MS29-P5 Inner and outer electrical field and dipole moment of a polar molecular crystal

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The inner and outer electrical field distribution and the macroscopic dipole moment are calculated for a polar molecular crystal such as 4-iodo-4'-nitro-biphenyl (INBP) crystallizing in Fdd2 (crystal class mm2). In INBP, the molecules pack head-to-tail parallel to the polar axis, leading to an ideal built up of opposite surface charge densities on the polar faces. At atmospheric ambient conditions, the surface charges can be compensated, implying a dipole opposed to the crystal dipole.

We simulated various nano-crystals of linear dimensions up to 20 nm, with and without surface charge compensation. We calculated, with gas-phase density functional theory, each molecule in the mean field generated by all the others in the nano-particle, thus enabling the calculation of an individual dipole moment for each molecule. This procedure is different from the classical calculation of an ideally infinite crystal and periodic boundary conditions. It was iterated until convergence was found (typically, within 10 cycles a root mean square smaller than 0.1 D on the molecular dipole is obtained).

The ideal crystal packing of this molecule is such that, at variance from other species, the molecular dipole is smaller (by about 20%) with respect to the molecular dipole in the gas phase. This is caused by the internal crystal field, which opposes the molecular dipole due to the lateral interactions that overwhelm the head-to-tail motif.

If the charge compensation is taken into account, two additional effects occur: the field generated by the surfaces enhances the molecular dipole but the additional dipole due to these charges contrast the crystal dipole (sum of molecular dipoles). As a result, the average molecular dipole increases, but the total dipole (i.e. sum of all molecular and surface dipoles) can be 80% smaller than the sum of the gas phase molecules. These results strongly depend on the surface definition, in particular at which distance from the external atoms the charge carriers will be accommodated. Because the nature of these particles is not known, and very likely strongly variable with the atmospheric conditions, the estimation is very approximate and the dipole compensation can be even much larger, thus reducing the observable crystal dipole to a very small value.

Keywords: Polar crystal, dipole moment, electrical field, surface charge density

MS29-P6 Molecular interactions in crystal packing of dipeptide gels

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A gel is defined as a non-fluid colloidal network or polymer that is expanded throughout its whole volume by a fluid[1]. This network can be obtained by either intermolecular - or by interfibrillar - crosslinks[2]. In general peptide hydrogels are a promising class of soft biomaterials for cell culture, regenerative medicine, or drug delivery applications having advantages in biocompatibility, biodegradability and injectability[3,4]. So far, many different longer peptide hydrogel systems like Max1 and P_{11}-2[4] are well studied but the publications about dipeptide hydrogels are limited. Dipeptide gels have certain advantages over longer peptide gels being less cost intensive, more versatile and easier to synthesize in high quantities. The most commonly studied one is the Fmoc-Phe-Phe dipeptide[5]. The major driving force of the self-assembly of such peptides is proposed to be π-π stacking. Other forces known to play a role are hydrophobic interactions, ionic interactions, hydrogen bonding and electrostatic interactions[6,7]. Nevertheless, a better understanding of the self-assembly process would allow a more rational design for specific applications. In our work, we found that a dipeptide based on two β-alanine groups, hence excluding π-π stacking, was able to form a gel-like state. In order to explore this phenomenon, we specifically target the different driving forces by changing the protecting or end groups of the dipeptide. Additionally, solvents of different polarities, salts and pH are tested. The main goal is to synthesize the different dipeptide systems depicted in figure 1, to analyze their chemical, physical and mechanical characteristics, using techniques like Small-angle X-ray scattering, X-ray Single crystal - and X-ray powder diffraction, to show the major differences and to perform mathematical models.

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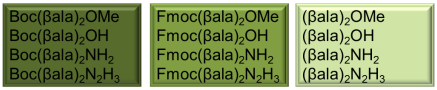

Figure 1. Scheme of the different dipeptides