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Crystal Engineering

Growing Molecular Crystals on Inorganic Crystals: Polar Structure Induced by Noncentrosymmetric Templates**

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Crystal growth can be strongly influenced by the templating effect of the surface on which it occurs. For example, the growth of calcium carbonate on self-assembled monolayers (SAMs) has been extensively studied, in this system the organic surface promotes the growth of specific structures,[1] morphologies,[2] and orientations.[3] Other inorganic crystals studied include zinc oxide, lead sulfide, and calcium phosphate.[4] SAMs have been the surface of choice for the growth of molecular crystals as they enable control of the structure[5] and orientation,[6] yield meta/less stable polymorphs,[7] and induce enantioselectivity.[8] Molecular crystal growth on templates such as plastics and carbon,[9] at air/water interfaces with Langmuir films,[10] and on other molecular crystals through epitaxy[11] have also been investigated. Interestingly, there are very few reports where the potential templating effect of inorganic crystals is exploited for crystal growth. Selected polymorphs of calcite have been grown by epitaxy from aragonite-type inorganic substrates.[12] The few studies of molecular crystal growth on inorganic crystal surfaces have addressed mechanisms of nucleation/growth,[13] morphology and orientation control,[14] and heterogeneous nucleation effects.[15] To the best of our knowledge, inorganic crystal surfaces have not been used to induce the growth of specific molecular crystal polymorphs, which is a problem of fundamental interest. Due to the unique combination of accessibility, ease of fabrication, and wide choice of chemical compositions and symmetries that could exert rational control on the growth of guest crystals, inorganic crystals should prove superior to templates such as SAMs and Langmuir films. Many simple inorganic crystals can be grown easily with good size and quality, often from an aqueous medium, and provide excellent surfaces for growing molecular crystals. The wide range of centrosymmetric, noncentrosymmetric, and chiral inorganic crystals available should facilitate the exploration of the utility of their surfaces for the growth of specific guest molecular crystals. This is particularly significant in view of the predilection of molecular crystals to form centrosymmetric lattices[16] and the need for noncentrosymmetric crystals in quadratic nonlinear optical, ferroelectric, and piezoelectric applications.

A particularly interesting test of the impact of an inorganic crystal surface would be the growth of polar (and hence noncentrosymmetric) and centrosymmetric molecular polymorphs on different types of crystals, since the former is likely to be especially sensitive to the substrate on which the growth is initiated. Mechanisms and models for polar crystal growth have been investigated extensively by Hulliger and coworkers.[17] We have shown previously that (4-pyrrolidinopyridyl)bis(acetylacetonato)zinc(II) (ZNPPA) exhibits dimorphic structures with extreme molecular orientations (Figure 1): centrosymmetric ZNPPA1 (**1**; *C*2/*c* space group) and perfectly polar ZNPPA2 (**2**; *Fdd*2 space group).[18,19] These dimorphs possess distinct morphologies: **1** is cuboid and **2** has a truncated pyramid shape. Dimorph **2** shows a second harmonic generation (SHG) comparable to that of urea, while **1** is inactive. Investigation of the crystallization in a number of solvents showed that **1** is the predominant structure in most cases.[19] Whereas, only **1** grows from methanol solution, **2** is not obtained exclusively in any solvent; even in the more polar water/methanol mixture where **2** is formed, it grows mostly as microcrystals of poor quality. In view of these facts, we envisaged that the induction of the growth of **2** from pure methanol solution, on a logically chosen inorganic crystal, would be a critical test of the template concept.

