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Directed Nucleation of Molecular Crystals on Self-Assembled Monolayer Surfaces

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The nucleation and growth of four types of molecular crystals (4,4′-diiodobiphenyl, 2-methyl-4-nitroaniline, 3-nitroaniline, and 2-amino-5-nitropyridine) on gold-thiol self-assembled monolayers (SAMs) of 4′-X- and 3′-X-4-mercaptobiphenyl (X = I and NO_2) is described herein. In each case, crystals were found to nucleate heterogeneously on the SAM template and adopt specific growth orientations with respect to the underlying monolayer surface. The preferred orientations observed in these and other systems can be rationalized on the basis of coincident epitaxy and complementary NO···I interactions across the SAM/crystal interface.

Keywords: crystal growth; nucleation, self-assembled monolayer; template

INTRODUCTION

The first key step in any crystallization process is nucleation. Heterogeneous nucleation is generally thought to prevail over homogeneous nucleation, because the surface energy required to form stable nuclei of critical size is lower. An increasingly popular strategy toward controlling crystal form, size and/or orientation, has been to target crystallization at the early nucleation stage by introducing ordered 2-dimensional templates into the growth solution. A variety of templates including the surfaces of polymers [1], single crystals [2–4], Langmuir monolayer films [5–7], and gold-thiol self-assembled monolayers (SAMs) [8,9–19], have each been shown effective at influencing the crystallization process.

We would like to thank Stephen W. Varney for the synthesis of the 3′ series of thiols. We thank Amy A. Sarjeant at Johns Hopkins University for solving the structure of 4,4′-diiodobiphenyl and Victor G. Young, Jr. at the X-Ray Crystallographic Laboratory at the University of Minnesota for solving the structure of 2-methyl-4-nitroaniline.

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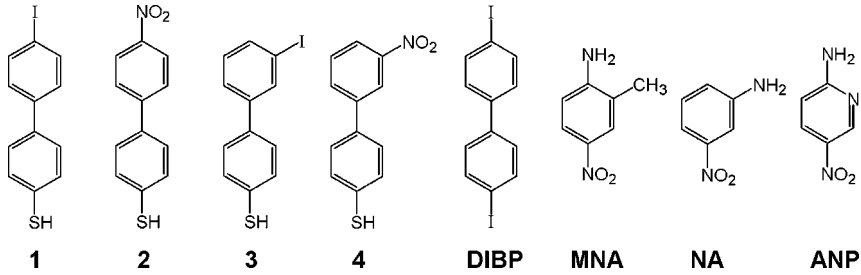
The present study focuses specifically on the use of SAM templates. We reasoned that the 2D templates most effective at directing heterogeneous nucleation should be those which have similar 2-dimensional lattice geometries and complementary chemical functionalities with distinct molecular crystal planes. While alkanethiol monolayers are by far the most ubiquitous, their 2D surface lattice dimensions tend to be smaller than the typical cell parameters for most organic molecular crystals. The tilt angle made between the long axis of the thiol and the surface normal can also vary quite substantially depending on the alkyl chain length, head group and solvent choice, thus altering the monolayer surface periodicity [20,21]. On the other hand, 4′-substituted-4-mercaptobiphenyls have larger cross sectional areas, and are expected to yield SAMs with 2D lattice periodicities that are somewhat larger and closer to that of most molecular crystals. Previous work by others [22–24] has demonstrated that in such monolayers, the biphenylthiols assemble more perpendicular to the surface, often adopting herringbone-type arrangements so that close-packing requirements are met. In addition to compatible lattice geometries, the surface chemistry of biphenylthiols can also be manipulated through synthetic means so that complementary interactions across a crystal/SAM interface can be integrated into the template design scheme. Short iodo. . .nitro contacts (3.4 Å, $-5.7\,\mathrm{kJ\,mol^{-1}}$) [25] are frequently observed in the structures of aromatic compounds bearing such groups. This "synthon" can also be exploited at a crystal/SAM interface, if SAMs bearing either nitro or iodo functionalities are prepared.

