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Organic Electro-optic Single-Crystalline Thin Films Grown Directly on Modified Amorphous Substrates**

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Organic single crystals grown directly on substrates with desired orientation of molecules are important for fundamental and applied chemistry[1,2] and numerous nonlinear optical[3] and optoelectronic[4] applications. For integrated photonic applications such as microresonator filters and modulators, single crystalline thin films with a thickness in the range of 0.2–10 μm are required.[5] Such crystalline films can be grown by epitaxial growth methods, for which lattice matching is an important parameter for obtaining high-quality single-crystalline thin films without defects on other materials (or substrates).[6] Therefore, epitaxial growth is usually limited to lattice-matched crystalline substrates and cannot be simply used on amorphous substrates. Only a few approaches have been reported on the growth of organic crystals on non-crystalline substrates, for example by using graphoepitaxy on amorphous SiO_2 substrates,[7] chemical epitaxy on ordered gold-thiol self-assembled monolayers,[1] and shear-induced polar interaction on silica (fused quartz).[8] Moreover, the epitaxial growth based on the lattice matching technique usually combines two very similar materials[9] and therefore does not allow for a high refractive index contrast needed, for example, for micro-ring resonators and photonic crystal structures.[3,5] In order to overcome these restrictions we report here on the growth of organic nonlinear optical single-crystalline thin films using surface-specific interactions combined with a capillary method on amorphous glass substrates. The surface of the substrates has been modified with functional groups of chromophores to mimic the crystal surface of a growing crystal.

A series of acentric configurationally locked polyene (CLP) crystals has been developed recently with large macroscopic nonlinearity and high thermal stability.[10,11] For the growth of thin films on the substrates we choose one of the chromophores 2-{3-[2-(4-dimethylaminophenyl)vinyl]-5,5-dimethylcyclohex-2-enylidene}malononitrile (DAT2, see Fig. 1a) due to a noncentrosymmetric crystal structure (monoclinic $P2_1$ space group)[12] that leads to large macroscopic nonlinearities.[10]

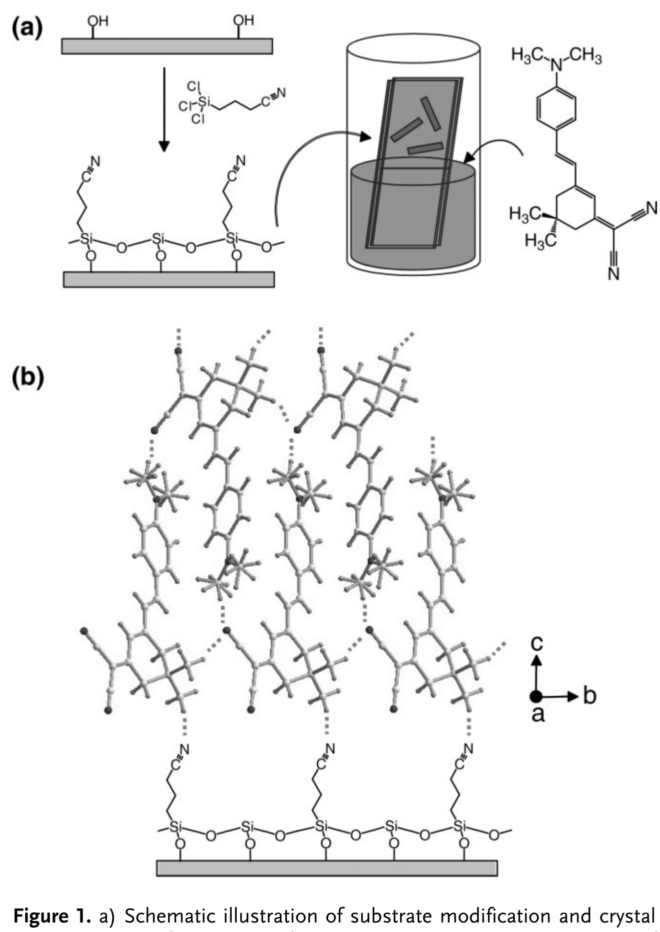

Figure 1. a) Schematic illustration of substrate modification and crystal growth method of DAT2. b) Self-assembly and crystal packing diagram of DAT2 on CN-modified substrate. Hydrogen bonds are indicated by dotted lines.

The main supramolecular interactions of DAT2 crystals are weak hydrogen bonds of C≡N···H-C with distances in the range of 2.8–3.4 Å. The C–H groups on the equatorial and axial methyl groups in the hexatriene bridge and one of methyl groups on dimethylamino group act as hydrogen bond donors. The CN groups act as hydrogen bond acceptors (see Fig. 1b).[10] To induce specific interactions with DAT2 molecules, a hydrophilic surface of amorphous glass substrates was modified by silanization with 4-(trichlorosilyl)-butyronitrile

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according to the literature.[13] The silanized treatment leads to a CN-functionalized surface, which mimics the crystal surface of a growing crystal including the important hydrogen-bond acceptor CN groups in the crystalline state (see Fig. 1). Therefore, the CN-modified surface can interact specifically with the DAT2 molecules in solution. As illustrated in Figure 1a, single-crystalline thin films grow by slow evaporation and the capillary effect that pulls up the liquid between the two CN-modified glass substrates immersed in acetone solution. During the crystal growing process, DAT2 molecules in the solution are supposed to recognize the CN-modified surface of the substrate as a crystal surface of a growing DAT2 crystal and then start to nucleate and grow on the substrate. For comparison purposes we also investigated the growth on unmodified hydrophilic amorphous glass substrates treated only with piranha solution (see Supporting Information for experimental details).

