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Self-Assembly in Ultrahigh Vacuum: Growth of Organic Thin Films with a Stable *In-Plane* Directional Order

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Most self-assembled organic thin films are formed in solution,[1] where the adsorbate molecules approach the film surface via diffusion that also makes the intermolecular interaction in the solution inevitable. Therefore, due to the competing aggregation in solution, well-ordered thin films are very difficult to grow continuously in solution at a reasonable rate although they have been formed by repeating the sequential activation−adsorption steps in different solutions.[2] On the other hand, molecules can approach a target without diffusion, i.e., without intermolecular interaction, in ultrahigh vacuum ($<10^{-8}$ mbar). This is a unique feature of organic molecular beam deposition[3] (OMBD, Figure 1A) that allows a one-component self-assembly growth of ordered thin films in a continuous and rapid way. In addition, OMBD has many other advantages over the solution-based techniques, such as negligible contamination and in situ growth control (Figure 1A). Moreover, as we demonstrate here for the first time to our knowledge, an organic thin film can be ordered in situ in any desired direction within the substrate plane by OMBD.[4,5]

Organic thin films with a non-centrosymmetric order have been intensively studied for applications in nonlinear optics.[6,7] Described here is a novel approach to form such thin films by OMBD. We have designed chromophores so that they are strongly hydrogen-bonded to each other *in a head-to-tail fashion* to form linear supramolecular assemblies[8] in the solid state. Such materials can be sublimated in ultrahigh vacuum (Figure 1B) if the hydrogen bonds can be broken while the molecules are intact at elevated temperatures. The sublimated molecules form a molecular beam and travel without interacting with each other before arriving at the film surface where they start to self-assemble in a head-to-tail fashion. To orient each chain in the film along the same direction, substrate surfaces which selectively bond only one end of the adsorbate molecules are used. Our preliminary results were obtained with 4-[pyridin-4-yl)ethynyl]benzoic acid (**1**)[9] and amorphous glass substrates.

The intermolecular hydrogen bonding of **1** (powder) was probed by solid state ^{15}N NMR spectroscopy.[10] The only ^{15}N signal of **1** appears at −105 ppm relative to that of $CH_3{}^{15}NO_2$ (0 ppm). This chemical shift is between that of a free pyridyl group, for example, methyl ester of **1** (−67 ppm) and pyridine (−63 ppm), and that of protonated pyridine (ca. −180 ppm). It is characteristic for strongly hydrogen-bonded pyridyl groups, indicating the presence of a strong COOH···N linkage in the solid state of **1**. On the other hand, the presence of free pyridyl groups as the end groups of short head-to-tail hydrogen-bonded oligomers or head-to-head hydrogen-bonded dimers of **1**, which should have resulted in additional ^{15}N signal, is negligible. Therefore, long head-to-tail chains are probably dominant in the solid state of **1**. In addition, the low molecular weight **1** has a high melting point (300 °C) and is hardly soluble in common organic solvents at room temperature. On the other hand, the powder of **1** becomes slightly soluble in hot DMSO and sublimates at 180 °C/0.01 mbar, implying that the hydrogen bond networks can be broken at elevated temperatures.

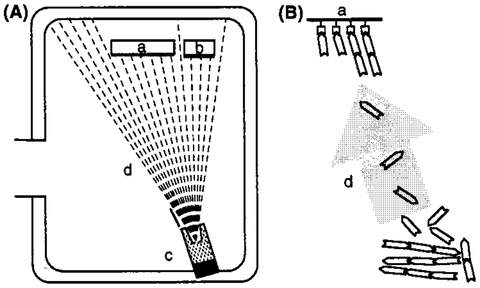

Figure 1. (A) Illustration of OMBD. An organic thin film on the substrate (a) is growing out of the molecular beam (d), formed by evaporating the material in the effusion cell (c) into the chamber in ultrahigh vacuum ($<10^{-8}$ mbar). The growth rate and the film thickness are monitored in situ with monolayer sensitivity by the quartz microbalance (b). In our home-built chamber, the distance between the beam source and the substrate is 26 cm, and the incident angle is ca. 26°. (B) Illustration of the self-assembly growth of ordered thin films.