In previous work [26–28], we have demonstrated that SAMs of either 4′-X-4-mercaptobiphenyl and/or 3′-X-4-mercaptobiphenyl ($X = NO_2$, I) can be used to direct the nucleation of various crystal systems. For instance, the crystal structure of the compound 4-iodo-4′-nitrobiphenyl (INBP) (*Fdd2*: $a = 8.200$ Å, $b = 18.887$ Å, $c = 14.385$ Å) [29,30] is polar and acentric. When INBP crystals are nucleated on a SAM of 4′-nitro-4-mercaptobiphenyl, the absolute crystal growth direction emerging from the template is along the –*c* crystallographic axis while INBP nucleation on a SAM of 4′-iodo-4-mercaptobiphenyl yielded crystal growth along the +c crystallographic axis [26].

In addition to controlling the absolute growth direction of polar crystals, SAM templates can be used to both reduce the number of crystal phases and selectively control the growth of polymorphs. We have previously reported using SAM templates to selectively nucleate only the less stable polymorph of 2-iodo-4-nitroaniline (INA) [27]. INA grows concomitantly from supersaturated ethanol solutions as orthorhombic plates (*Pbca*: $a = 7.422$ Å, $b = 12.676$ Å, $c = 16.464$ Å) and triclinic needles (*P-1*: $a = 7.16$ Å, $b = 7.96$ Å, $c = 8.05$ Å, $\alpha = 67.91^\circ$,

$\beta = 86.96^{\circ}$, $\gamma = 65.74^{\circ}$) [31]. Exclusive growth of the less stable orthorhombic plates was achieved on SAM templates of 3′-iodo-4-mercaptobiphenyl and 3′-nitro-4-mercaptobiphenyl. More complex polymorphic systems were also explored. The crystal system 1,3-bis(*m*-nitrophenyl) urea (MNPU) is known to exist as three nonsolvated forms (α, β, and δ) [32–34] and one monohydrate phase (γ) [34]. Recently, we demonstrated that three out of the four forms can each be selectively nucleated and grown on appropriately functionalized 4′-substituted-4-mercaptobiphenyl SAM templates [28].

The present study provides details on the template-directed nucleation observed when each of four different crystalline substances, 4,4′-diiodobiphenyl (**DIBP**), 2-methyl-4-nitroaniline (**MNA**), 3-nitroaniline (**NA**), and 2-amino-5-nitropyridine (**ANP**), are crystallized in the presence of SAMs made from 4′-X and 3′-X-4-mercaptobiphenyl (X = NO_2 or I).



METHODS

The preparation and characterization of gold-thiol self-assembled monolayers of (**1**) 4′-iodo-4-mercaptobiphenyl, (**2**) 4′-nitro-4-mercaptobiphenyl, (**3**) 3′-iodo-4-mercaptobiphenyl, and (**4**) 3′-nitro-4-mercaptobiphenyl have been described elsewhere [26,27]. The four crystalline compounds utilized in the study – 4,4′-diiodobiphenyl (**DIBP**) (Aldrich, 90%), 2-methyl-4-nitroaniline (**MNA**) (Aldrich, 97%), 3-nitroaniline (**NA**) (Aldrich, 98%), and 2-amino-5-nitropyridine (**ANP**) (Aldrich, 97%)) – were commercially available and used without further purification.

Crystal growth of **DIBP**, **MNA**, **NA**, and **ANP** was achieved from the room temperature slow evaporation of supersaturated solutions in the absence and presence of SAMs **1–4**. SAMs were positioned vertically against the side of the vials, so that they would not lay flat on the bottom. The addition of SAMs **1–4** to these solutions resulted in crystal

growth directly on the template surfaces. For each crystal system examined, visible sized crystals were observed on only one out of the four different templates, usually within a period of 3–5 days. Crystal growth was not observed on the other three SAMs even over significantly longer periods. The unit cells of both solution-grown and SAM-grown crystals were obtained from single crystal X-ray diffraction and compared against their known crystal structures. X-ray goniometry was used to characterize the morphology of all solution grown crystals and to establish the orientation of crystals which nucleated on the SAM templates.