DAT2 crystals grew between two glass substrates as illustrated in Figure 1a. Figure 2 shows a photograph of typical DAT2 crystals grown on unmodified and CN-modified glass substrates after removing the other glass substrate. The crystals on the CN-modified glass substrate are in the shape of rectangular plates with side lengths in the range of 5–10 mm and regular thicknesses in the range of 1–40 μm, and are therefore of suitable size and thickness for fabrication of integrated photonic devices. Moreover, the whole surface area of DAT2 crystals grown by the above method is well attached on one of the modified substrates, even during patterning by photolithography and other experiments for determining physical properties, which is also an advantage for stable and easy handling of brittle crystalline thin films. Comparing CN-modified substrates with unmodified glass substrates using same growing conditions, we only observed DAT2 crystals of small number, small size and bad quality using the latter (see Fig. 2a). In addition, by a slow evaporation method without using the capillary effect, i.e. only one substrate was immersed in the solution, we obtained bad-quality crystals with rough surfaces, meaning that the capillary effect between the substrates gives regular material transport and prevents perturbations of growing conditions.

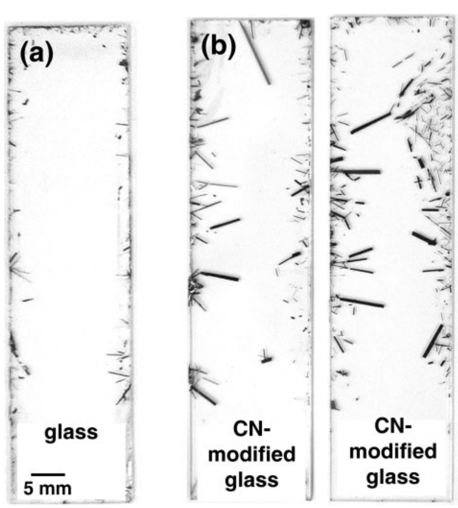

Figure 2. DAT2 crystals grown on a) unmodified, and b) CN-modified glass substrates (two examples are shown).

Figure 3 shows one of the DAT2 crystals grown on a modified CN glass substrate. The crystal has a regular thickness of 6.89 ± 0.03 μm, as measured by a profilometer along 5 mm of the long crystal axis. We investigated DAT2 crystals between crossed polarizers using a microscope. As shown in Figure 3, the whole crystal region shows a homogeneous transparency. We have also observed the same changes of the transmittance when rotating the crystal using polarized light, meaning that the crystal is single crystalline with good optical quality. Figure 3a shows the transmittance curve in the range of 600–2000 nm measured with light polarized along the long-axis (*a*-axis) of the crystal. The measured values (circles) of the transmittance spectrum show good agreement with the theoretical curve (solid line) considering multiple reflections at the surfaces (crystal–air, crystal–glass and glass–air) and neglecting the absorption. This indicates that the crystals grown on the substrate have good optical surfaces and are free from scattering centers. Comparing the UV-vis/IR transmission along the two main axes of the DAT2 crystals grown on the substrate and bulk plate-like crystals[10] we can conclude that the largest crystal face is in both cases the *c*-face. Therefore, the crystal preferentially grows normal to the crystallographic *c*-face, which is due to the supramolecular interactions between the CN groups on the modified surface and the *c*-face of crystals, as illustrated in Figure 1b.

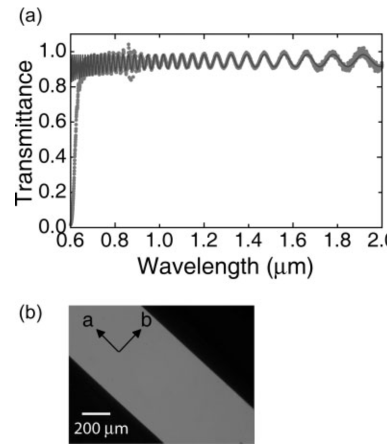

Figure 3. A typical DAT2 single-crystalline thin film on a CN-modified glass substrate: a) transmittance curve measured by the polarized light along the long-axis (*a*-axis), and (b) microphotograph as observed between the crossed polarizers for a film of about 7 μm thickness.

In summary, we have reported on the production of high-quality single-crystalline thin films of DAT2 on amorphous CN-modified glass substrate, which is a mimic crystal surface of a crystal, by slow evaporation and capillary method. This technique is useful to obtain crystalline thin films with desired orientation not only for nonlinear optical applications but also for optoelectronic and other areas where single crystalline films are required. Further studies will focus on controlling the direction and position of nucleation and crystal growing on modified substrates.

Experimental

Experimental details have been provided as Supporting Information.

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[12] X-ray data for DAT2 crystal: $C_{21}H_{23}N_3$, M_r = 317.42, monoclinic, space group $P2_1$, point group 2, a = 6.1303(7) Å, b = 7.4239(9) Å, c = 20.258(4) Å, α = 90°, β = 96.750(8)°, γ = 90°, V = 915.6(2) Å^3 , T = 295 K, CCDC-278087.

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