

## Extended-chain lamellar crystals of monodisperse polyfluorenes

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### ABSTRACT

Polymer single crystals of monodisperse poly (9,9-dioctylfluorene)s (PFOs) with actual molecular weights of 6220, 12,437 and 24,874 Da corresponding to the numbers of fluorene repeating units of 16, 32 and 64, respectively, were grown from chloroform/ethanol solutions. In the single crystals, polymer chains adopt lamellar packing motif. The crystal structure determined by electron diffraction is identical for all three PFOs, and the single crystal has an orthorhombic unit cell with lattice parameters of  $a = 2.16$  nm,  $b = 1.28$  nm, and  $c = 3.36$  nm. In these lamellar crystals, PFO backbones are arranged perpendicular to the lamellar surface and alkyl side chains are along the crystal-growth direction. The lamellar thickness is identical to the extended chain length of the corresponding polymer as demonstrated by atomic force microscopy (AFM) measurements. It is noteworthy to point out that F64 still maintain extended-chain packing habit even when the chain length is as long as 53 nm. Therefore, our results demonstrated that chains remain extended in this system.

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### 1. Introduction

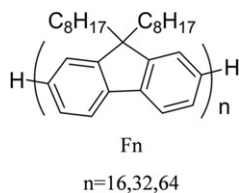
Conjugated polymers (CPs) have attracted much attention for their great potential in the application to low-cost optoelectronic devices that are prepared by solution processing [1–3]. It is well-documented that the performance of devices based on CPs heavily depends on the solid-state structure of CPs and the preparation process such as the solvent-evaporation rate [4–6] and annealing conditions [7–9]. From this viewpoint, understanding the crystallization mechanism and crystal structures of CPs is critically important. Nevertheless, the understanding for CP crystallization is still obscure and has to be learned from the past knowledge gathered on flexible chain polymers [10–15]. Among various crystallization behaviours of CPs, polymer chain folding or nonfolding behaviour has been one of the major subjects of intensive investigations. Chain folding phenomenon [16] has been observed in a wide variety of flexible chain polymers such as polyethylene [17–19], and was accepted as a characteristic feature of polymer crystallization. Nevertheless, rigid CPs exhibit different behaviours from flexible chain polymers. A revitalized interest in chain nonfolding in CP crystals has been stimulated by recent studies [20,21]. From a fundamental viewpoint, single crystals are ideal substances to investigate the crystallization behaviours of polymers, since they can

not only provide the fundamental structural information but also elucidate polymer chain interactions and molecular packing in the bulk materials. In despite of these, there was very limited literature on CP single crystals. Although single crystal structures of regioregular poly (3-butylthiophene) (P3BT) [20], poly (3-hexylthiophenes) (P3HT) [22,23], poly (3-octylthiophene) (P3OT) [24] and thioacetate substituted poly (para-phenylene ethynylene) (TA-PPE) [5] were studied to some extent, the data are not sufficient to prove that polymer chains are extended or folded. Chain folding of poly (3-alkylthiophene)s (P3ATs) has been experimentally evidenced by scanning probe microscopy [25–28] and transmission electron microscopy (TEM) [21,29,30], but it is still a great challenge to clarify chain behaviours in single crystals from solution crystallization [20,31]. The difficulty may come from the polydisperse nature of CPs, originating from the polymerization method, which introduces new parameters that significantly affect the physics of crystallization. Moreover, the molecular weight, side chain length, rigidity of conjugated backbones, and crystal growth conditions such as the choice of solvent, have an effect on the crystallization process.

To overcome the problem, monodisperse CPs with the defined chain length is an ideal system for studying the polymer crystallization and crystal structure. Based on this consideration, monodisperse poly (9,9-dioctylfluorene)s (PFOs) [32–36], one kind of the most extensively studied CPs, were chosen to investigate the crystallization mechanism and crystal structures of PFOs. Although most of them are concentrated on the morphology and structure in solutions [37–39] and crystalline films [40–45] in the pioneering

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**Chart 1.** Structure of monodisperse PFOs, which abbreviated as Fn.

studies of PFOs, there is still lacking knowledge about the polymer chain behaviour in the single crystals.

In this study, we used monodisperse PFOs with the number of fluorene units of 16, 32 and 64 as samples, respectively. (Chart 1, abbreviated as F16, F32 and F64) By the crystallization of these samples from dilute solutions, we obtained rod-like crystals of micrometre sizes. Selected area electron diffraction (SAED) patterns demonstrated that the single crystals have an orthorhombic unit cell with lattice parameters of  $a = 2.16$  nm,  $b = 1.28$  nm, and  $c = 3.36$  nm. There are four chains in the unit cell, and the crystals have a density value of 1.112 g/mL. A combination of the scanning electron microscopy (SEM) and atomic force microscopy (AFM) leads to the observation of the lamellar morphology, and the individual lamellar thickness is almost the same as the extended chain length of the corresponding polymer. These lamellar features could be originated from the strong interactions of alkyl side chains. Most importantly, we first demonstrate the conjugated backbone of PFO is stacked perpendicularly to the lamellar surface with extended-chain conformation, regardless of polymer chain lengths.