The program EpiCalc [35] was used to confirm that for the first three SAM/crystal interfaces described, the 2-dimensional lattice parameters of the contacting surfaces are geometrically related by coincident epitaxy. In the fourth case, the periodicities of the surfaces at the SAM/crystal interface do not appear to be coincident. The 2D lattice parameters of the crystal surface were determined from the unit cell parameters of the known crystal structures. The 2D lattice parameters of the SAMs used in these calculations were ones previously reported for SAMs of 4′-methyl-4-mercaptobiphenyl ($4.8 \times 10.0\,\text{Å}$, $\alpha = 90^\circ$) [36] and/or 4′-chloro-4-mercaptobiphenyl ($5.5 \times 8.0\,\text{Å}$, $\alpha = 90^\circ$) [37]. The crystal morphology pictures presented in Figures 1–4 were generated using the program WinXMorph [38].

RESULTS AND DISCUSSION

For each of the systems described below, the same general approach was adopted. Crystal growth was first attempted from a variety of solutions in order to determine the ones appropriate for each system. All solution-grown crystals were examined by optical microscopy, single crystal X-ray diffraction, and further characterized with differential scanning calorimetry to ensure phase purity. Crystal growth was also attempted in the presence of each SAM **1–4**. Crystals grown on SAM templates were carefully removed from the surface with tweezers, mounted on an X-ray goniometer head, and a sufficient number of reflections were collected so that accurate unit cell parameters could be determined. The cells were compared against known structures and used to assign Miller indices to all the natural faces. Each of the four crystal systems examined in this study are described in separate sections below.

A. 4,4′-Diiodobiphenyl (DIBP)

The structures of substituted biphenyls have attracted the interest of crystallographers for over three decades. Biphenyl [39] and the

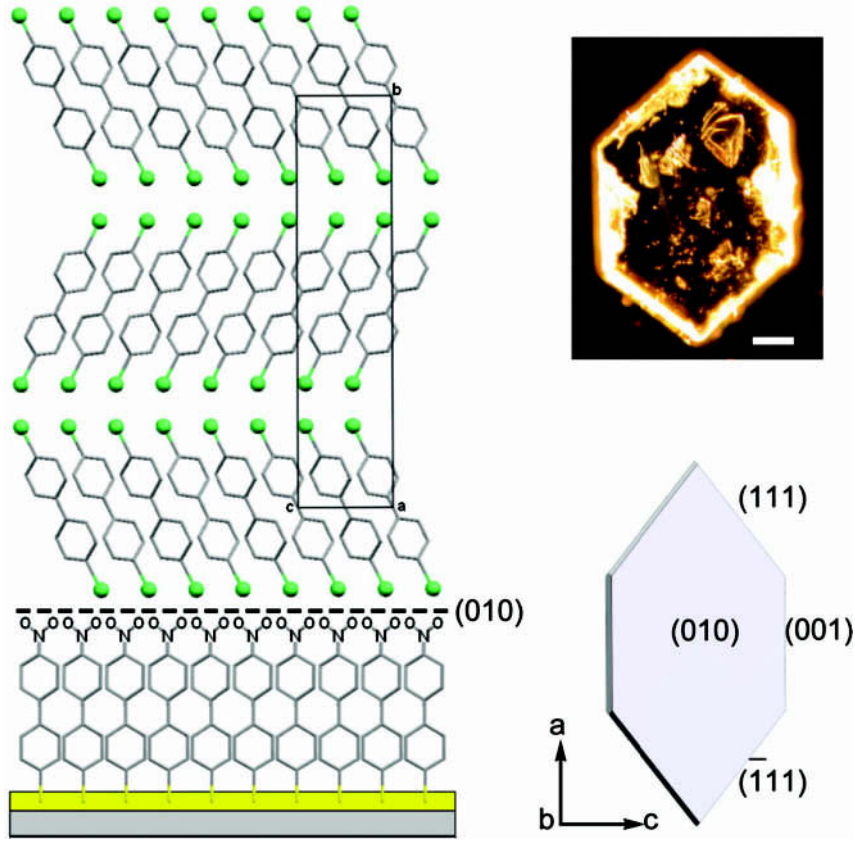


FIGURE 1 Oriented growth of 4,4′-diiodobiphenyl (DIBP). (left) Schematic of the **DIBP** (010)/SAM **2** interface with hydrogen atoms omitted for clarity; (top right) Micrograph of **DIBP** nucleated on SAM **2**, scale bar = 0.2 mm; (bottom right) Morphology with Miller indices assigned.

