

# Orientation-controlled growth of molecular organic thin films

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The control of the structure and preferential orientation of molecular organic thin films might be achieved by the selection of suitable substrates that, in general, have to be designed. Langmuir–Blodgett (LB) and self-assembled monolayers (SAMs) films are good candidates as substrates due to the chemical versatility of their surfaces. We illustrate an example of the selection of either of the two energetically most probable preferential orientations of polycrystalline neutral tetramethyltetraselenafulvalene (TMTSF) thin films by the choice of different substrates. The films (thickness  $\sim 1 \mu\text{m}$ ), obtained by sublimation of TMTSF microcrystals in high vacuum ( $\sim 10^{-6}$  mbar), are dominated by (0–21)- and (100)-oriented microcrystals when using KBr (100) and methyl-terminated films, respectively.

## 1. Introduction

Molecular engineering is an increasingly expanding field due to the appealing possibility of tailoring the electronic, magnetic and optical properties of molecule-based materials by selecting and modifying their molecular constituents. The crystal packing of such materials results from a complicated balance of several interactions within a narrow energy range of less than 1 eV, including hydrogen bonding,  $\pi$ -overlap, electrostatic and van der Waals interactions, *etc.*<sup>1</sup> Thus, in order to build molecular assemblies with predetermined physical properties, the packing that prioritizes the relevant interactions needs to be obtained. For example, in conducting molecular solids, effective  $\pi$ -overlap is a critical feature. However, the dominant interactions leading to a given structure do not necessarily determine directly the physical properties of interest,<sup>2</sup> so that crystal engineering is far from being a mature research field. Similar issues apply when forming heterostructures like organic thin films and organic–inorganic interfaces, where the interactions at the interfaces should be taken into account in addition to balancing the interactions between molecules within the crystals. Control over crystal orientation relative to the substrate can be of great importance, especially for the preparation of thin films of anisotropic materials, in order to spatially define the direction of the associated anisotropic property. The controlled preparation of oriented thin films of well-defined crystallographic phases<sup>3</sup> is essential for future technological applications in areas such as solid-state photonics, microelectronics and biotechnology.<sup>4</sup> This control might be achieved through the judicious selection, or design, of suitable substrates.

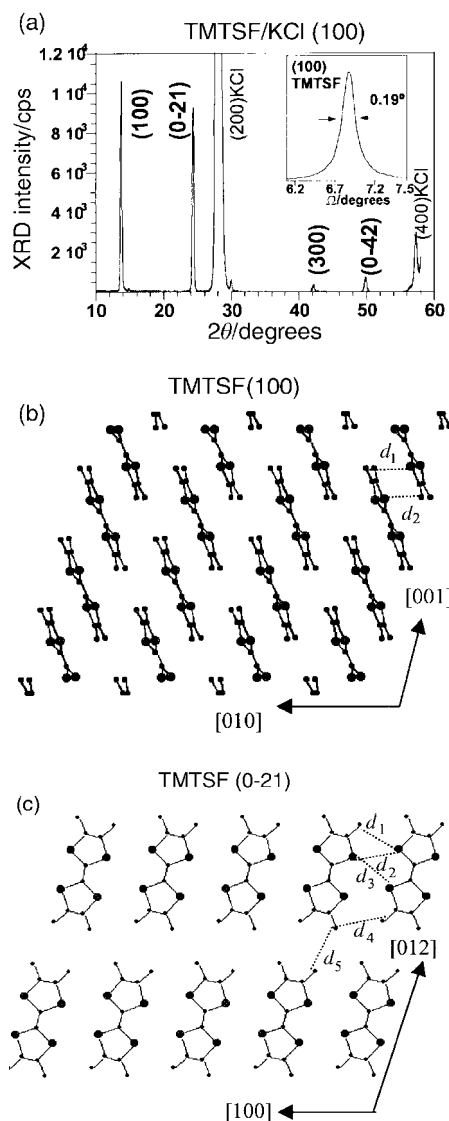
We present results on the selection of the preferential orientation of vapor deposited thin films of neutral  $\pi$ -donor tetramethyltetraselenafulvalene (TMTSF)<sup>5</sup> by the choice of different substrates. TMTSF was chosen for study because crystallographically  $a \approx c$  and because it is an essential component of the Bechgaard salts, a series of quasi-one-dimensional conductors with general formula (TMTSF)<sub>2</sub>X, where X stands for monovalent inorganic anions. The first discovered ambient-pressure organic superconductor was

(TMTSF)<sub>2</sub>ClO<sub>4</sub> with  $T_c = 1.2 \text{ K}$ .<sup>6</sup> Bechgaard salts with monovalent anions such as ReO<sub>4</sub>, PF<sub>6</sub> or AsF<sub>6</sub> undergo also a superconducting transition but at hydrostatic pressures ( $> 6 \text{ kbar}$ ).<sup>7</sup> The results presented here for TMTSF films should have general implications for the vapor deposition of molecular thin films.

