CHAPTER 2

Polar Assembly of Dipolar Molecules in Crystals and Thin Films of Metal Complexes
**Papers published**

  Perfectly Polar Assembly of Molecular Dipoles in Crystals of Zn(II)(DMAP)(acac): A Case of Self-Poling.

  Impact of Molecular Structure Change on the Hierarchy of Intermolecular Interactions Leading to Polar/Centrosymmetric Crystals.


  Thin Films of Perfectly Polar Crystallites with Uniaxial Orientational Ordering.

- **Anthony, S. P.; Porel, S.; Rao, D. N.; Radhakrishnan, T. P. (Submitted).**
  Thin Films of Metal-Organic Compounds and Metal Nanoparticle Embedded Polymer for Nonlinear Optical Applications.
2.1 INTRODUCTION

There has been intense research activity in recent years, in the area of molecular materials focusing on the design and systematic alteration of the structure of the constituent molecules with a view to realize specific materials properties.\(^1\) Synthetic chemistry provides great scope for the structural modification of the molecular materials both at the molecular level and at the organization level, i.e. the level where we wish to control the assembly of molecules in the solid state.\(^2\) Bulk properties of molecular materials are often directly related to the relative orientation and organization of the constituent molecules. Molecular materials based on dipolar molecules with a polar organization of the molecules, form an important class of materials, since many technologically useful solid state properties such as ferroelectricity, pyroelectricity, piezoelectricity and second order nonlinear optical effects could be realized in them.\(^3\) A brief account of the relevance of molecular orientation to many solid state properties was presented in Sec. 1.4. We have developed a novel family of metal-organic compounds with a push-pull structure which forms perfectly polar assemblies in the crystal lattice. Interesting cases of polymorphism and oriented growth of crystallites in vapor deposited thin films were observed with these molecular materials. All the materials show moderate second harmonic generation.

Fabrication of polar molecular materials often requires special techniques. For example, parallel alignment of molecular dipoles in doped polymer films is achieved through electric field poling.\(^4\) Approaches towards polar molecular assembly in crystals have relied on the use of a supporting framework structure. In Sec. 2.2, we describe the synthesis of a new class of coordination complexes of zinc which exhibit perfectly polar organization of the molecular dipoles in the crystal lattice. The polar ordering of the single component system can be described as a case of ‘self-poling’, and is discussed on the basis of a hierarchy of anisotropic intermolecular interactions in the three-dimensional crystal lattice. We discuss two of the new materials in Sec. 2.3.

In Sec. 2.4, we describe the polymorphism observed in another complex in this series; it forms perfectly polar as well as centrosymmetric crystal structures depending sensitively on the solvent and the rate of crystallization. A suitable choice of solvents
provides crystals exhibiting an unusual cogrowth of polar/centric as well as polar/polar domains. Semiempirical computational modeling studies of molecular clusters of the dimorphic structures gives useful insight into the delicate balance of energetics involved in the solvent polarity preference of the extreme structures. The SHG of microcrystalline powders of the different compounds are presented in Sec. 2.5.

In Sec. 2.6, we discuss the fabrication of thin films of these metal-organic systems on amorphous glass substrates by vapor deposition method. X-ray diffraction studies reveal orientational ordering of the perfectly polar crystallites in these films. Position and distance of the substrate from the sublimation boat is shown to be the critical factors controlling the crystallite orientation. Morphology of the films was studied by scanning electron microscopy. Optical second harmonic generation measurements on the thin films clarify further, the uniaxial orientational ordering of the crystallites and the random orientation within the plane. Sec. 2.7 summarizes the work presented in this chapter.

### 2.2 SYNTHESIS AND CHARACTERIZATION

The new zinc complexes we have developed and present in this chapter are: (4-dimethylaminopyridyl) bis(acetylacetonato) zinc(II) (ZNDA), (4-morpholinopyridyl) bis(acetylacetonato) zinc(II) (ZNMPA) and (4-pyrrolidinopyridyl) bis(acetylacetonato) zinc(II) (ZNPPA). The structures and synthesis are depicted in Scheme 2.1. Morpholinopyridine, pyrrolidinopyridine and Zn(acac)$_2$$\cdot$H$_2$O were synthesized following the procedures reported in the literature. General procedure for the preparation of ZNDA, ZNMPA and ZNPPA is as follows. The compounds were prepared by the direct addition of the solution of 1 mmol of the appropriate pyridine ligand in 10 ml methanol to a solution of 1 mmol of Zn(acac)$_2$$\cdot$H$_2$O in 50 ml methanol. The mixture was stirred for 5 min at room temperature and the white microcrystalline product obtained was filtered, washed with cold methanol and vacuum dried. Characterization of each of the compounds is listed below.

(4-dimethylaminopyridyl)bis(acetylacetonato)zinc(II) (ZNDA): Yield: 90%; M. P: 237-240°C; UV-Vis (methanol): $\lambda_{\text{max}}$ ($\lambda_{\text{cut-off}}$) = 282 nm (330 nm); FT-IR (KBr pellet):
\( \tilde{\nu}/\text{cm}^{-1} : 3078.7, 2918.6 \) (C-H stretch), 1608.8 (aromatic C=C stretch), 1010.8 (C-H bend); \(^1\)H NMR (CDCl\(_3\)): \( \delta/\text{ppm} = 1.85 \) (s, 12H), 2.98 (s, 6H), 5.25 (s, 2H), 6.67 (d, \( J=6\text{Hz}, 2H \)), 8.01 (d, \( J=6\text{Hz}, 2H \)); \(^{13}\)C NMR (CDCl\(_3\)): \( \delta/\text{ppm} = 28.0, 46.1, 99.1, 107.1, 148.5, 153.6, 191.8 \).

