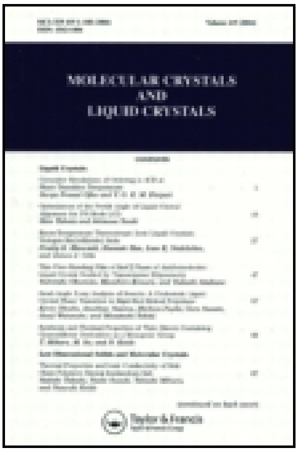

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Photo-Conversion and Structural Properties of the Drop-Cast Films of 6,13-Pentacene Diketone

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Published online: 11 Sep 2013.

To cite this article: C. Ohashi , H. Yamada & K. Nakayama (2013) Photo-Conversion and Structural Properties of the Drop-Cast Films of 6,13-Pentacene Diketone, Molecular Crystals and Liquid Crystals, 580:1, 103-109, DOI: 10.1080/15421406.2013.807724

To link to this article: http://dx.doi.org/10.1080/15421406.2013.807724

Mol. Cryst. Liq. Cryst., Vol. 580: pp. 103–109, 2013

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.807724

Photo-Conversion and Structural Properties of the Drop-Cast Films of 6,13-Pentacene Diketone

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6,13-pentacene diketone is a unique material which can be converted to pentacene only by photo irradiation. Drop-cast films of this soluble precursor of pentacene were prepared and their thin film properties were studied. The effect of solvent and photo irradiation conditions on photo-conversion behavior and film structures were investigated, compared to spin-cast films. The drop-cast films exhibited large plate-like crystals having a size of several microns, and showed intense peaks in X-ray diffraction. The electrical measurement using a field-effect transistor was also performed.

Keywords Drop-cast film; organic field-effect transistor; pentacene; soluble precursor; X-ray diffraction

Introduction

Organic thin-film transistors (OTFTs) have been interested due to their advantages in low-cost, flexible, and large-area production. In particular, organic field-effect transistors (OFETs) have been extensively studied in various fields of production techniques [1–3], materials, and electronic applications such as complementary circuits [4,5], displays [6], and sensors [7,8]. Many researches on FET materials have been classified into two categories, polymer semiconductors and small molecule semiconductors. The former is suitable for solution process, while the carrier mobility is generally lower. The latter can form highly crystalline film; however, it is difficult to be prepared by solution process. In general, high carrier mobility leading to high performance OFETs can be obtained in highly crystalline films. Therefore, "oligoacene" molecules like pentacene are ideal for OFET "devices" however, such rigid and large π-conjugated molecules tend to be insoluble. To improve low solubility of pentacene, some attempts have been made by synthesizing substituted pentacene molecule like TIPS-pentancene [9] and soluble precursor of pentacene [10–12]. We have proposed 6,13-pentacene diketone (PDK) [13] which is a soluble photoprecursor of pentacene. The PDK molecules can be converted to pentacene only by photo irradiation

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in solution and solid film. Thus far, OFET performance of the photo-converted pentacene films from PDK solution has been investigated in the spin-cast films [14]. However, the spin-cast films show poor crystallinity.

In this study, we investigated drop-cast films of photo-converted pentacene. The effect of solvent and photo irradiation conditions on the photo-conversion behavior and film structures were investigated and compared to spin-cast films. The OFET performance of the drop-cast films was also measured. The drop-cast films exhibited higher crystalline structure composed of large plate-like crystals and intense peaks in X-ray diffraction measurement. The difference of photo-conversion process in spin-cast and drop-cast films is discussed from the viewpoint of drying process of the cast solution.

Experiment

Figure 1 shows the experimental setup for preparation of photo-converted pentacene films. A glass substrate was employed for investigating UV/VIS absorption spectra, and *n*-type heavily doped Si wafer with a SiO_2 layer for evaluating OFET performance and film structures. The surface of SiO_2 was treated with 1,1,1,3,3,3-hexamethyldisilazene (HMDS) supplied from Sigma-Aldrich. The gold source and drain electrodes were prepared by vacuum deposition through a metal shadow mask. The channel length (L) and width (W) were 50 μm and 5.5 mm, respectively. The 6,13-pentacene diketone (10 mg/mL) was drop-cast and spin-cast from chloroform and *o*-dichlorobenzene solution. The cast films were irradiated with high brightness LED area lamp (Edmund Optics) with a wavelength of 470 nm, typical intensity of 200 mW/cm^2, and typical irradiation time of 30 min in a nitrogen glove box system where the concentrations of H_2O and O_2 are less than 1 ppm. UV/VIS spectra of the organic thin films were measured by spectrophotometer (JASCO, V-650).