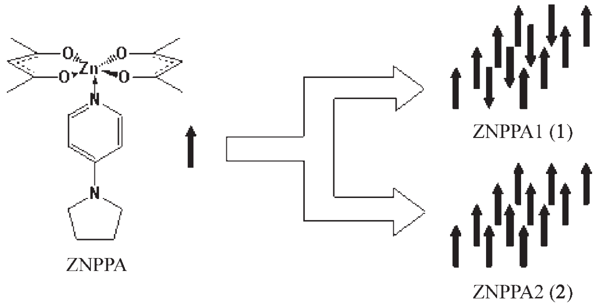

Figure 1. The molecular structure of ZNPPA and a schematic representation of the molecular assembly of the dimorphic structures **1** and **2**.[18]

We selected template inorganic crystals with the following characteristics: insoluble in methanol, non-hygroscopic and non-efflorescent, colorless, and transparent; all were grown from water. Well-formed crystals with dimensions of around 0.5–2.0 mm[19] were chosen for the experiments. In a typical

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Supporting information for this article (details of crystal growth and SHG experiments, SEM images, and crystal morphology) is available on the WWW under http://www.angewandte.org or from the author.

run, between five and ten crystals of a given template were placed at the bottom of a beaker into which 2.5 mL of an approximately 0.01 M solution of ZNPPA in dry methanol was introduced; the area of the template top surface available for the growth of ZNPPA crystals was around 1–2 mm^2 per template crystal. The beaker was covered with a Petri dish and left under ambient atmosphere at a controlled temperature of 24–25 °C.[19,20] Growth of ZNPPA crystals on the template crystals was observed within 10–15 min and confirmed by observation under an optical microscope; crystal growth on the glass surface of the beaker occurs almost simultaneously. In a few cases, the growth on the template was found to occur slightly (about 1 min) before that on the beaker, thus possibly indicating the influence of the template surface on nucleation.[15] Very slow evaporation over 60–90 min resulted in the growth of appreciable numbers of ZNPPA crystals on the surface of the inorganic crystals as well as in the solvent at the bottom of the beaker. The crystal growth was not continued beyond this time interval as the template crystal surfaces showed signs of degradation; this may be due to traces of moisture picked up by the solvent from the atmosphere or very slight solubility in methanol itself. Except for the rare occurrence of powder particles with extremely small sizes, nearly all the well-formed crystals of ZNPPA had a largest dimension of about 100 μm; the polymorph-growth statistics presented below are based on the count of such crystals.

The identity of the individual crystals (**1** or **2**) was established as follows. The solvent was removed carefully with a syringe, the crystals dried in a stream of nitrogen gas, and the beaker placed on a scanner stage. The crystals were then examined individually for their SHG response using a vertically aligned fundamental beam from an Nd:YAG laser (1064 nm, 6 ns, 10 Hz);[19] the precautions exercised for specific templates are described at the appropriate points below. The morphology of the crystals was examined by scanning electron microscopy (SEM). ZNPPA crystals harvested from the beaker or removed from the inorganic crystal surface were tested again to verify their SHG response and selected crystals were indexed on an X-ray diffractometer.

Table 1 shows the aggregate results from several batches of crystal growth in the presence of template crystals; the total number of crystals of **1** and **2** observed on the template and away from the template (designated as "in the solvent") are listed. The crystallization runs were repeated until the total count of crystals in the solvent was about 200; in all cases these were found to outnumber those formed on the template.[20] Figure 2 shows the percentage of **1** and **2** in each environment. A preliminary insight into the template effect was provided by experiments using potassium dihydrogen phosphate (KDP, noncentrosymmetric space group, $I\bar{4}2d$) and potassium sulfate (K_2SO_4, centrosymmetric space group, Pmcn). In both cases, nearly all the ZNPPA crystals formed in the solvent are **1**, which is consistent with earlier observations.[18] The results obtained on the surface of K_2SO_4 are similar. However, the fraction of **2** obtained on KDP crystals is quite appreciable (27 %). In the SHG test, since KDP itself is capable of showing a response, incidence of the laser beam in the phase-matching direction of the KDP crystal was avoided and the laser intensity was kept low enough to ensure that only the stronger SHG from **2** was visible.

Table 1: Total number of crystals of **1** and **2** formed in the two environments during growth in the presence of inorganic template crystals, and their ratio.