(4-morpholinopyridyl)bis(acetylacetonato)zinc(II) (ZNMPA): Yield: 90%; M. P: 228-230° C; UV-Vis (methanol): \( \lambda_{\text{max}} (\lambda_{\text{cut-off}}) = 283 \text{ nm (323 nm)} \); FT-IR (KBr pellet): \( \tilde{\nu}/\text{cm}^{-1} : 3078.7, 2918.6 \) (C-H stretch), 1610.7 (aromatic C=C), 1010.8 (C-H bend); \(^1\)H NMR (CDCl\(_3\)): \( \delta/\text{ppm} = 1.85 \) (s, 12H), 3.31 (t, 4H), 3.68 (t, 4H), 5.25 (s, 2H), 6.92 (d, 2H), 8.05 (d, 2H); \(^{13}\)C NMR (CDCl\(_3\)): \( \delta/\text{ppm} = 28.0, 45.6, 65.8, 99.1, 108.3, 148.9, 155.6, 191.8 \).

\[
\begin{align*}
\text{H} & \quad \text{O} \\
\text{H} & \quad \text{H}
\end{align*}
\]
\[
\begin{align*}
\text{Zn} & \quad \text{O} \\
\text{O} & \quad \text{Zn}
\end{align*}
\]

\[
\text{R} = \text{NHCCH}_3
\]

\[
\text{ZNDA}
\]

\[
\text{R} = \text{NCH}_4
\]

\[
\text{ZNMPA}
\]

\[
\text{R} = \text{NCH}_5
\]

\[
\text{ZNPPA}
\]

Scheme 2.1
(4-pyrrolidinopyridyl)bis(acetylacetonato)zinc(II) (ZNPPA): Yield: 90%; M. P: 245°C; UV-Vis (methanol): $\lambda_{\text{max}}$ ($\lambda_{\text{cut-off}}$) = 282 nm (322 nm); FT-IR (KBr): $\bar{v}/\text{cm}^{-1}$: 3074.9, 2949.7 (C-H stretch) 1606.7 (aromatic C=C), 1009.3 (C-H bend); $^1$H NMR (CDCl$_3$): $\delta$/ppm = 7.98 (d, 2H), 6.36 (d, 2H), 5.29 (s, 2H), 3.29 (t, 4H), 2.05 (m, 4H), 1.98 (s, 12H); $^{13}$C NMR (CDCl$_3$): $\delta$/ppm = 25.0, 28.9, 47.1, 99.4, 107.0, 148.2, 152.6, 192.9.

2.3 PERFECTLY POLAR ORGANIZATION OF DIPOLAR MOLECULES IN CRYSTALS OF ZNDA AND ZNMPA

The formation of molecular assemblies possessing a polar axis, is one of the most remarkable aspects of solid state organization. This unique solid state phenomenon has no counterpart in liquid or gas phase where molecules can undergo relatively ready reorientation. Molecular materials with a polar organization of the constituent dipoles are of interest in the development of novel electro-optic (EO) and photo-refractive devices and nanoscale components such as molecular rectifiers. Inclusion compounds have been investigated in the past with a view to develop new strategies for designing polar solids.

It is essential that the molecular chromophores are arranged noncentrosymmetrically in the crystalline state to have a nonvanishing macroscopic second order nonlinear optical response from the material. Molecular crystals show a strong predilection towards centrosymmetric organization. Special design strategies are often employed to induce noncentrosymmetricity. Still rarer are highly polar molecular crystals with molecular dipoles aligned parallel to a single axis. Strategies such as cocrystallization, salt formation, host-guest complexation and framework systems have been developed for achieving polar molecular assembly in crystals. These approaches require a supporting structure to achieve parallel alignment of molecular dipoles, which reduces the density of the active component in the bulk and invariably leads to less effective utilization of the bulk materials to achieve desired solid state properties. Crystal engineering strategies have been utilized in the development of single component systems with polar organization of molecular dipoles. Parallel alignment of
molecules has been achieved in crystals of some zinc complexes. A molecular design strategy proposed by Hulliger in involves a dipolar backbone with an optimal decoration that dictates weak or non-bonding lateral recognition, leading to a polar crystal lattice. A potential candidate for such an approach would be a 'screw'-shaped molecule with a dipolar axis and 'head' which curtails lateral interactions without obstructing one-dimensional head-to-tail Coulombic interactions. We have developed the simple metal-organic compounds, ZNDA, ZNMPA and ZNPPA that form perfectly polar organization of molecular dipoles in the crystals. In these compounds, the pyridyl-zinc combination forms the polar entity and the acetylacetonate ligands, the 'head' structure. We have analyzed the crystal structure of these compounds and the intermolecular interactions which appear to promote the parallel orientation of the molecular dipoles in the three-dimensional supramolecular assembly. We discuss the structure of ZNDA and ZNMPA in this section.

**Crystal Structure Investigations**

**ZNDA**

Colorless crystals of ZNDA could be grown by slow evaporation of methanol solution. X-ray analysis showed that the crystals belong to the orthorhombic space group Fdd2 with half a molecule in the asymmetric unit; the C2 operation generates the other half. The basic crystallographic data are presented in Table 2.1. The molecular structure of ZNDA is shown in Fig. 2.1. Zinc and the coordinated pyridine nitrogen, the para carbon and dimethylamino nitrogen atoms on 4-dimethylaminopyridine (DMAP) lie on special positions on the c-axis. Zn(II) has distorted square-pyramidal coordination with normal bond parameters. The space filling model of the molecular structure shows the 'screw'-shaped structure clearly (Fig. 2.2). More interestingly, the molecules pack into a perfectly polar lattice with the dipoles aligned along the c axis (Fig. 2.3) by virtue of the special position of Zn and DMAP and the space group operations. The origin of this organizational motif may be sought in the interplay of intermolecular interactions in the ZNDA lattice.
ZNDA is expected to have a sizeable dipole moment due to the push-pull nature of the DMAP-Zn(II) combination; AM1 calculation\(^2\) on the molecular geometry taken from the crystal structure, gives a value of 8.919 D. The electrostatic interaction between the dipoles directs the head-to-tail chain formation along the c axis. This is augmented by weak intermolecular H-bonds\(^2\) between the carbon atoms of the dimethylamino groups of the DMAP ligand and oxygen atoms of the \textit{acac} ligand of neighboring.

