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Alignment of PHTP–DNAA inclusion crystals by zone casting

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ABSTRACT

Inclusion compound of perhydrotriphenylene (PHTP) and polar N,N-dimethyl-4(4-nitrophenylazo)-aniline was grown from solution into oriented crystalline layers using a zone casting technique. The parallel orientation of channel axes in the direction of the casting was investigated by means of a combination of optical absorption, polarized visible light and a pronounced SHG response. The maximum of the SHG signal of an oriented needle-like crystal was observed along the channel axis. A phase sensitive second harmonic generation (PS-SHG) experiment has demonstrated a bi-polar state of PHTP/DNAA growth from solution. Experimental evidence is provided, that unipolar layers can be obtained.

1. Introduction

Fabrication of highly ordered thin layers of organic molecules is of fundamental interest in many opto-electronic applications. Macroscopic long-range order (and thus orientation) for organic materials can be achieved via solution processing using a *zone casting* technique. In this method, solution is continuously supplied onto the substrate withdrawn at a controlled rate and solvent evaporation takes place from the surface of a meniscus formed between a flat nozzle and the substrate (see Fig. 2) [1–7].

Due to the presence of a gradient of the solute concentration, its solidification proceeds within the narrow zone localized in the meniscus. Under such conditions an anisotropic layer with uniform long-range order extending over the centimeter scale can be continuously deposited on a substrate. Different materials such as low molecular weight (semi)conductors, discotic molecules, and block copolymers may be successfully processed using this technique. Some of these materials were already shown to have good properties as active layers in field effect transistors [3,5].

In this work the application of the *zone casting* for depositing oriented layers of the inclusion compound perhydrotriphenylene/*N,N*-dimethyl-4(4-nitrophenylazo)-aniline (PHTP/DNAA) (Fig. 1) [8,9] showing nonlinear optical properties is demonstrated. DNAA was selected, because upon growth from solution, this inclusion system forms rather easily. This is important because zone casting imposes enforced conditions.

In case unipolar layers could be obtained, these materials would show a pyroelectric effect to be used for heat detection. Unipolar deposition can be verified by phase sensitive second harmonic generation [10] and scanning pyroelectric microscopy [11,12].

2. Experimental

PHTP was synthesized as described in [13]. The N,N-dimethyl-4-(4-nitrophenylazo)aniline (DNAA) guest molecule was prepared according to Ref. [14]. Toluene was purchased from Aldrich and used as received. Fresh solutions of PHTP–DNAA were filtered with a PTFE (0.2 μm) membrane before use. Zone casting of PHTP/DNAA was performed by means of a device used earlier for other systems [2,3,15] (Fig. 2).

A solution of PHTP + DNAA (7:1) in toluene (concentration: 7 mg/ml) was deposited through a flat nozzle (slit-like, width 3 cm) onto a moving glass support at 45 °C. The cover glasses (35×50 mm from Fisher Scientific) used as substrates. Before use they were immersed in ethanol (ultrasonic bath, 10 min) then rinsed thoroughly with distilled water and dried under a nitrogen stream. The distance between the nozzle and the substrate was of 1.0 mm. The solution supply (Fig. 2) was realized by pushing the piston of an injector (capacity of 1 ml) at a constant rate using step motor. The rates of withdrawal (range of 2–5 μm/s) and solution deposition (range of 2.7×10^{-5}–0.7×10^{-4} ml/s) were optimized to attain stationary layer solidification conditions.

UV–visible measurements were carried out using a Hewlett–Packard 8453 spectrophotometer. The second harmonic generation (SHG) measurements were performed using a Q-switched Nd:YAG-Laser (Surelite I-10, Continuum) providing a repetition rate of

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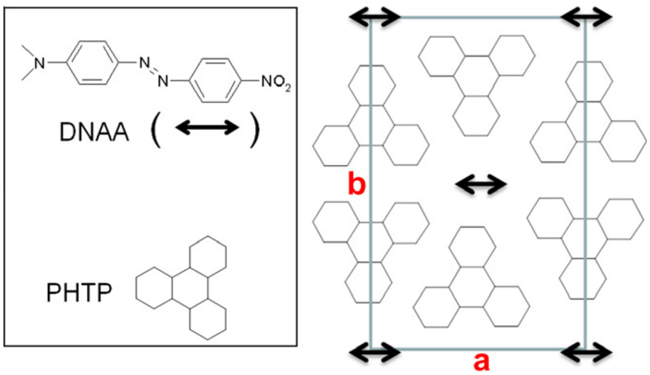

Fig. 1. Schematic representation of the structure of the host/guest compound PHTP/DNAA. Guest molecules show dipole alignment along channels of the inclusion compound.

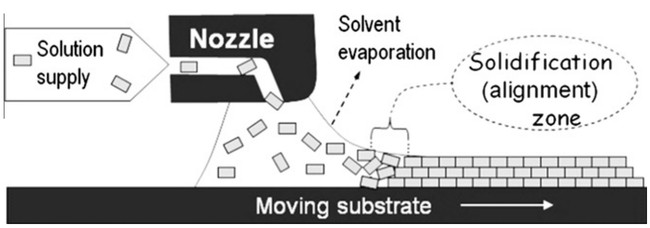

Fig. 2. Schematic presentation of the zone casting process [1–7].