isostructural 4,4′-difluorobiphenyl [40] crystallize in monoclinic $P2_1/a$ structures in which molecules adopt planar conformations and assemble into discreet layers. Many of the other symmetrically substituted 4,4′-biphenyls, including the 4,4′-dichloro- [41], 4,4′-dibromo- [42,43], and 4,4′-dimethyl [44] derivatives adopt an isostructural $P2_1/n$ structure which is different from that of biphenyl. The orthorhombic structure of **DIBP** (*Pccn*: $a = 7.418$ Å, $b = 25.667$ Å, $c = 5.965$ Å) (REFCODE = FAYHET) recently reported by Britton [45], is not isomorphous with any of the other known dihalobiphenyl compounds, though it shares some structural similarities with other diiodoaromatics.

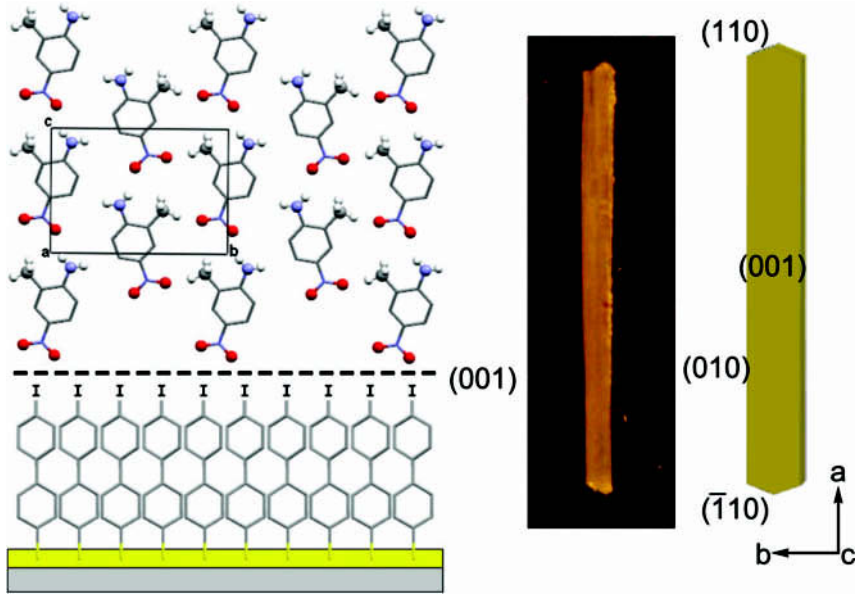


FIGURE 2 Oriented growth of 2-methyl-4-nitroaniline (**MNA**). (left) Schematic of the **MNA** (001)/SAM **1** interface with some hydrogen atoms omitted for clarity; (middle) Micrograph of **MNA** crystal nucleated on SAM **1**; (right) Morphology with assigned Miller indices assuming a space group *Ia*.

Our own efforts to crystallize **DIBP** by traditional methods (e.g., slow evaporation and/or cooling of a wide variety of solutions) typically yielded soft plate-like hexagonal crystals that were severely twinned. Those grown from supersaturated ethanol solutions in the presence of SAM **2** seemed to be of generally higher quality, such that a complete structure determination was possible. Our structure was identical to that previously reported. Ethanol-grown crystals of **DIBP** exhibited large (010) faces and smaller (001) and (111) side faces. The (010) plate face of the crystal was always found in contact with the underlying SAM **2** template. Despite repeated attempts, SAMs **1**, **3** and **4** did not seem to support heterogeneous nucleation.

