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Engineered Growth of Organic Crystalline Films Using Liquid Crystal Solvents

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Thin films of organic molecular crystals (OMCs) have drawn widespread attention for their scientifically interesting and potentially useful properties, with applications ranging from mechanically flexible circuitry to inexpensive photovoltaics, light emitting diodes, transistors, and chemical sensors.[1] However, because the properties of OMCs are extremely sensitive to structural imperfections, domain size, and crystallographic orientation,[2] preparation of high-quality thin films with controlled microstructural organization under technologically favorable conditions has long been a bottleneck toward practical applications and better controlled fundamental studies.[3] Here we introduce a new approach for fabricating OMC films that comes close to achieving these demanding objectives. The main advance is the combined use of vapor-phase deposition into a thermotropic liquid crystal (LC) solvent, which is applied as a thin coating onto a supporting substrate, providing an organized fluid environment in which OMCs nucleate and grow. The technique produces large crystals, enables control over crystallographic orientation, growth habit, and size, and involves near ambient conditions compatible with a variety of substrates and organic materials.

Films were prepared by spin coating a thin layer (1−10 μm) of a thermotropic LC onto a solid substrate, which was then placed in a sealed chamber and exposed to a thermally generated vapor of the OMC solute (Figure 1).[7] Deposition was carried out at ambient pressure to prevent evaporation of the LC. By delivering the solute in this way, solution-phase growth of even highly insoluble compounds becomes possible, and since diffusion is more facile in a fluid than on a bare substrate, lower temperatures (<50 °C) can be used to grow large crystals, enabling compatibility with a broader range of substrate materials, including polymers.[4] In addition, by using a LC in conjunction with an alignment layer, the technique affords a high degree of control over three-dimensional crystallographic orientation. After deposition, LC can be removed by rinsing, leaving behind an oriented film of micrometer-sized crystals adhering to the solid substrate.

Here we present results for tetracene, a linear fused-ring organic semiconductor from the archetypal polyacene family;[5] similar results were also obtained in a smaller number of experiments using anthracene and pentacene. Several substrates were employed, including Si(100), Si(111), glass, polyimide, polyester, polyacetal, and indium-tin-oxide-coated polyethylenephthalate, each treated in a number of different ways to control the alignment of the LC. For uniaxial in-plane alignment, substrates were spin coated with thin films of polyvinyl alcohol (PVA) and mechanically rubbed. Rubbing of bare, thermally annealed polyacetal also gave comparable results. To produce random in-plane alignment, substrates were spin coated with lecithin, unrubbed PVA, or in some cases used without an alignment layer. All substrates wetted by the LC resulted in crystals with similar shapes and sizes, showing that crystal growth was substrate independent.

A long-recognized advantage of solution-phase crystallization is the ability to tune growth characteristics via chemical interactions with the solvent.[6] Accordingly, several nematic solvents were investigated, and it was found that the choice strongly affected crystal growth. Different LCs produced morphologies ranging from compact lozenge shapes, to platelets, thin needles, and amorphous aggregates. Several examples are collected in Figure 2a−c. Substrate temperature was also influential, affecting primarily the size of crystals. At fixed coverage, crystallite size increased roughly exponentially from a few hundred nanometers up to 100 μm between room temperature and 50 °C. The scope of accessible morphologies was thus more diverse and the limiting crystal sizes were larger than those typically produced by conventional vacuum deposition of OMC films.

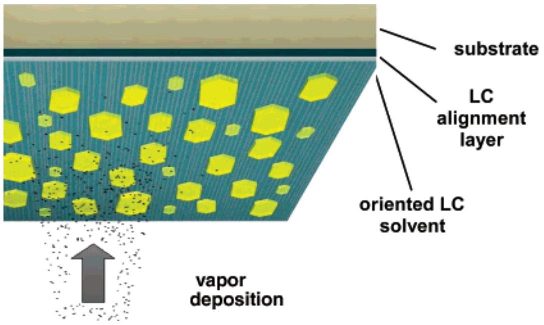

Figure 1. Coating solid substrates with a thin layer of LC solvent enables growth of OMC films composed of larger crystals, with controlled habit and three-dimensional crystallographic orientation under near ambient conditions. In-plane order is established by an alignment layer, which dictates the crystallographic orientation via interactions mediated by the LC solvent.

Perhaps the most striking aspect of these films is their high degree of long-range, in-plane orientational order, clearly visible as a large birefringence in polarized optical microscopy. Hereafter we discuss films like the one in Figure 2a, prepared using the LC ZLI-3417, a multicomponent nematic mixture used in commercial LC display applications (nematic range < −20 to 94 °C). X-ray diffraction measurements[7] of such films agreed with tetracene's previously reported bulk triclinic structure and indicated that the *ab* plane oriented almost exclusively parallel to the substrate, with the long molecular axis inclined by about 20° from the surface normal.

To determine the in-plane component of orientation, crystals' interior angles were analyzed to assign the crystallographic identity of individual faces. This procedure revealed two types of crystals, representative examples of which are shown in Figure 2d. They occurred in equal amounts and were related to one another by a mirror plane along the director, as required by the uniaxial symmetry of the nematic phase. The results from shape modeling as well as polarized UV−vis spectroscopy on crystalline films indicated that the [110] axis aligned parallel to the director, with the unit cell adopting the overall three-dimensional orientation shown in Figure 2e. On the basis of this symmetry, the degree of orientational order was measured using the parameter $s = \langle\cos(2\theta)\rangle$, where θ is the angle between the [110] axis of a given crystal and the mean orientation of all crystals, and the brackets denote an average overall observation. The quantity *s* ranges from 0 to 1 for perfect disorder