Films of **1** with a thickness of 100−400 nm were grown on amorphous glass substrates by OMBD with a growth rate of 4 nm/min.[11] The films appeared homogeneous and transparent. The absorption maximum (λ_{max}) of the films was at 336 nm, and the cutoff edge (90% transmission) was at 400 nm. Most interestingly, the films had a directional order within the film plane. As shown by second harmonic generation (SHG) experiments,[6] the second harmonic intensity ($I^{2\omega}$, Figure 2) reached its maximum when the projection of the molecular beam on the substrate surface (the X_3 axis) became parallel to the electric field vectors of the fundamental (E^{ω}) and the second harmonic ($E^{2\omega}$).

At different places over the large film area (2.5 × 3 cm), $I^{2\omega}$ varied within 10% which was within the experimental error. In addition, $I^{2\omega}$ increased quadratically with the film thickness up to at least 400 nm (Figure 3A). Both behaviors are characteristic for films having a uniform and long-range non-centrosymmetric order that does not decrease with increasing film thickness.[2] Particularly noteworthy is that $I^{2\omega}$ only slightly diminished when the temperature was increased to 180 °C (Figure 3B), indicating a high thermal stability of the ordering. This stability can be attributed to the close packing of **1** in the film and the high melting and sublimation temperature of the material. The nonlinear optical coefficient d_{33} of the films was determined to be 0.75 pm/V (reference value $d_{11} = 0.3$ pm/V of quartz at $\lambda_0 = 1064$ nm) by

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(11) Base pressure: 5×10^{-9} mbar; sublimation temperature: 200 °C; substrate temperature: 30 °C. The glass substrates (2.5 × 4 cm microscope slides) were cleaned under ultrasound in acetone (5 min) and ethanol (5 min) and dried at 120 °C/10^{-6} mbar for 0.5 h.

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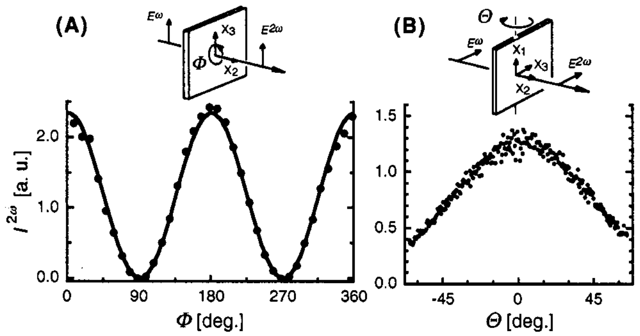

Figure 2. SHG intensity ($I^{2\omega}$) as a function of the sample rotation angle Φ (A) and incident angle Θ (B) of the fundamental ($\lambda_0 = 1064$ nm) incident on a 400-nm (A) and a 200-nm (B) film of **1** grown on glass substrates at 30 °C by OMBD. X_3: projection of the molecular beam on the substrate surface; X_2: the surface normal and rotation axis for (A); X_1: perpendicular to both X_2 and X_3. $\Phi = 0°$ or $\Theta = 0°$ denotes that both E^{ω} and $E^{2\omega}$ are parallel to X_3. The curves are typical for all films of **1** grown under similar conditions.

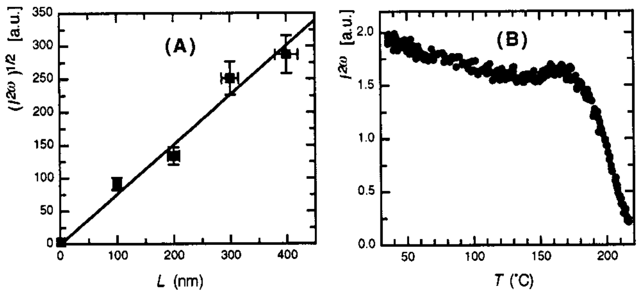

Figure 3. (A) Square root of the SHG intensity [$(I^{2\omega})^{1/2}$] for films of **1** grown on glass substrates at 30 °C by OMBD as a function of the film thickness (L). The experimental data were obtained using the setup shown in Figure 2A with $\Phi = 0°$. The result is not contrary to that in Figure 2B: note that the projection and transmission factors contribute much more to $I^{2\omega}$ than the film thickness in Figure 2B.[6,7] (B) SHG intensity ($I^{2\omega}$) for a 200-nm film of **1** grown on glass at 30 °C by OMBD as a function of temperature (T) with a heating rate of 7.2 K/min. Both experiments used a fundamental light of $\lambda_0 = 1064$ nm.

