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MS29-O2 Molecular interactions and configurational entropy determining the macroscopic polar state of molecular crystals

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Advanced physical characterization of as grown molecular crystals made of dipolar molecules by scanning pyroelectric and phase sensitive second harmonic microscopy has revealed the true macroscopic polar state of molecular crystals: Supported by configurational entropy, i.e. 180° orientational disorder, molecular crystals (and similarly organized materials) grow into a *bi-polar macroscopic state* (for a review, see [1] or basics [2]). This means, experimentally at least two adjacent domains showing opposite average polarization may be observed. Theoretically, this phenomenon is well understood by analytical models (Markov chain, 2D anisotropic Ising model), force field based calculations for defect energies and Monte Carlo (MC) simulations. Both the thermalized state (concerning 180° disorder) of nano sized seeds and e.g. layer by layer grown crystals were investigated by MC. In case of a *seed* undergoing 180° disorder, a bi-polar state is found. In case of a kinetically controlled nucleation of a *mono polar seed*, growth should lead to a *reversal transition*, experimentally confirmed for bi-phenyls [3]. For 4-iodo-4'-nitro-biphenyl (INBP) the reversal of molecular axes 2 takes place over a transition zone of about 150 micron. The combination of anomalous X-ray scattering & pyroelectric measurements allows us to determine the absolute polarity of such bi-polar objects. The experimentum crucis supporting the *reversal* mechanism consisted in the investigation of solid solutions by adding symmetrical molecules (e.g. 4,4'-di-iodo-biphenyl) to the nutrient. Here, the absolute polarity of the as grown bi-polar state was found to be inverted. The result is in agreement with qualitative arguments about main intermolecular interactions at attachment sites [3]. Force field calculations for para substituted benzenes undergoing 180° orientational disorder at growing faces have provided quantitative data in favour of a *reversal transition*. When analysing the source for driving energies, we find that the main part for the electrostatic interaction stems from a dipolar to quadrupole interaction.

[1] J. Hulliger et al., New J. Chem. 37, 2229-2235, 2013

[2] J. Hulliger et al., Cryst. Growth Des. 12, 5211-5218, 2012

[3] M. Burgener et al., CrystEngCom 15, 7652-7656, 2013

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