### Table 2.1 Crystallographic data for ZNDA and ZNMPA

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<td>1.001</td>
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<td>0.1189</td>
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Figure 2.1 Molecular structure of ZNDA from single crystal analysis. 95% probability thermal ellipsoids are indicated; H atoms are omitted for clarity.

Figure 2.2 Space-filling model of the molecular structure of ZNDA determined from single crystal analysis.
Figure 2.3  View of the unit cell of ZNDA viewed along the b axis; H atoms are omitted for clarity.

Figure 2.4  Intermolecular close contacts (broken lines) in the sheets of ZNDA molecules in the bc plane; H atoms are omitted for clarity.
molecules ($r_{C7\cdots O12} = 3.679\ \text{Å}; \theta_{C7-H7B\cdots O12} = 158.7^\circ$). A further network of weak intermolecular H-bonds ($r_{C4\cdots O8} = 3.612\ \text{Å}, \theta_{C4-H4\cdots O8} = 139.6^\circ; r_{C7\cdots O8} = 3.526\ \text{Å}, \theta_{C7-H7A\cdots O8} = 155.6^\circ; r_{C4\cdots O12} = 3.585\ \text{Å}, \theta_{C4-H4\cdots O12} = 151.0^\circ$) between DMAP and acac binds the ZNDA molecules into a sheet parallel to the $bc$ plane (Fig. 2.4). The sheets are well separated in the $a$-direction with a distance of $\sim 7\ \text{Å}$ between adjacent DMAP planes (Fig. 2.5).

Neither strong nor even the weak bonding interactions present within the sheets are observed between the sheets. Thus the three-dimensional lattice structure of ZNDA is built from electrostatic interactions along the $c$ axis and weak noncovalent interactions within the $bc$ plane leading to sheet structures with no bonding recognition between the sheets in the $a$ direction. This bulk organization can be viewed in terms of the Hulliger model\textsuperscript{17} for the generation of polarity in supramolecular systems.

![Figure 2.5](image.png)

**Figure 2.5** Projection of the crystal lattice of ZNDA onto the $ab$ plane; H atoms are omitted for clarity.
ZNMPA

Crystals of ZNMPA grown from methanol are found to belong to the polar monoclinic space group, Cm with half a molecule in the asymmetric unit. The basic crystallographic data are presented in Table 2.1. The molecular structure is shown in Fig. 2.6. Zn(II) has similar distorted square-pyramidal coordination environment as found in ZNDA. The space-filling model of the ZNMPA molecule clearly shows the ‘screw’-shaped structure in this molecule as well (Fig. 2.7). Two carbon atoms of the morpholine ring in chair conformation show disorder due to ring flipping. The molecules assemble into a perfectly polar lattice with the molecular dipoles aligned along the [1 0 1] direction (Fig. 2.8).

Figure 2.6 Molecular structure of ZNMPA from single crystal analysis. 95% probability thermal ellipsoids are indicated. The disordered position of C10 and C13 are shown; H atoms are omitted for clarity.
Similar to the situation in ZNDA, this can be analyzed in terms of the intermolecular interactions in the lattice. A weak coordinate bonding interaction between the morpholino oxygen and the zinc metal of the neighboring molecules ($r_{O-Zn} = 2.628 \AA$) directs the head-to-tail chain formation. The polar chain is further supported by the weak intermolecular H-bonds between the morpholino carbon atoms and oxygen atoms of acac ligands ($r_{C-O} = 3.279, 3.366 \AA$) (Fig. 2.9). A further network of weak intermolecular H-bonds ($r_{C-C} = 3.402, 3.569 \AA$) between the morpholinopyridine and acac in the $ac$ plane binds the ZNMPA molecules into a sheet structure. The lattice can be visualized in terms of the stacking of the polar sheets along the $b$ direction. The mirror plane $(ac)$ ensures that the sheets are oriented in the same direction. The sheets are well separated in the $b$ direction with negligible interactions between ZNMPA molecules (Fig 2.10). The three-dimensional polar structure of ZNMPA is built from weak coordinate bonding as well as noncovalent interactions within the $ac$ plane leading to sheet structures with no bonding recognition.

*Figure 2.7* Space-filling model of the molecular structure of ZNMPA determined from single crystal analysis; only one of the (disordered) conformation of cyclohexane is shown.
Figure 2.8  Perfectly polar assembly of molecules in crystals of ZNMPA viewed along b-axis; $H$ atoms, the methyl C atoms of the acac ligand and the disordered positions of two C atoms in the morpholine group are omitted for clarity.

Figure 2.9  Intermolecular close contacts (broken lines) in ZNMPA crystal lattice ($R_1 = 2.628$, $R_2 = 3.279$, $R_3 = 3.366$, $R_4 = 3.402$, $R_5 = 3.569$ Å).
Figure 2.10 Projection of the crystal lattice of ZNMPA onto the ab plane; H atoms, the methyl C atoms of the acac ligand and the disordered position of the two C atoms in the morpholine group are omitted for clarity.

between the sheets in the b direction. It once again establishes the tendency of this family of molecules to form polar assemblies without the assistance of counterions, cocrystallization partners or a host lattice. As noted earlier, the model for polarity generation developed by Hulliger and coworkers\textsuperscript{13,17} provides a basis to understand the perfectly polar assemblies of these 'screw'-shaped molecules in the crystal lattice.

