Chinese Chemical Letters 27 (2016) 523–526

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Original article

Solution-grown aligned crystals of diketopyrrolopyrroles (DPP)-based small molecules: Rough surfaces and relatively low charge mobility

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ARTICLE INFO

Article history:
Received 31 December 2015
Received in revised form 25 January 2016
Accepted 30 January 2016
Available online 12 February 2016

Keywords:
Diketopyrrolopyrrole
Crystals
Solution processing
Organic field-effect transistors
Morphology

ABSTRACT

Field-effect transistors (FETs) of three diketopyrrolopyrroles (DPP)-based small molecules, 3,6-bis(5-phenylthiophene-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4-dione (PDPPP), 3,6-bis(5-(4-fluorophenyl)thiophene-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4-dione (FPDPPPF) and 3,6-bis(5-(4-*n*-butylphenyl)thiophene-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4-dione (BuPDPPPBu), have been studied in this work. Well aligned crystals of the three molecules were grown from *para*-xylene by droplet-pinned crystallization method. FETs based on these aligned crystals exhibit a hole mobility up to 0.19 $cm^2 V^{-1} s^{-1}$ and electron mobility up to 0.008 $cm^2 V^{-1} s^{-1}$. The achieved hole mobility is of the same order of magnitude as reported highest hole mobility for DPP-based small molecules, but it is much lower than that of the high-performance DPP-based polymers. The relative low mobility is mainly attributed to the rough crystal surfaces with steps and, thus, non-smooth charge transport channels at the interfaces between the crystals and the dielectrics. This work has implications for understanding the low charge mobility of DPP-based small molecules.

1. Introduction

Over the past decades, organic semiconductors in field-effect transistors (FETs) have attracted great attention for their low-cost, flexible and large-area electronic applications such as memory devices [1,2], displays [3] and sensors [4]. Nowadays great achievements in FETs have been obtained based on small molecules and polymers through molecular design and device optimization [5–16]. Among organic semiconductors, diketopyrrolopyrroles (DPP)-based small molecules and polymers have aroused significant concern due to their promising application in organic FETs [17–19]. Experimentally, DPP-based polymer semiconductors show amazing performance. Liu *et al.* combined a highly-extended (E)-2-(2-(thiophen-2-yl)vinyl)thiophene (TVT) unit with the dithienyl-DPP unit, the co-polymer exhibited a high hole mobility up to 8.2 $cm^2 V^{-1} s^{-1}$ [20]. Lee *et al.* have developed a dithienyl-diketopyrrolopyrrole (TDPP) and selenophene containing polymer with hybrid siloxane-solubilizing groups (PTDPPSe-Si) [21]. After tuning the alkyl spacer length of the hybrid side chains, high hole and electron mobilities up to 8.84 and 4.34 $cm^2 V^{-1} s^{-1}$ have been obtained [22]. Li *et al.* developed a very high molecular-weight DPP-DTT-based polymer, which exhibited a very high mobility up to 10.5 $cm^2 V^{-1} s^{-1}$ in organic thin-film transistor (OTFT) devices [23]. Kim *et al.* investigated the relationship between molecular structure and electrical properties, and obtained remarkably high hole mobility up to 13.9 $cm^2 V^{-1} s^{-1}$ [24]. Besides, DPP based polymers showed good performance in electron transport as well. Li *et al.* added two 1-pyridinyl groups onto DPP core to alleviate steric interaction with the DPP core, and obtained the ambipolar performance with a high electron mobility value of 6.3 $cm^2 V^{-1} s^{-1}$ in OTFT devices [25]. Kwon *et al.* reported impressively high electron mobility up to 7.0 $cm^2 V^{-1} s^{-1}$ in polymer OFETs by introducing one nitrile group to the vinylene moiety to obtain PDPP-CNTVT [26]. Although great achievements have been made in DPP-based polymers, the performance of DPP-based small molecules is much lower. Currently, DPP-based small molecules exhibit the highest hole mobility of 0.7 $cm^2 V^{-1} s^{-1}$ in thin films prepared by vacuum deposition [27] and the highest electron mobility of 0.96 $cm^2 V^{-1} s^{-1}$ in crystals formed through the solvent–vapor evaporation crystal growth method [28]. The