Epitaxy calculations based on geometric lattice-matching suggest that the (010) **DIBP** surface lattice parameters (5.965×7.419 Å, $\beta = 90^{\circ}$) should be coincident with SAMs made from 4′-X-4-mercaptobiphenyls [23]. The lattice periodicities of the 3′-substituted SAMs are not known, though ellipsometry measurements indicate that the molecules are also oriented nearly perpendicular to the surface and

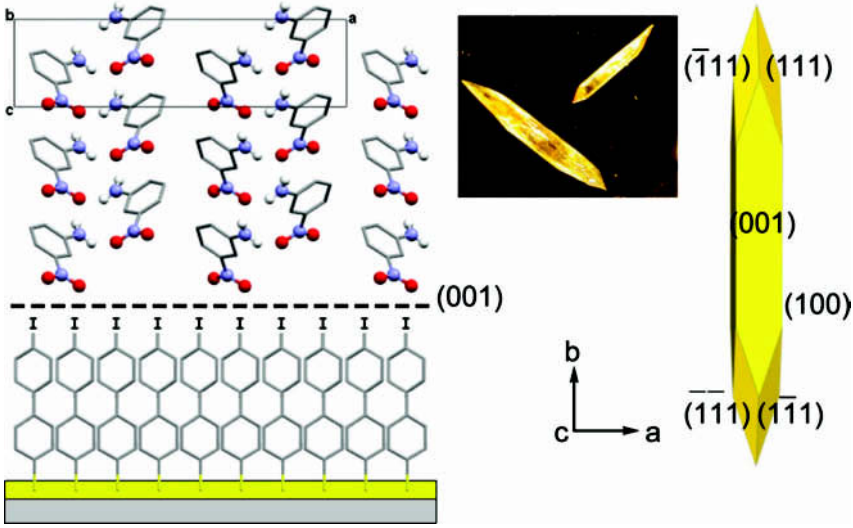


FIGURE 3 Oriented growth of 3-nitroaniline (**NA**). (left) Schematic of the **NA** (001)/SAM **1** interface with some hydrogen atoms omitted for clarity; (middle) Micrograph of **NA** crystals nucleated on SAM **1**; (right) Morphology with assigned Miller indices.

therefore likely give surface periodicities that are of a similar order of magnitude. The fact that only SAM **2** was able to support heterogeneous nucleation suggests that chemical interactions at the interface likely play an important role in directing crystal nucleation. Of all the naturally occurring crystal faces, the (010) surface presents the highest density of iodo groups. The C-I bonds project out from the (010) **DIBP** surface at a 63° angle (assuming no surface reconstruction). Nucleation on a SAM terminated with 4′-NO_2 groups would enable intermolecular $NO_2 \cdots I$ contacts to form across the SAM/crystal interface. Hypothetical $I \cdots I$ contacts across the interface of SAM **1** are expected to be less energetically favorable, despite the fact that the crystals themselves contain such interfaces. The fact that nucleation was not observed on SAM **4** is more difficult to explain, but it likely due to a less favorable orientation of NO_2 groups on the surface, or possibly to a difference in the long-range 2-dimensional ordering of 3′-X-SAMs versus 4′-X-SAMs.

B. 2-Methyl-4-nitroaniline (MNA)

The first entry for **MNA** in the Cambridge Structural Database (CSD) is a 1981 report by Lipscomb et al. [46] (REFCODE = BAJCIY).