## 2. Experimental section

### 2.1. Materials

The synthesis of F16, F32 and F64 was reported previously [46]. Chloroform and ethanol were purchased from Beijing Chemical Works and used without further purification.

### 2.2. Preparation of single crystals

The glass substrates (Corning 7059) with the size of  $1.0$  cm  $\times$   $1.0$  cm, were carefully cleaned by ultrasonic treatment in sequence of acetone, alcohol and deionized water. Finally, the substrates were dried with the stream of nitrogen. A mixed-solvent approach was employed for the growth of single crystals. Fn ( $n = 16, 32$  and  $64$ ) was dissolved into chloroform with a concentration of  $0.02$  mg/mL. Then ethanol was slowly added to tune the solubility parameter. The optimized chloroform/ethanol ratio (v/v) was 1:3 with a sample concentration of  $0.005$  mg/mL. Then the

**Table 1**

Summary of monodisperse PFOs with different molecular weights and contour lengths and average lamellar thickness in their prepared solution crystals.

Sample	$M_{MS}^a$ (g/mol)	PDI	Contour length <sup>b</sup> (nm)	Average lamellar thickness <sup>c</sup> (nm)
F16	6220.1	1.09	13.3	$14.2 \pm 2$
F32	12437.3	1.09	26.6	$26.5 \pm 3$
F64	24874.1	1.09	53.1	$54.6 \pm 3$

<sup>a</sup> Measured by MALDI-TOF mass spectrometry.

<sup>b</sup> Calculated according to the repeat distance of  $0.83$  nm [43] and the corrected  $M_{MS}$ .

<sup>c</sup> Determined by AFM, indicating a standard deviation.

solution was deposited onto the cleaned glass substrates placed on a platform inside a cylinder container with a radius and height of  $2.5$  and  $3.0$  cm, respectively, as shown in Fig. 1. The container was then carefully sealed for ensuring the crystal slow growth.

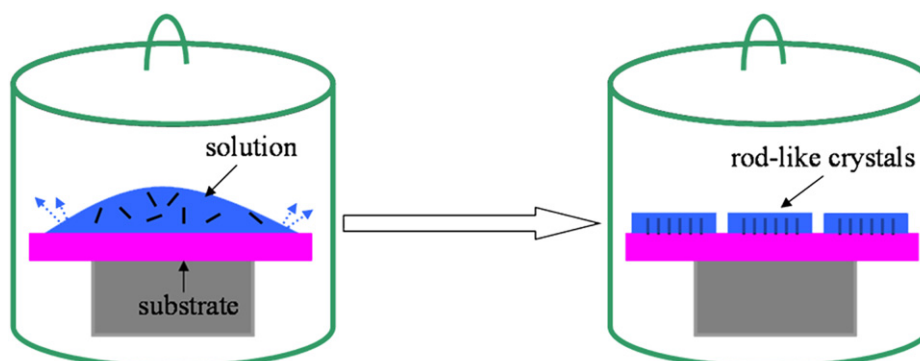
### 2.3. Characterization

The optical microscopy and SEM images were obtained using Zeiss Axio Imager A2m equipped with polarizer and FEL XL 30, respectively. TEM was performed on a JEOL JEM-1011 transmission electron microscope operated at an acceleration voltage of  $100$  kV. The grazing incident X-ray diffraction (GIXRD) measurement was performed using a Bruker D8 Discover Reflector (Cu  $K_{\alpha}$ ,  $\lambda = 1.54056$  Å) with generation power of  $40$  kV tube voltages and  $40$  mA tube current. AFM images were obtained using an SPA-300HV instrument with an SPI3800N controller (Seiko Instruments Inc., Japan) in tapping mode.

## 3. Results and discussion

The structures of Fn ( $n = 16, 32$ , and  $64$ ) are depicted in Chart 1, where  $n$  represents the number of fluorene units. The exact molecular weights obtained from MALDI-TOF mass spectrometry and the contour lengths are listed in Table 1. Fig. 1 shows the apparatus to grow single crystals. The solvent evaporation rate plays a vital role in the growth process. It could be noted that the closed jar slowed evaporation of the solvent and guaranteed polymer chains had sufficient time to grow into crystals. After one day, rod-like crystals were obtained for these samples.

Fig. 2a shows the optical images of the crystals of F16 with the typical dimensions of  $12$ – $600$  nm in height,  $0.2$ – $1.5$   $\mu$ m in width, and  $10$ – $200$   $\mu$ m in length. Their optical anisotropy was clearly observed under polarized light (Fig. 2b). Well-defined facets and smooth surface of the crystal of F16 can be seen from SEM (Fig. 2c and d). The SEM image of the crystal clearly shows a lamellar structure (Fig. 3a). Particularly, it is intriguing that the layer has been peeled off from the surface of the lamellar crystal of F16



**Fig. 1.** The apparatus to grow single crystals of Fn ( $n = 16, 32$ , and  $64$ ).

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