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http://dx.doi.org/10.1016/j.cclet.2016.01.054

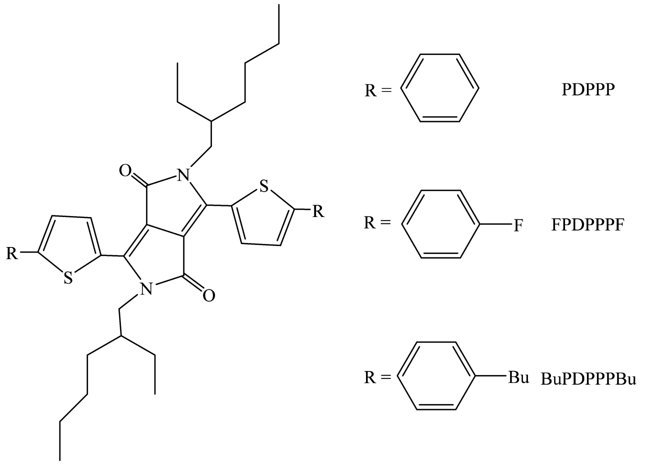

Fig. 1. The structures of DPP-based small molecules.

discrepancy between the DPP-based polymers and small molecules spurs investigation on the reason(s) for the low performance of the small molecules.

In this work, we studied three DPP-based small molecules with different substituent, diphenyl (PDPPP), di(4-fluorophenyl) (FPDPPPF) and di(4-*n*-butylphenyl) (BuPDPPPBu) groups (Fig. 1), respectively. We obtained well-aligned crystals by droplet-pinned crystallization (DPC) method [11]. Careful examination on the crystal morphologies reveals the rough and stepped crystal surfaces. FETs based on these aligned crystals showed hole mobility up to 0.19 $cm^2\,V^{-1}\,s^{-1}$ and electron mobility up to 0.008 $cm^2\,V^{-1}\,s^{-1}$ from PDPPP and FPDPPPF, respectively. The relatively low charge mobility is attributed to the non-intimate interface between the rough crystal surfaces and the substrate.

2. Experimental

PDPPP, FPDPPPF and BuPDPPPBu were synthesized according to the literature procedure and purified by chromatography on silica gel [29]. Orientated crystals were grown *in situ* on a piece of highly doped silicon substrate (1 cm × 1 cm) with 300 nm SiO_2. Divinyltetramethyldisiloxanebis(benzocyclobutene) (BCB) (Dow Chemicals) was modified on SiO_2, which was spin-coated from a mesitylene (Fluka) solution (V_{BCB}:$V_{mesitylene}$ = 1:30) and then thermally cross-linked on a hot plate in an N_2 glovebox. Organic semiconductors were dissolved in *para*-xylene (Sigma–Aldrich) with the concentration of 0.4 mg/mL. A solution (15 μL) was dropped onto the substrate with a piece of silicon wafer (0.3 cm × 0.3 cm, pinner) to pin the solution droplet. The substrate was placed on a Teflon slide inside a Petri dish (35 mm × 10 mm) sealed with parafilm on a hotplate of 30 ± 1 °C. After the solvent slowly evaporated, orientated crystals were formed in 30 min.

The morphology of crystals was characterized by optical microscopy (OM, Nikon LV100 POL) and atomic force microscope (AFM, Veeco). FETs were constructed in bottom-gate, top-contact configuration by depositing source and drain electrodes (80 nm Au), using a shadow mask with channel length (L) of 50 μm and width (W) of 1 mm. FETs performances were measured in an N_2 glovebox using a Keithley 4200-SCS semiconductor parameter analyzer. The measured capacitance of the BCB-covered SiO_2/Si substrate was 10 nF cm^{-2}, and this value was used for mobility calculation. For statistics, data of charge mobility are presented as mean ± SD.

3. Results and discussion

We used the DPC method [11] to grow crystals of the three DPP-based molecules of which the molecular structures as well as the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels have been shown in Fig. 1 and Table S1. Well-aligned long ribbons of several hundred micrometers in length were obtained from *para*-xylene (Fig. 2a–f). Crystal widths (about 10 μm) and heights (10's of nm) measured by atomic force microscopy (AFM) images from 10 ribbons are shown in Table 1.