the Maker-fringe method.[12] This rather low value is expected for the films of **1** and may be increased by using chromophores with stronger donor and acceptor substituents which are able to form strong head-to-tail hydrogen bonds. The degree of ordering cannot be quantified at this stage and may be improved by optimization of growth conditions, for example, substrate temperature, growth rate, and deposition angle.[13]

The origin of the *in-plane* directional order in our films is highly interesting. The order was dependent on the deposition coordinates defined in Figure 2 but not on the rotation angle of the substrate around its surface normal (the X_2 axis). Therefore, the order is not induced by the *in-plane* anisotropy of the substrate surface, if there were any. In fact, the direction of the *in-plane* order, i.e., along the X_3 axis, with respect to the substrate edges can be easily chosen in situ by substrate rotation around the X_2 axis. Films of several other dipolar chromophores without "sticky ends" were deposited by OMBD on glass, but none of them had any long-range order,[14] suggesting that the head-to-tail hydrogen bonding in **1** may be necessary for the ordering.

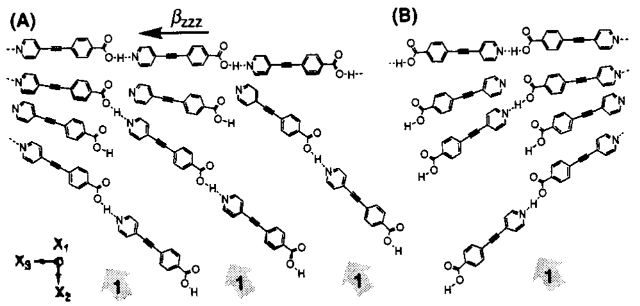

Figure 4. Illustration of two possible orientations (A and B) of **1** in the outermost layer of the film relative to the incoming molecular beam (the gray arrow), and the orientation and bonding of **1** in the film (upper part). {X_1, X_2, X_3}: the deposition coordinates defined in Figure 2.

We speculate that the growth is probably influenced by the following kinetic and thermodynamic aspects. The OH groups on the substrate surface may preferentially hydrogen-bond to the pyridyl instead of the carboxylic group of **1**,[15] exposing the carboxylic groups to the incoming molecules; however, at this stage, we cannot rule out the opposite selectivity, i.e., the carboxylic groups bond to the substrate surface, which does not contradict the present experimental results. The continuously arriving molecules then hydrogen-bond in a head-to-tail fashion to the film surface. The highest growth rate is expected when the molecules, hence the OH groups, in the *outmost* layer are oriented toward the incoming **1** (Figure 4A), whereas the growth may be retarded by the other orientations, for example, the one shown in Figure 4B, where the underlying active bonding sites are shielded from the incoming **1**. On the other hand, the incoming molecules should prefer to bond to the nearest and less crowded carboxylic groups, resulting in the formation of voids ("self-shadowing" effect[4]). To achieve a close packing, the molecules may tend to incline toward the substrate surface to fill the voids. The combination of these aspects may direct the molecules to align preferentially along the projected molecular beam direction on the substrate surface, i.e., the X_3 axis (Figure 4A). On the other hand, semiempirical calculation (see Supporting Information) suggested that the second-order polarizability of the linear "polymer" of **1** is completely dominated by its tensor component along the long molecular axis (β_{zzz}, Figure 4A). If this is true, the angle-dependent SHG (Figure 2) supports the proposed preferential direction of **1** in the films. The maximum $I^{2\omega}$ is obtained when the average direction of **1** in the film represented by the summation of β_{zzz} of all molecules becomes parallel to E^{ω} and $E^{2\omega}$.[6,7] Thus, Figure 2A indicates that this direction is in the X_3X_2 plane, while Figure 2B indicates that it is also parallel to the substrate plane; that is, the average direction of **1** is parallel to the X_3 axis.

In summary, we have described a novel approach for the self-assembly growth of organic thin films in ultrahigh vacuum and demonstrated for the first time, to our knowledge, that a thermally stable and *in-plane* directional order can be obtained by oblique OMBD. The ordering is probably due to the following three cooperating factors: the material, the oblique incidence of the molecular beam, and the substrate surface. This is an example of using physical means to direct a self-assembly process. Thin film waveguides can be fabricated in this way for nonlinear optics and electrooptics.

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Supporting Information Available: ^{15}N NMR and polarization angle-dependent SHG experiments, calculation, and synthesis of **1** (5 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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