2.4 EXTREME ORIENTATIONS OF DIPOLAR MOLECULES IN DIMORPHIC STRUCTURES OF ZNPPA

The process of crystallization is of great scientific and technological importance because the resulting crystal structures largely determine the solid state properties,\textsuperscript{22} the electronic, magnetic and optical attributes of materials. Molecules often adopt different packing arrangements that are close in energy leading to polymorphic crystal structures.\textsuperscript{23} Organization of molecules in crystals results from a complex, often subtle interplay of
intermolecular interactions, making accurate \textit{ab initio} prediction of crystal structures, a very difficult proposition.\textsuperscript{24} The problem is considerably compounded in the case of polymorphic structures where, even under apparently identical conditions as in concomitant polymorphs,\textsuperscript{25} the same molecule organizes in different crystalline assemblies. Particularly intriguing would be the case of polymorphs which manifest grossly different packing motifs. Such a situation could, in principle be encountered in the context of centrosymmetric and noncentrosymmetric polymorphic structures of dipolar molecules, the latter being of potential interest in quadratic nonlinear optical applications.\textsuperscript{26} Though several instances of such polymorphism are known,\textsuperscript{27} noncentrosymmetric lattices often involve small deviations from a centrosymmetric organization,\textsuperscript{28} leading to descriptions such as 'approximately centrosymmetric'.\textsuperscript{27} Optimal molecular orientations for applications like phase-matched second harmonic generation or electro-optic effect call for specific design strategies.\textsuperscript{29,11}

A case that merits special attention is the formation of perfectly polar molecular assemblies\textsuperscript{30,14,15} as described in the previous section. Such a situation where the molecules make exactly 0° angle with respect to a specific crystallographic direction would be the opposite extreme of the commonly encountered centrosymmetric formation,\textsuperscript{9} which by analogy can be described as constituted of 'perfectly antiparallel' molecular dipoles with equal numbers making 0° and 180° angles with respect to a specific crystallographic direction. Even though, polymorphism has been extensively studied in supramolecular chemistry, cases of such extreme molecular organizations in polymorphic structures are rare. One case that we are aware of is that of the dithiadiazolyl radical.\textsuperscript{31}

During our investigation of the perfectly polar compounds, we have observed that (4-pyrrolidinopyridyl)bis(acetylacetonato)zinc(II) (ZNPPA) shows extreme molecular orientation of dipoles in dimorphic structures.\textsuperscript{32} ZNPPA forms perfectly polar as well as centrosymmetric crystal structures depending sensitively on the solvent and the rate of crystallization. We have carried out semiempirical computational modeling of molecular clusters, incorporating solvation effects, to understand the energies involved in the solvent polarity preference of the extreme structures. We have observed an interesting cogrowth of the dimorphic structures as well as formation of twin polar domains in
monolithic crystals of ZNPPA. This observation suggests the possibility of realizing novel multidomain crystal architectures.

**Crystal Structure Investigations: Role of the solvent and rate of crystallization in the formation of the dimorphic structures and multidomain crystals**

ZNPPA was synthesized by mixing methanolic solutions of 4-pyrrolidinopyridine and Zn(acac)$_2$H$_2$O. The microcrystalline powder showed clear SHG, suggesting that the molecules are assembled in a noncentric lattice structure. However, the crystals of ZNPPA grown by slow cooling and evaporation of methanol solution were SHG inactive and found to belong to the centrosymmetric space group, C2/c; we will refer to this structure as ZNPPA1. The basic crystallographic data are collected in Table 2.2. The molecular structure of ZNPPA1 is shown in Fig. 2.11. Zn(II) has distorted square-pyramidal coordination with normal bond parameters as found in ZNDA and ZNMPA. Weak intermolecular H-bonds between the pyrrolidino carbons and acac of the neighboring molecules are observed in the polar chains formed along the $b$-axis. A further network of weak intermolecular H-bonds between 4-pyrrolidinopyridine and acac binds the ZNPPA1 molecules into a sheet parallel to the $ab$ plane (Fig. 2.12). Adjacent sheets are oriented in opposite directions leading to a centrosymmetric structure (Fig. 2.13).

The structure of ZNPPA1 was surprising since the perfectly polar crystals of the similar molecules, ZNDA and ZNMPA were grown from methanol and microcrystals of ZNPPA precipitated from methanol showed SHG. Semiempirical AM1 calculation on the molecular geometry taken from the respective crystal structures indicated that the dipole moment of ZNPPA (9.53 D) is higher than that of ZNDA (8.92 D). This suggested that the stronger dipole-dipole interactions in the case of ZNPPA might be screened more effectively in a solvent more polar than methanol. Slow evaporation of methanol-water (80:20) solutions of ZNPPA yielded crystals with two morphologies - nearly square plates and prismatic blocks in approximately 2:1 weight ratio. X-ray analysis of the square plates showed that they were ZNPPA1 crystals. Single crystal
studies of the prismatic blocks showed that they possess a new crystal structure belonging to the noncentrosymmetric space group, Fdd2; we refer to this polymorph as ZNPPA2. The basic crystallographic data are collected in Table 2.2. The molecular structure is

**Table 2.2 Crystallographic data for ZNPPA1 and ZNPPA2**

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Figure 2.11 Molecular structure of ZNPPA from single crystal analysis. 95% probability thermal ellipsoids are indicated; H atoms are omitted for clarity.

Figure 2.12 Intermolecular close contacts (broken lines) leading to polar sheets in the ab plane of ZNPPA crystal (R1 = 3.580, R2 = 3.356, R3 = 3.670, R4 = 3.610 Å).
Figure 2.13  Centrosymmetric assembly of molecules in ZNPPA1; H atoms are omitted for clarity.