Figure 1. The experimental setup for preparation of photo-converted pentacene films. Photochemical reaction scheme of PDK is also shown.

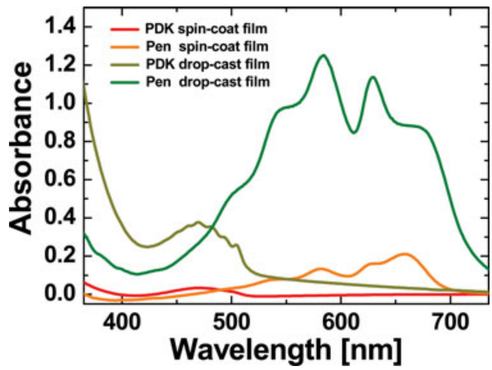

Figure 2. UV/VIS absorption spectra of the PDK (soluble precursor) films and photo-converted pentacene films prepared by spin-casting and drop-casting.

The film structures were evaluated by a digital microscope (Olympus, LEXT OLS4000), and X-ray diffractometer (Rigaku, SmartLab).

Measurements of OFET devices were carried out using a semiconductor parameter analyzer (Agilent, 4155C) in a nitrogen glove box. The mobilities were determined in the saturation regime by using an equation of $I_{DS} = (\mu WC_i/2L)(V_G - V_T)^2$, where I_{DS} is the drain-source current, μ is the field-effect mobility, W is the channel width, L is the channel length, C_i is the capacitance per unit area of the gate dielectric layer, and V_T is the threshold voltage. The channel length of L was adjusted based on each microscope image of the electrodes.

Results and Discussion

Figure 2 show the UV/VIS absorption spectra of the PDK (soluble photoprecursor) films and photo-converted pentacene films prepared by spin-casting and drop-casting from chloroform solutions. In the case of spin-cast film, a small amount of trichlorobenzene (1wt%) was added to the solution. The PDK films prepared by both spin-casting and drop-casting shows an absorption peak at 470 nm due to n-π^* electronic transition derived from the diketone moiety. The absorption spectrum is changed upon photo irradiation for 30 min with an intensity of 200 mW/cm^2. After photo irradiation, new absorption bands from 500 nm to 750 nm appears, while PDK absorption band at 470 nm disappears. This spectral change indicates that the PDK molecules can be converted to pentacene molecules even in thick drop-cast films. The thickness of drop-cast film is 1.5–2.0 μm, while that of spin-cast film is about 100 nm. The shape of each absorption spectrum is considerably different. Here, the absorption spectra can be identified with two notable absorption bands; one is a peak of a wavelength around 580 nm, that is assigned to molecular absorption of pentacene, and the other is a peak of a wavelength more than 650 nm, that is assigned to aggregated pentacene molecules. The wavelength of the latter absorption band is 660 nm for the spin-cast film and 675 nm for the drop-cast film, respectively. This red-shift by 15 nm may be attributed to higher crystallinity of the drop-cast film.

The effects of photo irradiation conditions on photo-conversion process are investigated. Figure 3 shows UV/VIS absorption spectra of the photo-irradiated films drop-cast from chloroform solution with four different photo irradiation conditions that are combination of two conditions of intensity (40 mW/cm^2 and 200 mW/cm^2) and two conditions