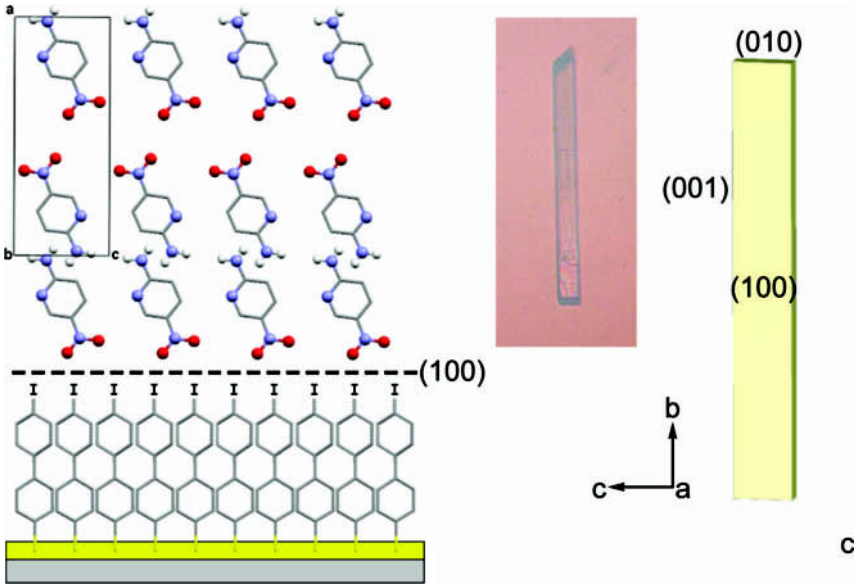


FIGURE 4 Oriented growth of 2-amino-4-nitropyridine (**ANP**). (left) Schematic of the **ANP** (100)/SAM **1** interface with some hydrogen atoms omitted for clarity; (middle) Micrograph of **ANP** nucleated on SAM **1**; (right) Morphology with assigned Miller indices.

A space group of *Cc* was reported, but no atomic coordinates. A more complete structure of **MNA** with atomic coordinates was later reported by Ferguson et al. [47] (REFCODE = BAJCIY01); in the non-standard setting *Ia*, where $a = 7.611\,\text{Å}$, $b = 11.630\,\text{Å}$, $c = 8.229\,\text{Å}$, and $\beta = 94.050^\circ$. Wondering whether this might be an indication of polymorphism, we embarked on our own growth studies of **MNA**. SAMs **1–4** seemed like a reasonable choice, given our previous study on SAM-templated growth of **INA** [27] which is similar in molecular shape.

Our growth of **MNA** from ethanol solutions yielded yellow rod-like crystals. Single crystal X-ray diffraction yielded a space group of *Cc* and unit cell parameters $a = 10.723\,\text{Å}$, $b = 11.574\,\text{Å}$, $c = 7.466\,\text{Å}$, and $\beta = 130.420^\circ$, similar to that reported by Lipscomb. Further close examination of the known *Ia* and our *Cc* structures, revealed the two to be identical, not polymorphic. The difference is the choice of the unit cell. Because there is a more extensive literature precedent [48] for using the *Ia* structure, Miller indices we report use this cell convention. The rod-like crystals we obtained were elongated about

the *a* axis, and bounded by large (001) faces and smaller (010), (110), and (−110) side faces (Fig. 2).

In ethanolic solutions containing SAM **1**, crystal nucleation and growth of **MNA** was supported. Template-directed nucleation is evidenced by the fact that all crystals grown on SAM **1** were oriented such that the contacting interface was always between **MNA** (001)/SAM **1**. (For reference, (001) in the space group setting *Ia* corresponds to (100) in space group setting *Cc*.) Despite our repeated attempts, growth was never observed on SAMs **2**, **3** or **4**.

Calculations using EpiCalc indicate that the lattice parameters for MNA (001) face (7.611 × 11.630 Å, $\beta = 90^\circ$) and the SAM are related by coincident epitaxy. However, since **MNA** crystals are polar, the (00-1) and (001) faces are chemically inequivalent. Nitro groups are projected in the –*c* direction while the amine and methyl groups are projected in the +*c* direction. In order to have stabilizing $NO_2 \cdots I$ interactions across the interface, we assume that the contacting face must actually be (001) and not (00-1) since NO_2−C bonds project outward from this surface at an angle of 71°. In this orientation they should be readily able to form intermolecular $NO_2 \cdots I$ interactions with the SAM **1** surface. This control of absolute polar growth direction is analogous to the polar orientation control observed previously for **INBP** [26].