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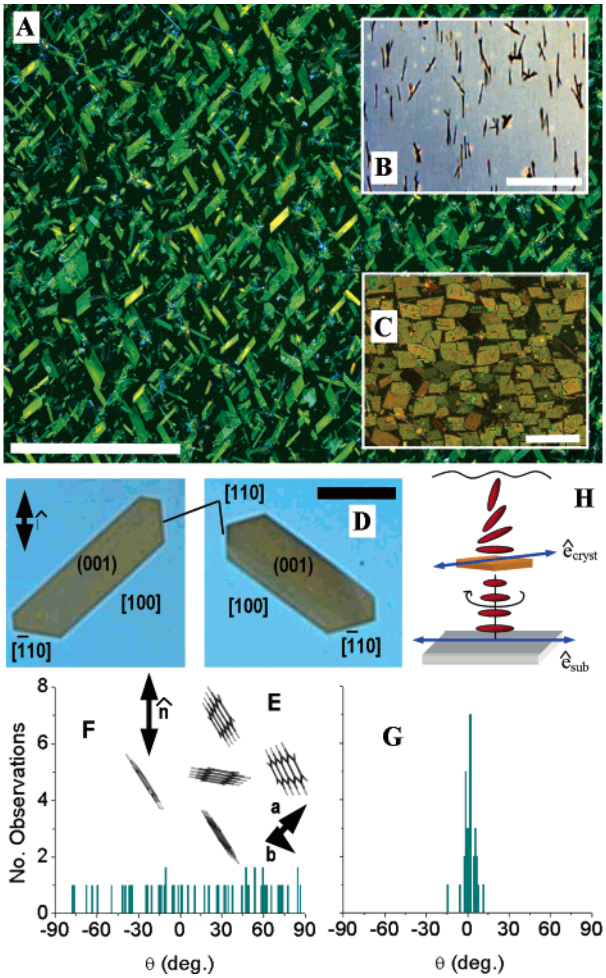

Figure 2. (A−C) Optical micrographs of tetracene films on Si(100) coated with rubbed PVA and LC solvent. (A) ZLI-3417, (B) E7, (C) MBBA. The director, $\tilde{n}$, which defines the average orientation of the LC, is vertical in all panels. Scale bars represent 100 μm. For experimental details, see ref 7. (D) Representative crystals from a film similar to that in part (A) at lower coverage. Scale bar is 20 μm. (E) Assignment of the three-dimensional unit cell orientation. (F, G) Orientational histograms of representative tetracene films grown in ZLI-3417 without (F) and with (G) a rubbed PVA alignment layer; θ is the angle between $\tilde{n}$ and tetracene [110]. (H) Representation of $\tilde{n}$ surrounding a misoriented crystallite.

and perfect order, respectively. The degree of order depended on deposition conditions and substrate treatment but was routinely greater than 0.9 and, in some cases, as large as 0.99, making these among the most highly oriented OMC films reported to date. As shown in Figure 2f, films deposited on substrates coated with lecithin or unrubbed PVA had essentially random long-range in-plane orientation ($s < 0.1$).

Because crystals grew free-floating, fully embedded in the LC (prior to LC removal, they could often be made to move or rotate by a small external perturbation), epitaxial interactions with the substrate are not the cause of alignment. Nor does anisotropic diffusion play a significant role because crystallite size, shape, and orientation were each uncorrelated. Instead it appears the dominant orientational influence is largely *mechanical* in origin, arising from a mechanism unique to ordered fluids, namely, a torque exerted on misaligned crystals as a result of surface anchoring and curvature elasticity. To understand this, we note that at the LC−gas interface anchoring was nearly homeotropic and azimuthally degenerate, while at the LC−substrate interface it depended on surface treatment but was normally fixed by the alignment layer to a single in-plane axis. Consequently, when the easy axis, $\hat{e}_{cryst}$, of a tetracene crystal (the axis along which the director prefers to orient) is coplanar but misaligned with that of the rubbed substrate, $\hat{e}_{sub}$, the intervening LC undergoes a twist distortion, raising its free energy (Figure 2H). On the basis of the elastic constants and thickness of the LC layer, we estimate the energy cost of misorienting a 10×10 μm crystal by just a few degrees exceeds $1kT$ at room temperature, consistent with the high degree of alignment observed in these films.

To test this hypothesis, experiments were conducted to determine whether free-floating crystals could be oriented by the action of the LC alone. Individual, micron-sized crystals were sealed in LC-filled cells constructed from two glass plates treated on their inner surfaces to give parallel, planar alignment. The cells incorporated two electrodes arranged to produce a field in the plane of the cell, perpendicular to the axis of orientation imposed by the walls. The director could thus be switched between two orthogonal orientations by applying or removing an AC field. Switching the director caused crystals to rotate, which then gradually relaxed to their original orientations when the field was removed. The rotational relaxation velocity measured in time-lapse movies for crystals of different sizes agreed with predictions from a simple model balancing LC-based torque and hydrodynamic drag, demonstrating that LC forces are strong enough to orient individual, free-floating organic crystals. These results also illustrate how patterned electrodes can be used to control local crystallographic alignment, possibly useful for constructing devices with increased architectural complexity.

In conclusion, this report introduces a new technique for engineered growth of organic crystalline films using thermotropic LC solvents. The method produces crystals larger than typical physical vapor deposition, enables control over crystallographic orientation and growth habit, and involves near ambient processing conditions compatible with a variety of substrates and organic materials. By combining the chemical diversity of thermotropic LCs[8] with methods for controlling LC alignment, the approach may enable preparation of OMC films with designer architectures, from micrometer to macroscopic length scales.

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Supporting Information Available: Experimental details, X-ray diffractogram, polarized UV−vis spectra, and fluorescence spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

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