Table 1
Thicknesses and widths of DPP-based crystals measured by AFM.

Crystals	PDPPP	FPDPPPF	BuPDPPPBu
Thickness/nm	18.9–59.7	17.9–50.4	16.6–38.8
Width/nm	8.6–17.2	5.0–14.1	4.1–17.6

Based on the aligned crystals, we proceeded to fabricate FETs by depositing Au source and drain electrodes through a shadow mask in a top-contact, bottom-gate configuration (Fig. 3d). Since the crystals did not fully cover the channel, the active W/L value was measured to calculate the mobility (Fig. 3e). All the devices were tested in the N_2 glovebox, and the saturation regime mobility was calculated. The saturation current (I_{SD}) can be obtained by Eq. (1), and then the saturation mobility (μ_{sat}) can be extracted using Eq. (2), where W is channel width, L is channel length, V_G is gate voltage, V_T is threshold voltage, and C is capacitance per unit area of the gate dielectric.

$$I_{SD} = \frac{W}{2L}\mu_{sat}C(V_G - V_T)^2 \tag{1}$$

$$\mu_{sat} = \frac{2L}{WC}\left(\frac{\partial\sqrt{I_{SD}}}{\partial V_G}\right)^2 \tag{2}$$

Here, we take PDPPP as an example. The typical transfer and output characteristics of PDPPP are shown in Fig. 3a and b, exhibiting good gate modulation. Histograms of hole mobility for 40 devices from 3 substrates are displayed in Fig. 3c. An average hole mobility (μ_h) of 0.079 ± 0.026 $cm^2\,V^{-1}\,s^{-1}$ (range: 0.036–0.15 $cm^2\,V^{-1}\,s^{-1}$, Fig. 3c, black bar) was obtained. After heating at 100 °C for 1 h and cooling down naturally, an obvious improvement in average hole mobility has been observed. The average hole mobility reached 0.090 ± 0.042 $cm^2\,V^{-1}\,s^{-1}$ (range: 0.036–0.19 $cm^2\,V^{-1}\,s^{-1}$, Fig. 3c, red bar). And on-to-off current ratio (I_{on}/I_{off}) > 10^5, threshold voltages (V_T) between −39 V and −62 V were also obtained. The FET characteristics of FPDPPPF and BuPDPPPBu are demonstrated in Fig. S1 in Supporting information. The FET performances of three molecules are summarized in Table 2. BuPDPPPBu molecular shows the average hole mobility of 0.013 ± 0.010 $cm^2\,V^{-1}\,s^{-1}$ (range: 0.0017–0.040 $cm^2\,V^{-1}\,s^{-1}$, Fig. S1g). Different from the other two molecules, FPDPPPF molecule exhibits ambipolar transport, with the average hole mobility of 0.036 ± 0.011 $cm^2\,V^{-1}\,s^{-1}$ (range: 0.017–0.063 $cm^2\,V^{-1}\,s^{-1}$, Fig. S1c) and average electron mobility of 0.0018 ± 0.0016 $cm^2\,V^{-1}\,s^{-1}$ (range: 0.00015–0.008 $cm^2\,V^{-1}\,s^{-1}$, Fig. S1f). The emergence of electron transport in this molecule is attributed to the lowered LUMO level due to the strong electron-withdrawing F substituents [30–33].

The achieved hole mobilities are among the highest values for the DPP-based small molecules, but they are much lower than the high-performance DPP-based polymers. In order to figure out the reason of the low mobility, we investigated the surface morphology of crystals with the aid of AFM (Fig. 2g–l). The AFM images of three crystals demonstrated their relative rough surface. In the detail images (Fig. 2j–l), the surface of the crystals is rough with many steps (RMS (root mean square) roughness ~1.2–4.6 nm). As a supporting evidence for the rough surface, the OM images of these crystals exhibit slightly different contrast along the crystals (Fig. 2a–f). The surface roughness is much larger than that of the typical spin coated polymer films (RMS roughness ~1 nm [34]). The rough crystal