10 Hz with a pulse width of 20–25 ns and a pulse energy of ~25 mJ (1064 nm, pulse intensity 10 MW/cm^2, beam diameter of 4 mm).

3. Results and discussion

Before applying zone casting, the crystallization of PHTP, DNAA and mixtures of PHTP and DNAA from toluene solutions was studied in drop casting experiments. The color and the shape of the crystals formed were examined using polarizing optical microscope.

It was found that DNAA crystallized as relatively small platelets or bundles of dark whiskers (Fig. 3a and b). A red color results from absorption of DNAA in a blue spectral range. PHTP crystallized in form of long ribbon-like crystals. PHTP does not absorb in the visible range and therefore the crystals are colorless irrespective of their orientation with respect to the light polarization (compare Fig. 3c and d).

By drying the droplets of PHTP/DNAA solutions, ribbon-like crystals similar to those of PHTP were found (Fig. 3e and f). Occasionally the precipitates of DNAA could also be noticed (compare area marked by a dashed line in Fig. 3e,f and Fig. 3a,b). Here, (Fig. 3e and f) the crystals appeared red when illuminated with light polarized parallel to their long axis, whereas perpendicular to light polarization crystals appeared colorless [16]. The observed dichroism implies that these are crystals of the PHTP/DNAA inclusion compound. DNAA guest molecules oriented in channels formed by stacks of PHTP give rise to anisotropic optical properties. A rather uniform red coloration of crystals is indicating a uniform distribution of DNAA chromophores in PHTP channels.

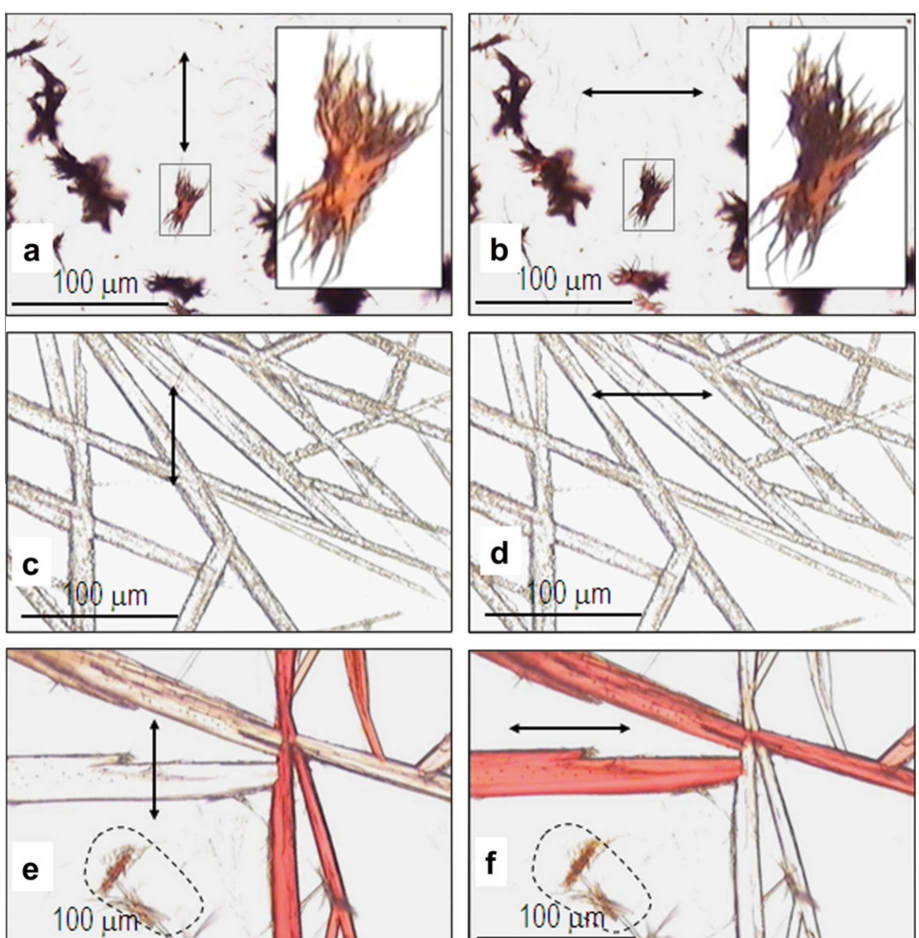

Fig. 3. Optical microscope images (illumination from the bottom with polarized light) of crystals formed on a glass substrate after evaporation of droplets made of different toluene solutions: (a), (b) DNAA (1 mg/ml); (c), (d) PHTP (10 mg/ml) and (e), (f) DNAA + PHTP (7:1, 7 mg/ml). Black double arrows indicate polarization.