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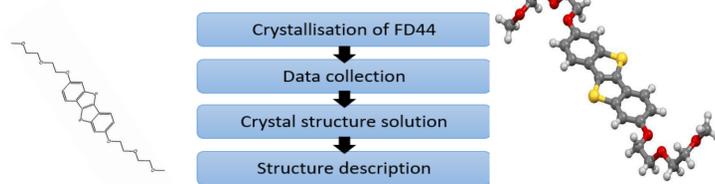
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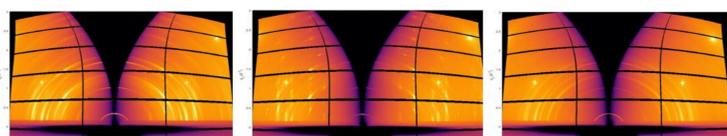
Abstract

Organic semiconductors are promising for thin-film transistor applications as they potentially offer distinctive advantages over their inorganic counterparts particularly in terms of its properties, processing techniques and cost-effectiveness. Small molecules with extended aromatic core and solubilizing long chains are budding candidates for solution-processed organic semiconductors. Here we investigate the crystal structure solution and film-forming properties of FD44, which is a [1]benzothieno [3,2-b]benzothiophene (BTBT) derivative. When we consider the structural aspect of the BTBT core, molecules arrange in a herringbone type packing which facilitates 2D carrier transport properties. The thin films were solution-processed by spin coating and drop-casting techniques from solvents with different boiling points. Chloroform and tetrahydrofuran are the low boiling point solvents used for the thin film preparations whereas chlorobenzene, 1,2-dichlorobenzene, o-xylene and cyclohexanone are the high boiling point solvents used. Morphologies of the thin films were different depending upon the type of solvent used for their fabrications. We obtained good quality films from the preparations and their crystal structure investigations were performed using both in house X-ray equipment and synchrotron. The crystal structure of FD44 was resolved from the single crystal and the Grazing Incidence X-ray Diffractions (GIXRD) were performed to determine the crystallographic structure within the thin film. All the observed peaks in the films were mapped well by the single crystal lattice. That is, the structure in the thin films was identical with that in the single crystal. Also, monolayer investigations of FD44 films were carried out in various solvents and the results were analyzed using X-ray reflectivity measurements in order to understand its monolayer formation at the substrate surface and thereby determine its polymorph formation due to the presence of a surface during the crystallization process.