Figure 2.14  Intermolecular close contacts (broken lines) leading to polar sheets in the ac plane of ZNPPA2 crystal lattice (R1 = 3.463, R2 = 3.400, R3 = 3.551 Å).
nearly identical to that observed in ZNPPA1. Weak intermolecular H-bonding networks between the pyrrolidinopyridine and acac ligand of the neighboring molecules leads to the polar sheet parallel to the $ac$ plane (Fig 2.14). The sheets are well separated along the $b$ axis. More significantly, the adjacent sheets assemble in a parallel fashion along the $b$ direction and lead to the perfectly polar organization with all molecular dipoles aligned along the $c$ axis (Fig. 2.15).

Crystals of ZNPPA1 and ZNPPA2 possess very similar two-dimensional formations of ZNPPA molecules in the $ab$ and $ac$ planes, respectively, bound through weak intermolecular interactions; the molecular dipoles are aligned parallel within the sheets. The critical differentiation between the two crystal packings arises at the level of organization of these molecular sheets, with net macroscopic dipole of adjacent sheets antiparallel in ZNPPA1 and parallel in ZNPPA2. The extreme molecular orientation of dipoles exhibited by the dimorphic structures (Fig. 2.16a) is illustrated by the linear array of molecules that may be envisioned using one from each sheet (Fig. 2.16b). ZNPPA2 is one more entry to the series of perfectly polar structures.

**Figure 2.15** Unit cell of ZNPPA2 viewed approximately along the $a$ axis; $H$ atoms are omitted for clarity.
Figure 2.16 Extreme orientations of molecular dipoles in ZNPPA₁ and ZNPPA₂ lattices (a) schematic view; (b) view from crystal structure analysis.
We have systematically explored the conditions promoting the formation of ZNPPA1 and ZNPPA2 in different solvent polarity environment. ZNPPA obtained by the direct addition of its components in methanol is inferred to be ZNPPA2, based on the SHG observed as well as the comparison of the powder x-ray diffractogram of the microcrystalline sample with the pattern simulated using the ZNPPA2 crystal structure (Fig. 2.17). However, as noted earlier, slow crystallization of ZNPPA2 from methanol yielded exclusively ZNPPA1; these crystals have nearly square plate morphology. The

![Figure 2.17. Powder x-ray diffractogram of ZNPPA2 (a) simulated from single crystal structure (b) recorded for microcrystalline sample obtained by direct addition of 4-pyrrolidinopyridine and Zn(acac)$_2$H$_2$O in methanol.](image)
exclusive formation of ZNPPA1 polymorph from methanol was also confirmed by the comparison of powder x-ray diffractogram with the pattern simulated using ZNPPA1 crystal structure (Fig. 2.18). Crystals grown from chloroform-toluene were also found to be ZNPPA1. This suggests that the formation of ZNPPA2 is promoted in more polar solvents. Since water-methanol mixture yields a mixture of the dimorphs as stated.

**Figure 2.18.** Powder x-ray diffractogram of ZNPPA1 (a) simulated from single crystal structure (b) recorded for microcrystals sample of ZNPPA1 obtained by recrystallization from methanol.
earlier, and ZNPPA has negligible solubility in pure water, we have investigated the use of DMSO as the solvent for crystallization. Fast precipitation by cooling produces SHG inactive material suggesting that ZNPPA1 is obtained. However, slow evaporation of dilute solutions yielded crystals of ZNPPA1 as well as new crystals of an unusual morphology (Fig. 2.19), which could not be indexed satisfactorily (the latter was approximately 25% by weight). However, this crystal can be smoothly cleaved to separate the cuboid and truncated pyramidal halves. Interestingly, the two domains could be independently indexed to the unit cells of ZNPPA1 and ZNPPA2 respectively, proving that the crystals from DMSO are indeed composite monoliths comprising of the extreme dimorphs. The cleavage plane corresponds to the (001) and (010) planes of the two

**Figure 2.19** Morphology of ZNPPA crystals: (a) centric (ZNPPA1) from methanol, (b) polar/centric from DMSO and (c) polar/polar from chloroform-DMSO. The scales indicate 500 μm and the arrows, the boundary between the domains.
Table 2.3  Crystallization condition and the polymorph of ZNPPA obtained; multidomain crystals are indicated with a slash.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Rate</th>
<th>Polymorph</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol*</td>
<td>Fast / Slow</td>
<td>ZNPPA1</td>
</tr>
<tr>
<td>CHCl₃-Toluene</td>
<td>Slow</td>
<td>ZNPPA1</td>
</tr>
<tr>
<td>Methanol-Water</td>
<td>Slow</td>
<td>ZNPPA1, ZNPPA2</td>
</tr>
<tr>
<td>DMSO</td>
<td>Fast</td>
<td>ZNPPA1</td>
</tr>
<tr>
<td>DMSO</td>
<td>Slow</td>
<td>ZNPPA1, ZNPPA1 / ZNPPA2</td>
</tr>
<tr>
<td>CHCl₃-DMSO</td>
<td>Slow</td>
<td>ZNPPA2 / ZNPPA2</td>
</tr>
<tr>
<td>CHCl₃-NMP</td>
<td>Slow</td>
<td>ZNPPA1, ZNPPA2 / ZNPPA2</td>
</tr>
</tbody>
</table>

*Direct synthesis of ZNPPA in methanol provides ZNPPA2, but only as microcrystals respectively which have a close registry as seen from the unit cell lengths (Table 2.2). When crystals of ZNPPA are grown from chloroform-DMSO mixture, a still different morphology is obtained. The different morphologies of the crystals are shown in Fig. 2.19. The bipyramidal crystal again could not be indexed as a whole, but when cleaved at the middle, the two parts could be indexed to ZNPPA2 crystal with the cleavage plane corresponding to (010). Crystals grown from chloroform-NMP mixture gives square plate (ZNPPA1) as well as bipyramidal (ZNPPA2) morphologies. The different crystallization conditions and the types of polymorphs formed are summarized in Table 2.3. It may be noted that the cogrowth of centric/polar domains exhibited by ZNPPA is different from situations such as statistical twinning where the demarcation of the polymorphic domains is not well defined and lamellar twinning involving mirror image domains of enantiomorphic molecules, where the molecular packing in the two domains are identical.
Semiempirical Computational Modeling of Molecular Clusters of ZNPPA1 and ZNPPA2

It is important to note that neither of the structures, ZNPPA1 and ZNPPA2, includes solvent molecules in the lattice. This has enabled us to compare the energetics of supramolecular assembly at the level of small clusters, which lead to the extreme cases of three-dimensional organization. The utility of such an approach in modeling the polymorphism of some nitroaniline derivatives have been demonstrated earlier. AM1 computations were carried out on molecular clusters (dimers to octamers) extracted from the crystal structures; H atom positions alone were optimized. The solvent environment during the crystallization was mimicked using the COSMO option; calculations employed dielectric constants of methanol and water representing environments with...