## 2. Experimental results

Highly-oriented polycrystalline TMTSF thin films (thickness  $\sim 1 \mu\text{m}$ ) have been obtained by sublimation in high vacuum ( $\sim 10^{-6}$  mbar) of recrystallized (in toluene) TMTSF small single crystals using different substrates held at room temperature.<sup>8</sup> The evaporation temperature was  $\approx 155^\circ\text{C}$ . With *ex situ* cleaved NaCl (100) and KCl (100) single crystal substrates, two TMTSF orientations are obtained, with (100)- and (0–21)-oriented microcrystals present in similar proportions. This point is made in Fig. 1(a), which shows a standard  $2\theta$  X-ray diffraction (XRD) pattern of TMTSF grown on KCl (100).<sup>9</sup> The (100) and (0–21) planes are parallel to the substrate surface and are highly oriented as indicated by the FWHM  $\Delta\Omega$  of the rocking curve in the inset of the figure. Note the low value of  $\Delta\Omega$  ( $= 0.19^\circ$ ) to be compared with the measured  $\Delta\Omega$  of the (200) reflection of the KCl single crystal used as substrate ( $0.13^\circ$ ). Van der Waals epitaxy has been earlier reported for many molecular organic materials on alkali halide substrates.<sup>10</sup> In general, thin films (or microcrystals) are oriented so that the most densely packed molecular planes are parallel to the substrate surface (see discussion below). The X-ray structure of TMTSF shows that the (100) and (0–21) planes contain the closest donor–donor interactions, making them the most favorable orientations in thin films (see Figs. 1(b) and 1(c)).<sup>5</sup>

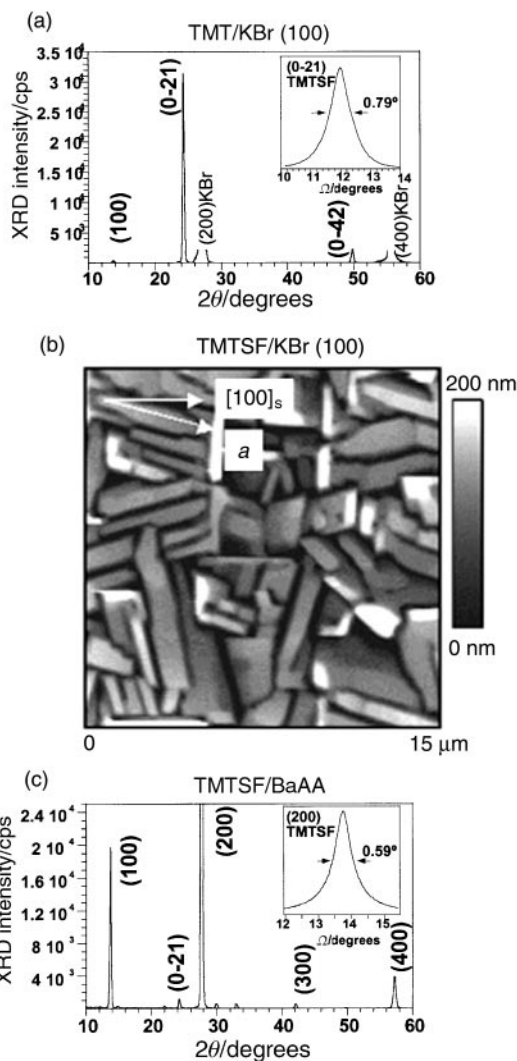
Fig. 2 illustrates an example of the preferential selection between the two energetically most probable plane orientations by the choice of different substrates. Fig. 2(a) shows the XRD pattern of a thin film grown on an *ex situ* cleaved KBr (100) single crystal substrate. In this case the films are largely dominated by (0–21)-oriented microcrystals ( $\Delta\Omega = 0.79^\circ$ ).