Introduction

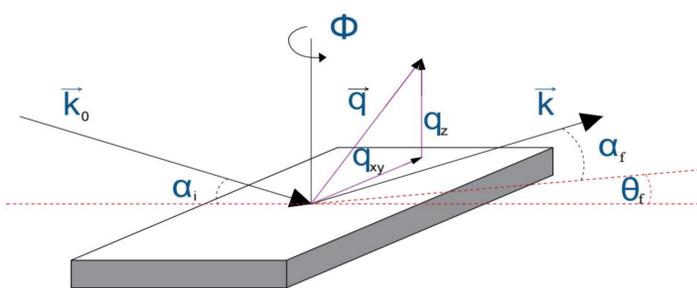


Thin-film transistors which are tailor-made of organic semiconductors (OSCs) have two features that can revolutionize the electronic industry. One, the π -conjugated core which improves the charge transport property and two, the solubilizing substituents in its functionalized core which enables them to be solution processed[1]. Among the various OSCs, molecules with [1]benzothieno [3,2-b]benzothiophene (BTBT) cores are identified as the best p-type semiconductors[2]. 2,7-bis(2(2-methoxyethoxy)ethoxy)benzo[b]benzo[4,5]thieno [2,3-d] thiophene (FD44) is a 2,7-Dialkyl derivative of BTBT type molecules with herringbone (HB) type stacking and thereby expected to show 2-dimensional charge transport behavior. The single crystals of FD44 molecules were grown on a Si substrate by slow evaporation of a high boiling point solvent cyclohexanone at room temperature. Single crystal X-ray analysis using XDS program package revealed a monoclinic phase (P 2₁/c) with unit cell parameter a = 18.635 Å, b = 7.6670 Å and c = 8.2930 Å. Here, the BTBT layers are positioned along the crystallographic a-axis. Moreover, the herringbone arrangement in the bc plane of the BTBT core facilitates 2D charge transport in this direction. FD44 thin films were solution-processed via simple and commonly used techniques such as spin coating and drop-casting followed by some post-deposition techniques like slow evaporation as well. The choice of solvents is a principal factor which influences the directionality of crystalline growth and the morphological outlook of the films[3,4]. Mochizuki et al. has reported that for C8-BTBT thin films prepared out of solvents with high boiling point produced high mobility[5]. To determine the crystal structure of the thin films, Grazing Incidence X-ray Diffraction (GIXRD) was performed and the corresponding reciprocal space map is showcased in fig. The mapping was indexed by a monoclinic unit cell whose lattice parameters are a = 18.635 Å, b = 7.6670 Å, c = 8.2930 Å, $\alpha = 90^\circ$, $\beta = 99.35^\circ$ and $\gamma = 90^\circ$, yielding a cell volume of 1169.1 Å³ which is identical to those obtained from the single crystals. When a material crystallizes at the interface of a solid substrate, we tend to witness polymorphism. That is, the interfacial layer seems to have a different crystal structure than the bulk. This interfacial phase is known as the substrate-induced phase or SIP[6]. Controlling the thin film morphology and their interfacial layer formation are very crucial for achieving the best performance in organic transistors[7]. Therefore by investigating the crystalline monolayers of FD44 prepared in various solvents, we can understand the film morphology and also the interfacial layer property thereby evaluating its suitability for transistor applications.



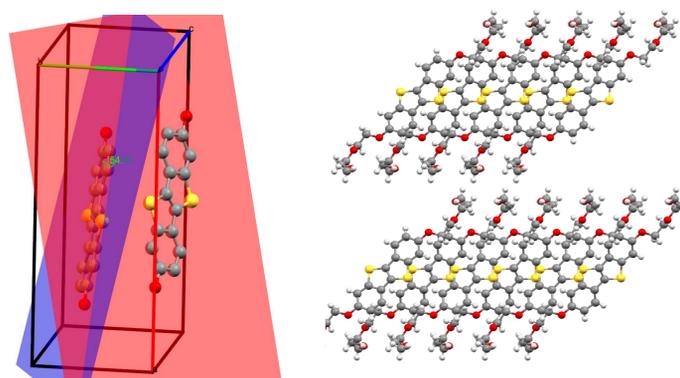
Reciprocal space map for drop casted FD44 films using 3 different solvents

Experimental



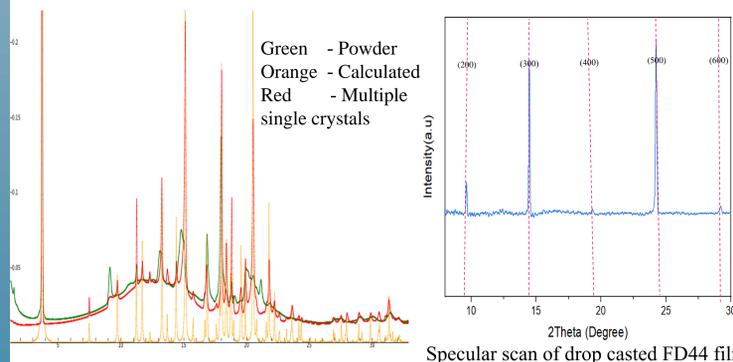
Principle of GIXD. The incident angle is close to the critical angle of the sample. Evanescent waves diffract in the plane of the sample. GIXD measurements were performed at the X-ray diffraction beamline (XRD2) of the Elettra Synchrotron, Trieste (Italy) using a monochromatic wavelength of 0.620 Å.

