Poster

Polymorph Screening at Surfaces of a Benzothienobenzothiophene Derivative: Discovering New Solvate Forms

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The class of benzothieno-benzothiophene (BTBT) molecules attracts large attention since it shows outstanding performance as organic thin film transistors. One specific derivative of BTBT-type molecules has oligoethylene-side chains attached at the terminal ends of the conjugated core. The chemical structure of the molecule is given in Figure 1. A classical polymorph screening procedure is performed to examine the variety of polymorph phases of this molecule [1]. Two polymorph phases and one solvate with dichloromethane were found (Figure 1). Expanding the methodology towards crystallisation at surfaces reveals the same polymorphs but also four additional unknown solvates; three solvates with dichloromethane and one solvate with dichlorobenzene [2]. A number of experimental techniques are used to probe the bulk properties of the solvates, including grazing incidence X-ray diffraction, X-ray fluorescence and Ramen spectroscopy.

Temperature-dependent experiments – i.e. hot stage microscopy and X-ray diffraction - reveal an interesting melt memory effect [3]. Starting from a specific solvate and heating it above the melting temperature and above the optical clearance temperature, then cooling down to room temperature causes crystallisation in the same specific solvate. Only at temperatures 50 K above the melting temperature and 20 K above the clearance temperature the melt memory is lost and the stable polymorph is formed during cooling. The underlying mechanism for the melt memory is explained by a strong interaction of the solvent molecule dichloromethane with the oligoethylene side chains of the molecule. In a subsequent step, thin film formation at silicon oxide surfaces is investigated. Considerable differences are found for films prepared by physical vapour deposition and by solution processing [4]. This work shows that including a surface into the polymorph screening process gives the possibility to observe unknown polymorphs, in our case solvates are found. These phases are not accessible by classical polymorph screening.

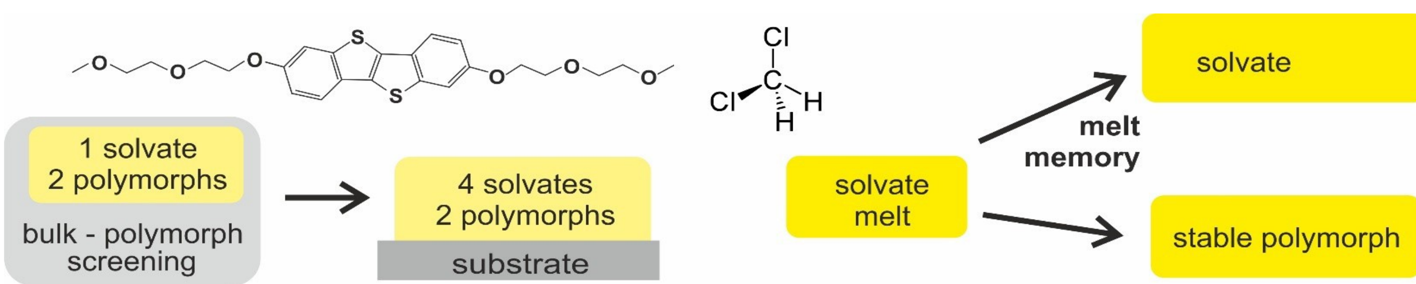

Figure 1. Classical bulk polymorph screening on the molecule oligioethyleneglycol-benzothienobenzothiophene reveals two polymorphs and one solvate with dichloromethane. Including a surface into the polymorph screening procedure reveals four additional solvates. These solvates show an interesting melt memory effect, since the initial solvate is formed from the isotropic melt. Only temperatures considerably higher than the clearance temperature cause the formation of the stable polymorph.

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The work was funded by the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 811284 (UHMob). The support by the Excellence of Science programme (EOS) of FNRS and FWO, through the 2D to 3D (No 30489208), and CHISUB (No 40007495) projects, is acknowledged.