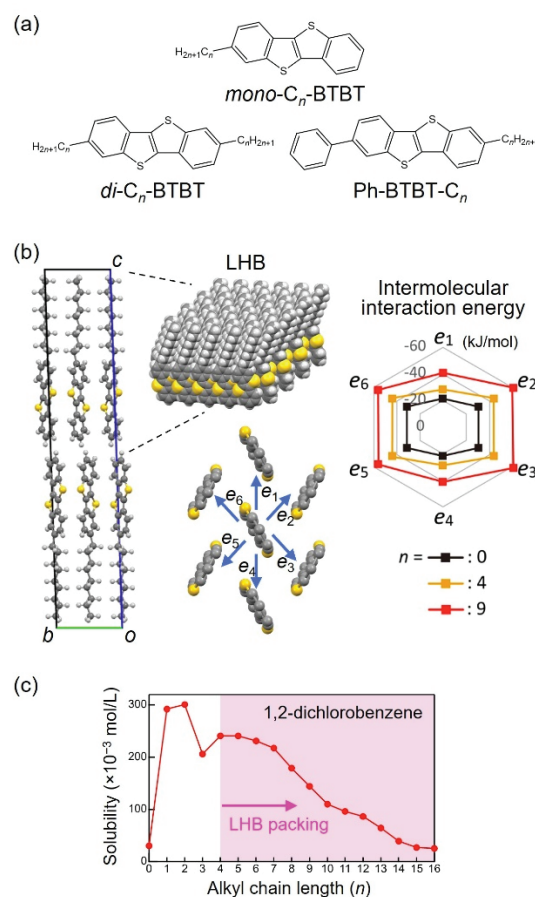


Fig. 2 (a) Alkylated BTBT derivatives. (b) Crystal structure (*mono*- C_9 -BTBT), LHB packing and calculated intermolecular interaction energy. (c) Solubility at 25°C of *mono*- C_n -BTBTs.

The diversity of organic materials and weak non-covalent intermolecular interactions between them are very complex to control and manipulate, but we have provided a basic understanding of general trends for high performance solution-processable OSCs. Recent active research on a wide variety of OSC materials will help to establish a fundamental knowledge on general material design for OSCs [10-13].

4 Conclusions

By using inkjet printing technique and OSCs that focused on the layered crystallinity, inkjet printing of single-crystal films and fabrication of high-performance OTFTs was successfully demonstrated. Basic understanding of general trends to induce layered crystallinity originating from LHB packing and tune material properties for alkylated BTBT derivatives was also reported. Deep insights into both materials and printing process conditions taking advantage of the diversity and designability of organic materials will lead to further progress toward practical applications.

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