Crystal structure

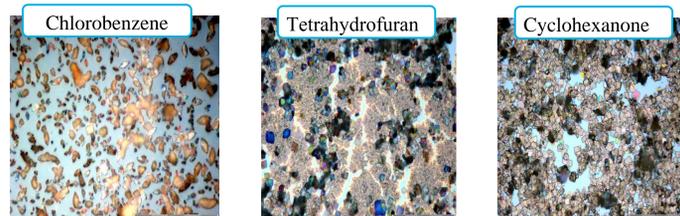


BTBT core of FD44 form a herring bone angle of 54.01°

Unit cell	FD44	Crystal Morphology	Thin Rods
a[Å]	18.635	Crystal colour	Pale yellow
b[Å]	7.6670	Solvent	Cyclohexanone
c[Å]	8.2930	Crystal size(mm)	0.100.0.050.0.020
α [°]	90	R factor	10.31%
β [°]	99.35	WR factor	23.7%
γ [°]	90	No. of reflections	2572
Volume[Å ³]	1169.14		
Z	2		

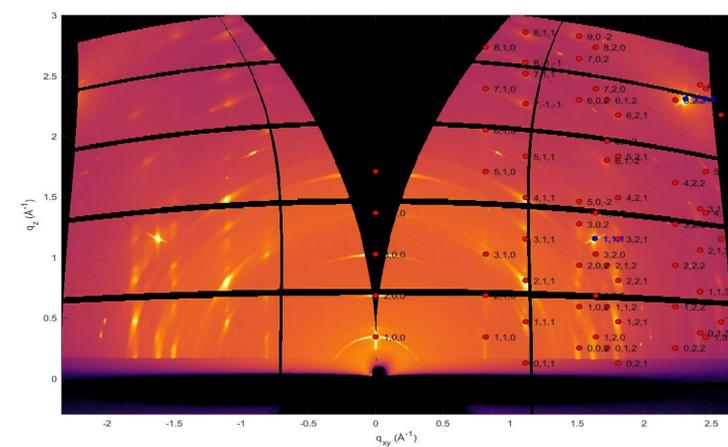


Specular scan of drop casted FD44 film

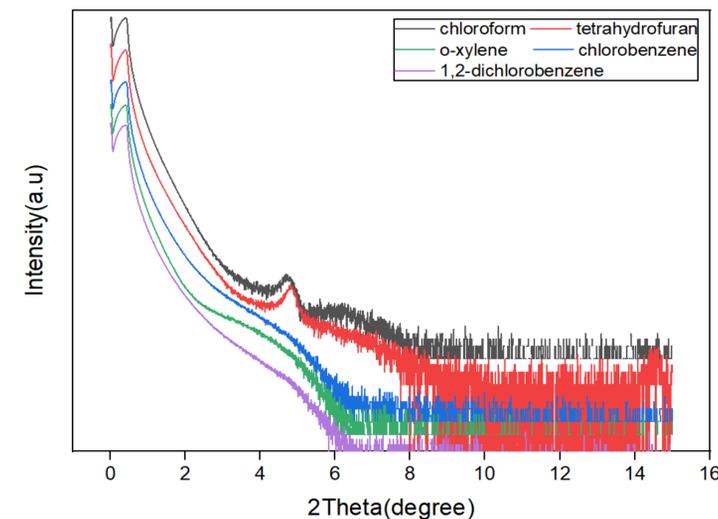


Optical microscopy images of drop casted FD44 films in 3 different solvents

Indexation



X-Ray Reflectivity



Conclusions:

- Crystal structure of FD44 was solved from the single crystals.
- GIXRD was performed on FD44 thin films and the reciprocal space map obtained was indexed using the monoclinic crystal structure obtained from the single crystals. The well mapped reciprocal space implies that the crystal structure in FD44 thin films is identical with that of its single crystal.
- The morphology of the films prepared from various solvents was different from one another.
- From the XRR studies, we could conclude that the films prepared using high B.P solvents gave a more well-defined monolayer structure.

Acknowledgements



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