Figure 2.20 AM1/COSMO computed enthalpies of formation (in water vs. methanol) of various molecular clusters of ZNPPA1 and ZNPPA2.
different polarities. The clusters from both the structures show higher stabilization in the more polar environment; however, the relative stabilization is slightly enhanced for ZNPPA2 compared to ZNPPA1 (Fig. 2.20). This suggests that even though the higher polarity preference of ZNPPA2 clusters is marginally more, solvent polarity control of the formation of the apparently extreme motifs in ZNPPA1 and ZNPPA2 are very closely balanced. Comparison of the enthalpies of formation of similar size clusters from the dimorphic structures in either solvent indicates that ZNPPA1 is always stabilized over ZNPPA2. The formation of both structures in water-methanol as well as DMSO, therefore suggests that thermodynamic factors alone do not determine the dimorph formation. It is interesting however, that ZNPPA1 is the major product in most of the cases (Table 2.3).

2.5 SHG STUDIES ON MICROCRYSTALLINE POWDERS OF ZNDA, ZNMPA AND ZNPPA2

ZNDA, ZNMPA and ZNPPA molecules possess a 'push-pull' electronic system with the amino group as the donor and the pyridinium unit involving the electropositive metal as the acceptor. AM1/TDHF calculations using the molecular geometry from crystal structures show a static hyperpolarizability of \( \sim 4 \times 10^{-30} \) esu for these molecules. Even though the hyperpolarizabilities are small and the polar organization is not the optimal arrangement for SHG, the noncentrosymmetric organization of molecules in the crystal lattice of ZNDA, ZNMPA and ZNPPA2 is expected to lead to solid state SHG in these materials. These compounds are found to have good thermal stability and stability towards laser radiation (at a power of \( \sim 1 \) GW cm\(^{-2}\)). SHG from microcrystalline powders was examined using the Kurtz-Perry technique. Details of the experiment are provided in Appendix C. Table 2.4 presents the powder SHG of ZNDA, ZNMPA and ZNPPA2 at various particle sizes. The particle size dependence of SHG indicates phase-matchable behavior of these materials.
Table 2.4 SHG of microcrystalline powders of ZNDA, ZNMPA and ZNPPA2 at different particle sizes. 1 U = SHG of urea having particle size > 150 μm.

<table>
<thead>
<tr>
<th>Compound</th>
<th>SHG (U)</th>
<th>Particle size (μm)</th>
<th>Average value at saturation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>100-150</td>
<td>150-200</td>
</tr>
<tr>
<td>ZNDA</td>
<td>0.92</td>
<td>0.91</td>
<td>1.02</td>
</tr>
<tr>
<td>ZNMPA</td>
<td>0.93</td>
<td>1.21</td>
<td>1.30</td>
</tr>
<tr>
<td>ZNPPA2</td>
<td>0.86</td>
<td>0.89</td>
<td>0.95</td>
</tr>
</tbody>
</table>

2.6 FABRICATION OF THIN FILMS WITH UNIAXIALLY ORIENTED MICROCRYSTALLITES AND OPTICAL SHG STUDIES

Acentric supramolecular assemblies of dipolar molecules are potential candidates for a multitude of information-processing and photonic applications, such as high speed electro-optic modulation, optical switches, and nonlinear optical waveguides for integrated frequency conversion. The desirable characteristics of thin films for frequency conversion and telecommunication applications are the following. (i) They must be noncentrosymmetric showing strong second order NLO effects, (ii) their thickness must be of the order of one micrometer, able to support waveguiding, (iii) they must be homogenous and of good optical quality over large areas of the order of square centimeters, and iv) they must have good photostability.

Thin films of dipolar molecules with noncentrosymmetric ordering have been grown using techniques such as LB and self-assembled monolayer method. The drawbacks of these approaches are that they are time consuming processes and the final material is usually fragile since the assembly is principally by van der Waals interactions. Vapor phase depositions techniques offer the advantages of high growth...
rates, good chemical purity due to vacuum conditions, in-situ growth monitoring, and layer thickness control.\textsuperscript{44} Thin films with oriented crystallites have been fabricated by sublimation onto oriented PTFE\textsuperscript{45} and cleaved single crystals\textsuperscript{46} and by mechanical dragging procedures.\textsuperscript{47} Günter and coworkers have used organic molecular beam deposition process to grow films of H-bonded molecules with preferred orientations.\textsuperscript{48} Oriented crystallites and thin films of NLO-phores have been fabricated through vapor phase assembly on functionalized substrates.\textsuperscript{49}