Template crystal	On the template no. of crystals **1**	**2**	Ratio **2**:**1**	In the solvent no. of crystals **1**	**2**	Ratio **2**:**1**
KDP[a]	22	8	0.36	211	5	0.02
K_2SO_4	50	1	0.02	197	6	0.03
$Ba(BrO_3)_2{\cdot}H_2O$	41	3	0.07	216	8	0.04
$KBrO_3$[a]	12	9	0.75	188	6	0.03
$NaBrO_3$[a]	21	30	1.43	218	11	0.05

[a] Noncentrosymmetric template crystals.

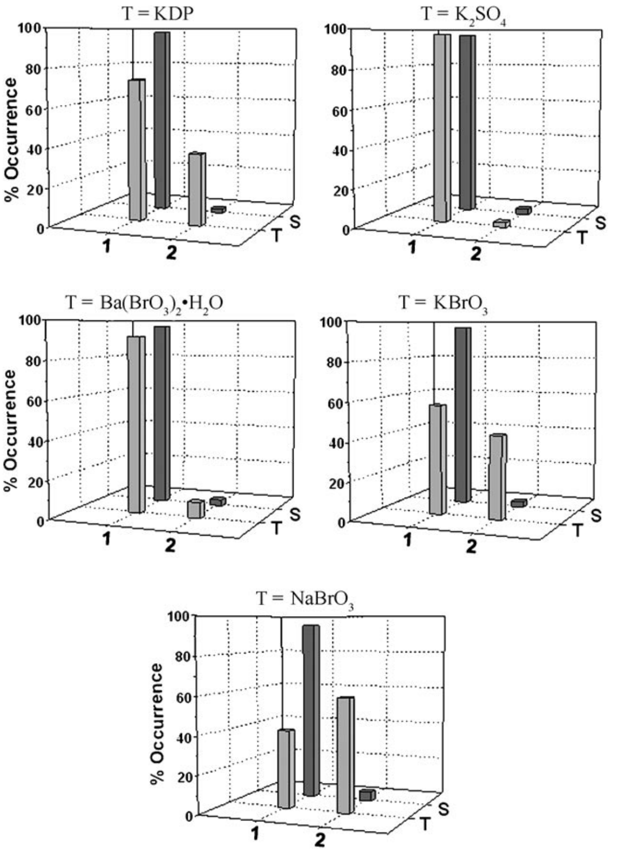

Figure 2. Percentage occurrence of the dimorphs ZNPPA1 (**1**) and ZNPPA2 (**2**) on the template crystal (T) and in the corresponding solvent medium (S); plots for T = KDP, K_2SO_4, $Ba(BrO_3)_2{\cdot}H_2O$, $KBrO_3$, and $NaBrO_3$ are shown.

Following these observations, which clearly indicated a template effect on the growth of ZNPPA crystals, the family of bromate salts $Ba(BrO_3)_2{\cdot}H_2O$ (centrosymmetric space group, C2/c), $KBrO_3$ (noncentrosymmetric but achiral space group, R3m), and $NaBrO_3$ (noncentrosymmetric and chiral space group, $P2_13$) was chosen as templates. Once again, the solvent shows nearly exclusive formation of **1** (Table 1,

Figure 2) in all cases. This polymorph also dominates on $Ba(BrO_3)_2{\cdot}H_2O$. In contrast, the noncentrosymmetric templates $KBrO_3$ and $NaBrO_3$ yield large proportions of **2** on their surface. In the case of $KBrO_3$, which itself shows visible SHG at the laser intensities used, the template was dissolved in water and the ZNPPA crystals released were washed, dried, and tested for SHG. $NaBrO_3$ is the most interesting template, with **2** being the dominant structure growing on its surface; several additional batches of experiments confirmed this.[19] The SHG tests are unambiguous since $NaBrO_3$ does not show any response at the laser intensities used. We experimented with $NaBrO_3$ crystals possessing cuboid as well as tetrahedral morphologies;[21] the preferential growth of **2** over **1** is slightly more pronounced in the case of the tetrahedral crystals.[19] $NaClO_3$ crystals were also found to promote the growth of **2**, however, the template surface shows signs of damage within a few minutes of the crystal growth, possibly due to slight solubility in methanol. Finally, we carried out coupled experiments where K_2SO_4 and $NaBrO_3$ crystals were both placed in the same beaker; the **2**:**1** ratio on each template was consistent with the value observed in independent experiments. The various experiments thus demonstrate the induction of the growth of polar crystal **2** on the surface of noncentrosymmetric inorganic crystals.