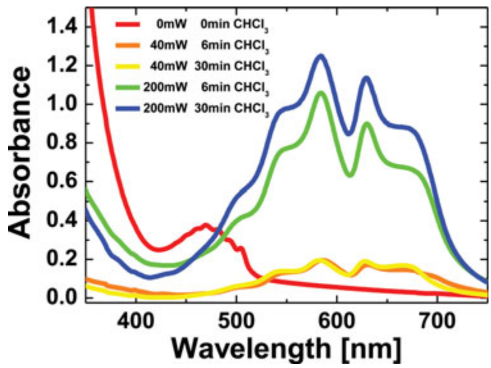

Figure 3. UV/VIS absorption spectra of the photo-irradiated drop-cast films from chloroform solution with different photo irradiation conditions.

of irradiation time (6 min and 30 min). In all the conditions, the PDK absorption band disappears and pentacene absorption band appears, and the spectral shape is almost the same. From these results with different intensity and time, we can discuss relationship between progress of the photo-conversion process and the number of irradiated photons. In general, more intense light and longer irradiation time are expected to promote photo-conversion. However, this is not true in Fig. 3. The number of irradiated photons should be the same in the case of 40 mW/cm^2 for 30 min and the case of 200 mW/cm^2 for 6 min. Nevertheless, absorption intensity of the pentacene is much higher for the latter case, which means that light intensity is more important rather than the total irradiated photon number. This result implies that drying process of cast solution strongly affects the photo-conversion process. We attribute this difference not to the film thickness or molecular arrangement, but to the film uniformity. The intense light (200 mW/cm^2) rapidly converts PDK to pentacene before drying up of solvent, which brings about a uniform purple film. In contrast, in the case of weak light (40 mW/cm^2), a transparent (thin yellow) PDK film is partially photo-converted to pentacene; however, after drying, the film changes to an aggregated, mesh-like and non-uniform film, resulting in apparent weak absorption. In addition, in the dried solid-state film, the photochemical reaction of PDK would be hindered by steric hindrance. Therefore, more intense light is more effective to convert PDK quickly before the cast solution dries up.

The electrical properties of the drop-casted films were measured using FET devices with bottom gate and bottom contact configuration. Figure 4 shows transfer (I_D-V_G) characteristics of the drop-cast films prepared from $CHCl_3$ and DCB solutions. The device prepared from $CHCl_3$ solution shows weak p-type modulation, the hole mobility of 5.5×10^{-4} cm^2/Vs, the on/off ratio of 7.2, and the threshold voltage of 30 V. In contrast, the device prepared from DCB solution shows the hole mobility is 2.6×10^{-3} cm^2/Vs, the on/off ratio of 4.5×10^2, and the threshold of 5.1 V. The FET mobility is improved by using DCB solution, which suggests that the film prepared from DCB solution should have higher crystallinity.

Figure 5 shows digital microscope images of the photo-converted films prepared from $CHCl_3$ and DCB solutions on Si/SiO_2 substrates. The photo-converted pentacene film composes of polycrystalline domains that can be observed as optical images. The film prepared from DCB solution exhibits larger crystalline domains having a size of several tens microns. The film structures were investigated also by out-of-plane and in-plane X-ray

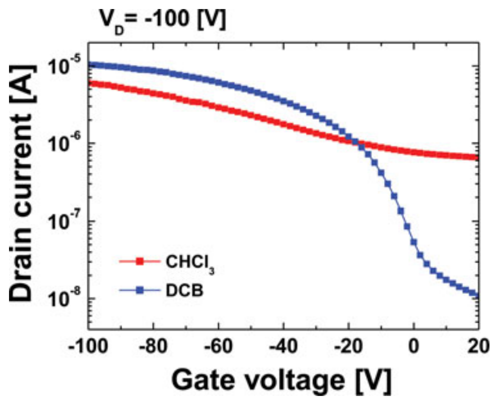

Figure 4. Transfer (I_D-V_G) characteristics of the drop-cast films prepared from $CHCl_3$ and DCB solutions. The films were irradiated with an intensity of 200 mW/cm^2 and irradiation time of 30 min.