In the previous sections we have described the novel, single component perfectly polar supramolecular organization of simple metal-organic compounds in crystals. In addition to possessing good optical transparency ($\lambda_{\text{cut-off}} < 330$ nm), these materials have good thermal stability and can be sublimed without decomposition. We envisaged that they would be ideal candidates for thin film assembly through vapor deposition on glass substrates. Examination of ZNDA, ZNPPA and ZNMPA showed that, not only is the perfectly polar crystal structure maintained in the thin films, but additionally the crystallites in the film show orientational ordering with respect to the substrate normal. Oriented crystallite growth through the vapor phase assembly on amorphous substrates is driven by intermolecular interactions rather than substrate control and hence is especially interesting from a molecular materials perspective. Distance of the substrate from the sublimation boat plays a critical role in effecting the crystallite orientation. Interestingly, ZNPPA films show the presence of both the dimorphic forms, ZNPPA1 and ZNPPA2. Morphology of the thin films were investigated by scanning electron microscopy (SEM). Polarization dependence of SHG is in agreement with the uniaxial orientational ordering of the crystallites in the films.\textsuperscript{45}

**Thin Film Fabrication and X-ray Diffraction Studies**

Microcrystalline powder of the compound to be sublimed was taken in a molybdenum boat. The glass substrate for deposition was cleaned by sonication in methanol followed by acetone and dried in oven at 100 °C for 1 h. Pressure inside the vacuum chamber was maintained at $\sim 10^{-6}$ mbar. Sublimation was achieved using typically 25 A current. The schematic diagram of sublimation set up is shown in Fig.
2.21. Different positions of the substrate, on and away from the normal to the sublimation boat were explored; the position directly above the boat was found to be the most suitable for obtaining oriented crystallites. Distance of the substrate from the sublimation boat was found to be the critical factor for effecting the crystallite orientation. We have checked the films for any signs of decomposition. The microcrystalline powders obtained by scratching the films off the substrate show the full diffraction pattern expected from the crystal structure of the material indicating that no chemical or crystallographic alterations occur during the fabrication process. The ir spectrum of the sublimed material also was consistent with that of the original compound.

![Schematic diagram of the sublimation setup](image)

**Figure 2.21** *Schematic diagram of the sublimation setup*

Thin films were fabricated by placing the substrate at different distances directly above the sample and its structural ordering was probed by x-ray diffraction. X-ray diffractogram of ZNDA film grown at different distances is shown in Fig. 2.22a. Comparison of the diffractogram to the pattern simulated using the single crystal structure of ZNDA (Fig. 2.22c) shows that the films show a high degree of crystallite orientational ordering. When the substrate is at the optimal distance of 5 cm, the film
Figure 2.22 X-ray diffractograms of ZNDA thin film fabricated at (a) different boat-substrate distances, $d$ and (b) at $d = 5$ cm (enlarged).
shows exclusively \((h\ 0\ 0)\) peaks (Fig. 2.22b) suggesting a preferential \(a\) axis orientation normal to the substrate \((h = 4n\) is imposed by the Fdd2 space group); at other distances, \((1\ 1\ 1)\) and \((2\ 2\ 0)\) peaks are also observed. From the x-ray diffraction data on the films and the single crystal structure it can be inferred that the molecular dipoles which point along the crystallographic \(c\) axis are oriented parallel to the substrate plane in the thin films of ZNDA.

The diffractogram of the films of ZNMPA grown at different distances are collected in Fig. 2.23a. ZNMPA grown at the optimal distance of 7 cm show exclusively \((h\ k\ 0)\) reflections \((h = k)\), suggesting crystallite orientation with the \([1\ 1\ 0]\) axis normal to the substrate (Fig. 2.23b). The x-ray pattern simulated using the single crystal structure of ZNMPA is shown in Fig. 2.23c. From the x-ray diffraction of the film and
the single crystal structure, it can be shown that the molecular dipoles are oriented at an angle of 50.8° with respect to the substrate in the thin films of ZNMPA.

![X-ray diffractograms of ZNMPA films formed at different boat-substrate distances, d.](image)

**Figure 2.23a** X-ray diffractograms of ZNMPA films formed at different boat-substrate distances, d.

In the previous section we have shown that crystals of ZNPPA form dimorphic structures with extreme dipole orientations. Interestingly, ZNPPA forms the dimorphic structures in the thin films as well. At nonoptimal distances, both centrosymmetric and noncentrosymmetric structures are obtained in the films as well (Fig. 2.24a); interestingly, both show preferred orientations. When the substrate is at 5 cm, the
Figure 2.23b  X-ray diffractogram of ZNMPA thin film fabricated at $d = 7$ cm

Figure 2.23c  Powder x-ray diffraction pattern simulated using ZNMPA crystal structure with peak indexing.
centrosymmetric structure ZNPPA1 is exclusively formed, with the $c$ axis oriented normal to the substrate (Fig. 2.24b). It is significant to note that the noncentrosymmetric structure could not be obtained exclusively in the film at any of the substrate position; this is reminiscent of the rarer formation of ZNPPA2 structure in crystallization experiments. The peaks are indexed using the powder x-ray diffractograms based on single crystal structures of ZNPPA1 (Fig. 2.24c) and ZNPPA2 (Fig. 2.24d). It is significant to note that in ZNDA and both the forms of ZNPPA, the crystallites are oriented with the longest unit cell axis normal to the substrate. These observations provides direct demonstration of the uniaxial orientational ordering of the polar crystallites with respect to the substrate normal, in the thin films of this family of metal organic compounds.

Figure 2.24a  X-ray diffractograms of ZNPPA films formed at different boat-substrate distances, $d$ ($C$ and $N$ correspond to ZNPPA1 and ZNPPA2 respectively).
Figure 2.24b  X-ray diffractogram of ZNPPA thin film fabricated at $d = 5 \text{ cm}$

Figure 2.24c  Powder x-ray diffraction pattern simulated using ZNPPA1 crystal structure with peak indexing.
Morphology of the Thin Films

We have examined the morphology of the films to gain insight into the crystallite organization. Films having thickness of 0.4-0.6 μm were examined after providing a thin gold coating. ZNDA film shows square or rectangular crystallites with sizes in the range of 60-200 nm (Fig. 2.25a). The micrograph clearly reveals a face-on orientation of the crystallites, but little ordering of the crystallite axes parallel to the substrate plane. We have also observed micron-sized, flat crystallites when the film thickness is increased. Scanning electron micrograph of ZNMPA film is shown in Fig. 2.25b. It shows that the film is formed from well-packed, flat, micron-sized crystallites, resulting in a smooth surface. The crystallites reveal a clear orientational preference with their flat face parallel to the substrate. The SEM image shows that there is no ordering of crystallite orientations within the plane. ZNPPA shows needle-like crystallites in the films (Fig. 2.25c). The widths are typically 1 μm and length 10 μm. We have not observed any
difference in the morphology of the crystallites in films of exclusively centrosymmetric or dimorphic structures of ZNPPA. Preferential orientation of crystallites perpendicular to the substrate plane is not as clear in these films as in the previous cases. The SEM images of the ZNDA and ZNPPA also show that there is no ordering of crystallite orientations within the plane in the films.