Figure 3 shows the SEM images of ZNPPA crystals formed on the surface of K_2SO_4 and $NaBrO_3$ crystals (see the Supporting Information for the images of other crystals); the morphologies of the dominant crystals, **1** and **2** in the respective cases, are highlighted. Dimorph **2** is often found to occur[19] as co-growth crystals.[18] Some of the dominant template faces on which growth occurs are: KDP (100); K_2SO_4 $(0\bar{1}1)$; $Ba(BrO_3)_2{\cdot}H_2O$ $(11\bar{1})$; $KBrO_3$ (001); $NaBrO_3$ [tetrahedral (111), cuboid $(\bar{1}00)$]. The contact face of **1** is (001) in most cases and occasionally $(\bar{1}10)$. The contact face of **2** for all the noncentrosymmetric templates is $(\bar{1}1\bar{1})$; this implies that the polar axis, *c*, of **2** is oriented at an angle of 40.2° with respect to the template surface.

In a broad sense, the inorganic template supports the heterogeneous nucleation of ZNPPA crystals with the possibility of epitaxial control and oriented growth. An earlier investigation of the melt growth of molecular crystals on inorganic crystal surfaces[15] has shown that, even though several factors might contribute to the reduction of supercooling and orientation control, interactions of the molecular dipole and anisotropic growth play a more dominant role than epitaxy. Although the atomic-level mechanism involved in the templated growth of ZNPPA crystals is not clear at the moment, it is likely that the polar nature of the noncentrosymmetric template crystal lattice, and its associated electrostatic field, promotes the oriented assembly of the dipolar ZNPPA molecules. The orientation of the growing crystals of **2** suggests that the oxygen atoms of the acetylacetonato ligand interact with the template surface atoms.[19] The influence of specific interactions and epitaxial effects cannot be ruled out, however, and these can be verified only through experimentation with selected template surfaces. The current observations suggest that a rational choice of inorganic crystal and solvent can be employed to harness selective templating effects and grow specific molecular crystals. The ease of fabricating a wide variety of such template crystals adds to the value of this tailored approach to crystal growth. Further investigations will clarify the generality of the impact of template symmetry on the growth of guest crystals. Exploitation of the symmetry attributes of the template crystal can be particularly significant for directing the growth of noncentrosymmetric, polar, or perhaps enantiospecific structural forms.

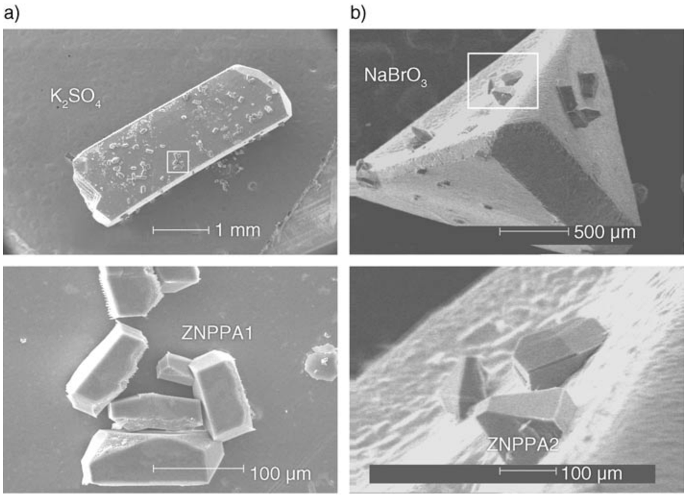

Figure 3. SEM images showing ZNPPA crystals growing on a) K_2SO_4 and b) $NaBrO_3$ template crystals; magnified images are also shown.

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