**Fig. 1** (a) XRD pattern of a TMTSF thin film (thickness  $\sim 1 \mu\text{m}$ ) grown on a cleaved KCl (100) substrate. The inset shows the rocking curve of the (100) reflection, with a FWHM  $\Delta\Omega = 0.19^\circ$ . (b) View of plane (100):  $d_1 = 3.90 \text{ \AA}$  ( $\text{Se}\cdots\text{CH}_3$ ),  $d_2 = 3.93 \text{ \AA}$  ( $\text{Se}\cdots\text{CH}_3$ ). (c) View of plane (0-21):  $d_1 = 3.87 \text{ \AA}$  ( $\text{Se}\cdots\text{CH}_3$ ),  $d_2 = 3.91 \text{ \AA}$  ( $\text{Se}\cdots\text{Se}$ ),  $d_3 = 4.04 \text{ \AA}$  ( $\text{Se}\cdots\text{Se}$ ),  $d_4 = 3.97 \text{ \AA}$  ( $\text{CH}_3\cdots\text{CH}_3$ ),  $d_5 = 3.98 \text{ \AA}$  ( $\text{CH}_3\cdots\text{CH}_3$ ).

KBr (100) is thus able to preferentially select one of the two energetically most probable molecular planes. These films are in-plane textured: the angle between the  $a$  axis of the TMTSF microcrystals (contained in the (0-21) plane) and the substrate surface equivalent [001] directions is  $16.3^\circ$  as indicated by  $\phi$ -scan patterns (not shown) and by tapping mode atomic force microscopy (TMAFM) measurements (see Fig. 2(b)).

Thin films with preferentially (100)-oriented microcrystals have been obtained by using methyl-terminated LB and self-assembled monolayers (SAMs) films as substrates. However, these films exhibit no in-plane texture. Fig. 2(c) shows the XRD pattern of a TMTSF film ( $\Delta\Omega = 0.59^\circ$ ) grown on a monolayer of barium arachidate (BaAA) deposited on a silicon wafer. Similar results were obtained when evaporating onto four bilayers of lanthanum octadecylphosphonate (La/OPA) deposited on a silicon wafer that had previously been made hydrophobic with a layer of octadecyltrichlorosilane (OTS)<sup>11</sup> ( $\Delta\Omega \approx 0.6^\circ$ ). BaAA and La/OPA were chosen because these LB films are stable to the high vacuum conditions employed during vapor deposition. Preferentially (100)-oriented thin films were also obtained on SAMs of methyl-terminated alkanethiols on



**Fig. 2** (a) XRD pattern of a TMTSF thin film (thickness  $\sim 1 \mu\text{m}$ ) grown on a cleaved KBr (100) substrate. The inset shows the rocking curve of the (0-21) reflection, with a FWHM  $\Delta\Omega = 0.79^\circ$ . (b) TMAFM image (topographic mode) of a TMTSF thin film grown on a cleaved KBr (100) substrate showing both the TMTSF  $a$  axis (triclinic) and the substrate (cubic) equivalent [001]<sub>s</sub> direction. (c) XRD pattern of a TMTSF thin film (thickness  $\sim 1 \mu\text{m}$ ) grown on a BaAA LB film. The inset shows the rocking curve of the (200) reflection, with a FWHM  $\Delta\Omega = 0.59^\circ$ .

Au (111) surfaces. We observe that the intensity ratio of the (100) to the (0-21) reflections is lower for the SAMs substrates as compared to the LB substrates, which should be ascribed to the larger surface roughness of the SAMs used in our experiments.<sup>12</sup> As an example of functionalized surfaces we have deposited thin TMTSF films on ethylenedithiotetrathiafulvalene (EDT)-terminated LB films. In this particular case a low degree of crystallinity and no preferential orientation are observed.

### 3. Discussion

The mechanisms governing the selection of orientation are rather complex and far from being understood. The growth of these films proceeds by an oriented nucleation,<sup>13</sup> which implies the formation of stable nuclei after a rather complicated kinetic process (surface diffusion, desorption, competition of intermolecular interactions inside the nuclei and at the nuclei-substrate interfaces, perhaps a reorientation of initially-formed nuclei, *etc.*) and the growth by incorporation of molecules to the more active sites like steps and kinks of the stable nuclei.<sup>14</sup> The final orientation and texture of these systems is essentially

a consequence of the balance of interactions at the film–substrate interface. In the case of alkali halide substrates the formation of anion-donor complexes is not excluded.

