Crystal Structure and Morphology Prediction of Organic Pigments

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Summary

Organic pigments are coloured organic compounds that are used in the form of insoluble powders in colouring of textile, paper, plastic and other materials, as well as in coatings. Colour is the most important characteristic of a pigment and depends strongly on the structure and morphology of the crystalline particles. The research presented in this thesis focuses on these two characteristics of organic pigment crystals.

Organic pigments, generally, have a very low solubility. This is one of the reasons why it is difficult to grow large enough single crystals, and consequently, it is in many cases not possible to determine the crystal structure using single crystal X-ray diffraction. Crystalline powders of pigments are also of low quality. The small particle size, and often the preferred orientation of the crystallites in the powder, result in low quality X-ray powder diffraction patterns, not suitable for structure determination. An alternative method, namely crystal structure prediction, can only be used for small molecules with few degrees of freedom and is rarely successful.

In chapter 2 the combination of crystal structure prediction and X-ray powder diffraction is presented as a powerful method, and used to predict the crystal structures of the three polymorphic forms of the organic pigment quinacridone (Pigment Violet 19).

This combined method turns out to be rather successful for quinacridone, which can be explained by the rigid molecular structure and, thus, the limited degrees of freedom. The results show that all three polymorphs of quinacridone were found within the first fifteen structures ranked in energy. Since the crystal structure of the stable gamma polymorph was known, it served as a test to evaluate the quality of the prediction. The structures of the beta and alpha polymorphs were not known at the moment of the study and the predicted crystal structure of the beta polymorph was later confirmed experimentally.

After the method was shown to be successful in predicting the crystal structure of the quinacridone polymorphs in chapter 3, three more pigments from different classes, Pigment Violet 23, Pigment Red 202 and Pigment Yellow 139, were subjected to the same prediction method. This was done to evaluate its general feasibility for pigment crystal structure prediction. For Pigment Violet 23, a bright blue pigment used in inks, the method solved the previously unpublished structure. The structure of the stable beta polymorph was predicted as number one in energy ranking and has, strikingly, no hydrogen bonds present in the structure, which is very unusual for organic pigments. The

crystal structure of Pigment Red 202, which is widely used for outdoor applications, was predicted as number two in the ranking. Pigment Red 202 is a substituted quinacridone, and its structural features resemble largely the structure of its unsubstituted analogue quinacridone. Finally, for Pigment Yellow 139, a pigment with an unknown crystal structure, number one in the ranking fitted best, having an unusually high symmetry space group Cmca. The structure was shown to consist of layers of strongly bonded molecules with a dense hydrogen bond network.

In chapter 4 a study on the crystal morphology of the blue pigments copper and metal-free phthalocyanine is presented. Both phthalocyanine pigments can be grown by sublimation at about 500C as long dark blue needles with a violet shine. The crystal morphology was indexed using optical goniometry. The crystals have a large flat basal face and several small side faces. The basal face was also investigated using Atomic Force Microscopy which revealed growth spirals on some of the crystals. Such long, thin anisotropic morphologies are usually not predicted well by conventional morphology prediction methods like the attachment energy method. Therefore, more sophisticated methods - kinetic Monte Carlo simulations and a step energy approach - were used to explain the crystal morphology of phthalocyanines. The results show that the time consuming kinetic Monte Carlo simulations, which simulate the growth of crystal faces for chosen driving force and temperature, lead to the most accurate prediction of the morphology. The calculations based on the step energies of the crystal faces, was shown to give reasonable results in a much shorter time.

Chapter 5 deals with polymorphism of quinacridone. In earlier crystal growth experiments the polymorph stability and nucleation order were not fully understood. The prediction of the crystal structures of three polymorphs of quinacridone in chapter 1 made it possible to investigate the nucleation behaviour of the polymorphs in a simulation study. For that, three-dimensional kinetic Monte Carlo simulations were conducted on the crystal structures of the three quinacridone polymorphs. The growth probability of three-dimensional molecular clusters at different driving forces and temperatures was determined. The gamma polymorph was found to be the most stable form, followed by the beta and alpha polymorphs. This stability order was confirmed by slurry experiments. In the simulations it was found that at high driving forces the beta polymorph has a lower surface energy, which results in a higher growth probability compared to the other polymorphs. This explains why only the beta polymorph was formed during sublimation, as in such experiments the driving force is very high. Furthermore, Ostwald's rule of stages was reversed by applying continuous grinding of the crystals in solution. In this way it was possible to obtain crystals of the metastable polymorph, starting from the stable gamma-form.

Chapter 6 deals with the crystal morphology of the three polymorphs of quinacridone and its three derivatives - Pigment Red 122, Pigment Red 202 and Pigment Red 209. The crystal structures of these pigments have several common features and were expected to show similar morphologies. The crystals were grown from the vapour and from solution. Solution experiments were performed by choosing a suitable solvent from the class of ionic liquids which turned out to enable the dissolution of the pigment in an amount

sufficient for crystal growth experiments. The grown crystals had a very thin platelet morphology. Morphology prediction with the conventional attachment energy method did not succeed in reproducing the large anisotropy of the morphology. Therefore, the kinetic Monte Carlo and step energy methods used in chapter 4 were applied, giving much better results. The morphology of unsubstituted quinacridone was, however, found to be complicated due to twin formation.

Chapter 7 describes the growth spirals observed using Atomic Force Microscopy on the largest face of the needle crystals of metal-free phthalocyanine. The spirals were analysed and compared with kinetic Monte Carlo simulations and a step energy analysis. A model describing an anisotropic rectangular growth spiral was proposed, relating step distances and step energies to the driving force for crystal growth. The spirals obtained using Monte Carlo simulations showed fair resemblance in anisotropy with the experimentally observed growth spirals. The model made it possible to estimate the experimental driving force which turned out to be much lower than was expected when using the Clausius-Clapeyron equation, based on the sublimation enthalpy. In case the experimental driving force is well known, the model can be used together with the step distances determined in the experiment, in order to find the anisotropy in the step energies on surfaces of anisotropic crystals.