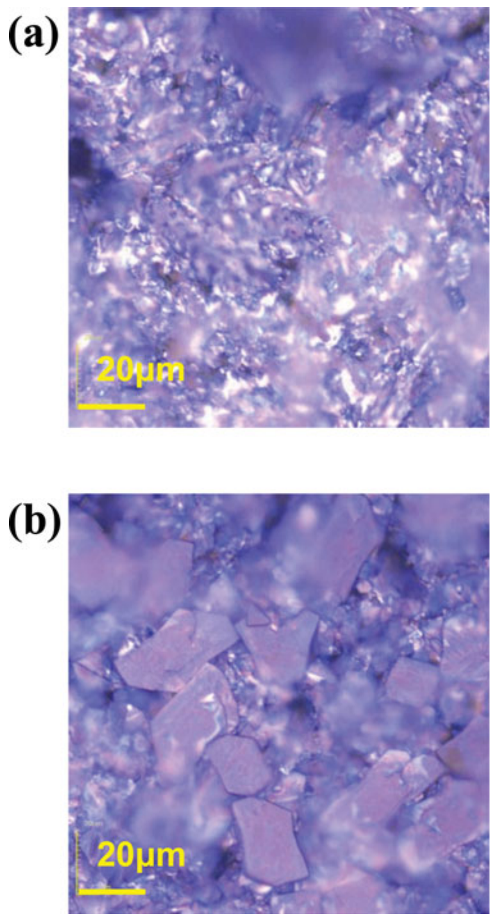

Figure 5. Digital microscope images of the photo-converted films prepared from (a) $CHCl_3$ and (b) DCB solutions.

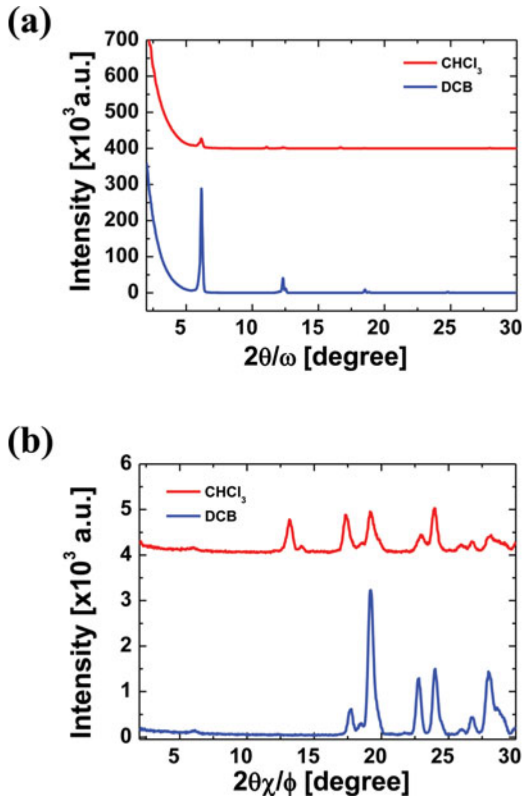

Figure 6. X-ray diffraction patterns of the photo-converted films prepared from $CHCl_3$ and DCB solutions on Si/SiO_2 substrates, (a) out-of-plane measurements, (b) in-plane measurements.

diffraction (XRD) patterns. In the out-of-plane measurements as shown in Fig. 6(a), both films show a diffraction peak at 6.16° that corresponds to c axis of pentacene crystal; however, the film prepared from DCB solution shows much intense peak and higher order diffraction peaks at 12.3° and 18.5°. Also in the in-plane measurements as shown in Fig. 6(b), more intense peaks were observed in the film prepared from DCB solution. The peak at 19.16° corresponds to herringbone packing of pentacene crystal.

From these results, it is obvious that the photo-converted pentacene film prepared from DCB solution has more crystalline film structure. The effect of solvent can be interpreted by crystal growth process during photo-conversion. In the case of DCB that has higher boiling point, the spin-cast solution is kept to be wet condition for long time. Therefore, the PDK and precipitated pentacene molecules can move and crystallize in the film.

Conclusion

The photo-conversion process, film structures and FET properties were investigated in drop-cast films of soluble photoprecursor of PDK. The drop-cast films showed higher crystallinity compared to spin-cast films, and using high boiling point solvent like DCB gave further crystalline films and better hole mobility in the FET devices. These observations point out an importance of wetness and drying process of the cast film in the photo-conversion materials.

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