Figure 2.25 SEM images of (a) ZNDA, (b) ZNMPA and (b) ZNPPA thin film on glass substrate
Optical SHG Studies of Thin Films

SHG from the thin films on glass substrates was examined in transmission mode. Details of the experimental set up are provided in Appendix D. It was ascertained that the glass substrate alone produces no detectable SHG. Since films of pure ZNPPA2 could not be prepared, we have studied only the ZNDA and ZNMPA films. Films with different thickness were prepared and the thickness was measured by a profilometer. The

![Graph](image)

**Figure 2.26** Dependence of the SHG of (a) ZNDA and (b) ZNMPA films on the thickness
Figure 2.27 Polar plots of the SHG of (a) ZNDA and (b) ZNMPA film in q-p (filled circle) and q-s (open circle) geometries (see text for details) as a function of the angle of rotation of the plane of polarization of the fundamental wave; the zero of the scale is chosen to coincide with one of the maxima in the q-p geometry, in each case.
SHG was examined at different regions and the variation was found to be within the experimental error, indicating good homogeneity of the film over the area (~2 cm$^2$). In addition, the SHG varies quadratically with the film thickness in both ZNDA and ZNMPA films (Fig. 2.26), indicating that the homogeneous organization is preserved with film growth.

Following the procedure developed by Zyss and coworkers,\(^4\) the SHG was measured in p and s-polarizations, in the so-called q-p and q-s geometries, when the plane of polarization of the fundamental wave is rotated. It may be noted that there is no special axis in the plane of the film imposed either by the substrate or by the fabrication protocol. The SHG intensity variation for the q-p and q-s geometries shows a 90° phase shift in both ZNDA and ZNMPA films (Fig. 2.27); this follows the pattern predicted for a collection of crystallites with uniaxial orientational ordering but random orientations within the plane.\(^4\) Thus the SHG study further corroborates the crystallite orientations revealed by the x-ray diffraction and morphological studies in these films of metal-organic compounds which exhibit the rare phenomenon of perfectly polar supramolecular assembly.

### 2.7 SUMMARY

The novel ‘screw’-shaped molecules with the ‘push-pull’ framework presented in this chapter exhibit the rare phenomenon of perfectly polar organization wherein the molecular dipoles are aligned parallel to one of the crystallographic directions. Examination of the crystal structures of ZNDA and ZNMPA in Sec. 2.3 revealed that these molecule form head-to-tail chains, promoted most likely, by dipolar interactions and polar sheet structures through weak intermolecular interactions between these chains. These sheets are organized into perfectly polar three-dimensional lattices. This bulk polar organization is in accord with the requirements put forth in the stochastic model\(^1\) for the generation of polarity in supramolecular systems. These compounds demonstrate the formation of single component perfectly polar molecular crystals with high density of active components, without the involvement of a supporting structure based on a framework lattice, counterion or cocrystallization partner. We have found that even with
the ‘screw’ shaped dipolar molecules, if relatively stronger lateral H-bonding interactions are incorporated, it results in the formation of antiparallel alignment of molecular dipoles in the crystal lattice.\textsuperscript{50} We have also observed that in a vanadyl complex, subtle modification of the ligand can have a drastic effect on the coordination geometry switching it between \textit{cis} and \textit{trans}, leading to a modification of the hierarchy of intermolecular interactions and changing the crystal organization from perfectly polar to a centrosymmetric one.\textsuperscript{51}

In Sec. 2.4, we have presented an interesting case of dimorphism involving extreme molecular orientations in the two structures. The polar and centric packings exhibited by ZNPPA provide an interesting demonstration of the close and subtle energetics and kinetics involved in supramolecular assembly. The studies of the multidomain crystals suggest the possibility of obtaining different polarity in cogrowth domains of monolithic crystals. The domain structure built up of SHG active and inactive regions can be mapped using techniques such as second harmonic microscopy.\textsuperscript{52} This would be an important direction for further work on these materials. If the orientational and spatial attributes of the domains can be controlled, it would be of considerable interest in developing crystals which simulate periodically poled structures for applications such as quasi phase-matched SHG.

In Sec. 2.6, we have described the fabrication of these novel compounds in the form of thin films by vapor deposition. Powder x-ray diffractogram studies demonstrated the orientational ordering of the perfectly polar microcrystallites in the films. The critical role of the substrate position with respect to the sublimation boat for effecting the crystallite orientation was demonstrated. Polarization dependence of the SHG from these films reveals the uniaxial orientational ordering of the crystallites with random orientation within the plane of the homogeneous thin films.\textsuperscript{45} The fabrication of homogeneous thin films with orientationally ordered crystallites, through the physical vapor deposition of a family of metal-organic compounds which form perfectly polar assemblies in crystals, demonstrates the generality of this effect for this class of materials. In addition to projecting a fundamentally interesting phenomenon, the current study presents materials of potential utility in opto-electronic applications.
REFERENCES


9. The latest update (version 5.26) of the Cambridge Crystallographic Database shows 75.5% of the entries to be centrosymmetric.


Chapter 2