The TMTSF films grow by the Volmer–Weber mechanism as expected for weak film–substrate interactions.<sup>15,16</sup> In this case the formation and growth of stable nuclei oriented with the planes exhibiting the lowest specific nuclei–substrate free-surface energies parallel to the substrate is favored.<sup>16</sup> These planes are thus the most energetic ones and contain the shortest donor–donor interactions. As a consequence the stacking parameters ( $a$  and  $c$ ) are contained in these planes. The strongest interactions are usually associated with the shortest intermolecular contacts. However, there are exceptions to this rule.<sup>17</sup> The crystal packing is a result of the contribution of all interactions between the molecules and is a matter of intensive theoretical studies.<sup>18</sup> In the case of the closely related tetrathiafulvalene (TTF)-based crystals it has been recently shown by means of *ab initio* calculations that S··S interactions, which are attractive and anisotropic, should contribute significantly to their cohesive energy competing effectively with other interactions such as hydrogen bonding.<sup>19</sup> To our knowledge no such studies have been performed for the Se··Se interactions. At the interface the interactions are weaker so that the analysis of the energetic balance leading to a selection of a given orientation becomes an extraordinarily complicated task because of the uncertainty in the determination of the strengths of the different and relatively weak interactions involved. This analysis would be further complicated because of *e.g.* the high mobility of methyl groups and the different flexibility/rigidity of the molecules.

Computationally-effective analytical methods based on the geometrical coincidence of the overlayer and substrate lattices<sup>20</sup> do not systematically reproduce the experimentally observed results. Monolayer and sub-monolayer molecular organic films have been recently studied with molecular resolution with scanning tunneling microscopy.<sup>21</sup> In this case the lattice periodicity of the film is determined but only limited and indirect information concerning the monolayer–substrate interactions is obtained. More information on the nature of the chemical bonding with conducting and narrow-gap semiconducting surfaces can be obtained *e.g.* with angle-resolved photoemission spectroscopy.<sup>22</sup>

From the thermodynamic point of view the similarity in the distribution of both (100) and (0–2 1) orientations in the case of NaCl (100) and KCl (100) substrates implies that the specific free-surface energies parallel and perpendicular to the substrates should be similar for both systems.<sup>16</sup> In the case of KBr (100), where a substrate-induced differentiation of the specific free-surface energies is found, the TMTSF molecules are lying flat on the surface. The in-plane texture evidences a high degree of van der Waals epitaxy although the system is incommensurate: at  $\approx 16^\circ$  the TMTSF  $a$ -axis is nearly parallel to the substrate [410] direction, and along this direction the anion–cation distance is 13.60 Å to be compared to  $2a = 13.87$  Å.

An important aspect of the LB and SAMs systems is that they are organic-modified substrates. Their use as substrates offers the possibility of modifying the end-groups and, to a certain degree, of designing the chemical nature of the surface and thus tailoring the surface properties. The chemical versatility of these engineered surfaces should enable control over the balance of interactions at the interface and permit manipulation of the structure and orientation of the vapor deposited thin films. This feature should be true for other types of organic films such as hyperbranched polymer films grafted on SAMs<sup>23</sup> that might also be used as substrates, showing the enhanced versatility of organic modifying layers over purely inorganic substrates.

## 4. Summary

We have shown that the selection of preferential orientations of vapor deposited molecular organic thin films can be achieved by choosing suitable substrates. We illustrate an example of the selection between two orientations of polycrystalline neutral TMTSF thin films by the choice of different inorganic and organic substrates. Among others, low vapor pressure LB and SAMs films are promising candidates as substrates due to the chemical versatility of their surfaces and because of their availability as large area substrates.

The control over orientation of thin films of neutral  $\pi$ -donor molecules may enable *e.g.* the preparation of organic superconducting thin films with their conduction axis parallel to the substrate surface by confined electrocrystallization,<sup>24</sup> which is under current investigation. Among others, thin films of Bechgaard salts are good candidates because neutral TMTSF and (TMTSF)<sub>2</sub>X exhibit similar structures.

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