C. 3-Nitroaniline (NA)

Structural studies of **NA** have interested crystallographers since the early 1970s, mainly because of the material's non-linear optical properties and interesting phase transitions at both low and high temperatures [49,50–52]. Wojcik and Holband examined the crystal structure of **NA** at several temperatures over a range from 90 to 350 K, but because our crystallization experiments are performed under ambient conditions, we cite the room temperature structure parameters – $Pca2_1$: $a = 19.361$ Å, $b = 6.502$ Å, $c = 5.068$ Å (REFCODE = MNIANL05) [52].

Growth from ethanol in the presence of SAM **1**, resulted in yellow prismatic needles of **NA** which are slightly elongated along the *b* axis. The contacting interface is always formed between **NA** (001)/SAM **1**. The assignment of Miller indices by X-ray goniometry revealed large (001) and (100) faces, and smaller (111) and (1-11) end faces. EpiCalc calculations suggest that the (001) face of **NA** (6.502 × 9.681 Å, $\beta = 90^\circ$) and the SAMs surface should be geometrically matched by coincident epitaxy. Because the polar axis in **NA** runs along +/−*c*, the (001) and (00-1) surfaces are chemically distinct. C−NO_2 bonds are projected from the (001) plane at an angle of 77°, but these groups are not expressed on the (00-1) surface. Only the interface between **NA**

(001)/SAM **1**, would be able to support $NO_2 \cdots I$ contacts. The absence of nucleation on SAM **3** suggests that either the orientation or 2D-spacing of NO_2 groups on this SAM surface is not as well suited for stabilizing the formation of critical nuclei.

D. 2-Amino-4-nitropyridine (ANP)

ANP is known to exist either in a monohydrate phase (REFCODE = GIVYAL) or as an anhydrous compound (REFCODE = GIVXUE) [53]. The anhydrous form crystallizes in the orthorhombic space group *Pnma*: with $a = 15.357$, $b = 6.080$, $c = 6.099$. Crystallization from ethanol yielded **ANP** with a structure identical to that previously reported. Morphologically, the crystals are yellow plates/blades with (100) plate faces, and smaller (001) and (010) side faces. Crystals are typically elongated in the crystallographic $\pm b$ direction.

The same crystals of **ANP** were found to nucleate on SAM **1**, always with the (001) face in contact with the template surface. On the other hand, SAMs **2**, **3** and **4** did not support crystal nucleation. Unlike the three previous examples, EpiCalc calculations indicate that the 2D surface lattice of **ANP** (6.080×6.099 Å, $\beta = 90^\circ$) is not coincidentally matched with the SAM surfaces. Two caveats should be offered for this result – there may be some local variability in the lattice dimensions of a SAM over large distances and epitaxy calculations do not account for the possibility of surface reconstructions. While epitaxy may or may not be a factor in this nucleation, the fact that crystals grown on SAM **1** are always preferentailly oriented, suggests that a favorable interaction exists at the SAM **1**/**ANP** {100} interface.

ANP crystals are centrosymmetric, so the (100) and (−100) surfaces are chemically identical. Molecularly smooth (100) surfaces are terminated either with C-NH_2 bonds projecting from the surface at an angle of 65°, or C−NO_2 bonds projecting 69°. If the crystal surface is terminated with monolayer steps, then regions exposing both functionalities may be present. Like the others, we presume that the orientational preference observed in this system originates from stabilizing $NO_2 \cdots I$ contacts across the SAM/crystal interface. However, it is more difficult to know the exact structure of the contacting crystal surface with certainty.

CONCLUSIONS

The present study adds to our growing number of examples in which molecular crystal nucleation on nitro- and iodo- terminated SAM surfaces is explored. **DIBP**, **MNA**, **NA** and **ANP** each crystallized in an

expected packing arrangement. Although no new polymorphs were identified, nucleation in the presence of SAMs did provide a viable means to control the crystal growth orientation. In the two systems which are polar and exhibit non-linear optical properties (**MNA** and **NA**), the absolute direction of the polar axis is also presumably controlled by the direction of the $NO_2 \cdots I$ interactions formed at the SAM/crystal interface. The results of these studies add to our working knowledge of the specific parameters that should be considered in future template design strategies.

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