

# Perfectly polar assembly of molecular dipoles in crystals of Zn(II)(DMAP)(acac)<sub>2</sub>: a case of self-poling†

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**Molecular dipoles assemble with a perfectly polar alignment in the crystals of the title complex and the hierarchy of intermolecular interactions in the lattice adheres to the requirements of a previously reported stochastic model for the production of polarity in supramolecular assemblies.**

Molecular materials with a polar organization of the constituent dipoles are of great current interest because a variety of technologically important solid state properties such as pyroelectricity, piezoelectricity and nonlinear optical (NLO) effects may be realized in them.<sup>1</sup> Such materials would be the basis for the development of novel electro-optic (EO) and photo-refractive devices<sup>2</sup> and nanoscale components such as molecular rectifiers.<sup>3</sup> Parallel alignment of molecular dipoles embedded in polymer films is achieved through electric field poling.<sup>4</sup> Non-centrosymmetric lattices are not common in molecular crystals;<sup>5</sup> special design strategies are often employed to induce noncentrosymmetry.<sup>6</sup> Still rarer are highly polar molecular crystals with molecular dipoles aligned parallel to a single axis. Marder *et al.* have developed the ‘salt methodology’ wherein the anion sheets provide the driving force favoring a net polar alignment of cation sheets;<sup>7</sup> the well-known NLO crystal DAST has molecular dipoles in the crystal *ab* plane oriented at *ca.* 20° on either side of the *a* axis.<sup>7b</sup> Optimal chromophoric orientation for EO applications has been achieved through co-crystallization approaches by Bosshard and coworkers.<sup>8</sup> Another successful strategy is the inclusion of polar guest molecules in channels of host molecules developed by Hulliger *et al.*<sup>9</sup> The latter have also carried out stochastic modeling of the growth of polar bulk structures.<sup>10</sup> One of the significant conclusions from their study is that polarity in supramolecular assemblies is a tunable property controlled by the energetics of intermolecular interactions in different directions. While bonding interactions are required to assemble chains or sheets of polar molecules aligned along the direction of polarity evolution, the lateral interactions are required to be non-bonding recognitions to achieve 3-D polar alignment. The low density of the active molecules in two-component salts, co-crystals and the host-guest inclusion materials leads to less effective utilization of the bulk material to achieve the desired solid state effects. If molecular design involves a dipolar backbone with an optimal decoration that dictates weak or non-bonding lateral recognition, the assembly should lead to a polar crystal lattice with a higher density of the active species, a situation ideally suited for EO applications.<sup>11</sup> A potential candidate would be a ‘screw’-shaped molecule with a dipolar axis and a ‘head’ which curtails lateral interactions without obstructing 1-D head-to-tail Coulombic interactions. We have realized this paradigm in the perfectly polar lattice of (4-dimethylaminopyridyl)bis(acetylacetonato)zinc(II) (ZNDA); DMAP–Zn forms the polar entity and the acac ligands the

‘head’. This material also possesses good thermal stability and transparency.

ZNDA was synthesized by the direct replacement of the water molecule in Zn(acac)<sub>2</sub>·H<sub>2</sub>O by DMAP. Colorless crystals could be grown from methanol. X-Ray analysis revealed the orthorhombic space group *Fdd2* with half a molecule in the asymmetric unit;<sup>12</sup> *C*<sub>2</sub> rotation generates the other half. Zinc and the coordinated pyridine nitrogen, the *para* carbon and dimethylamino nitrogen atoms on DMAP lie on special positions on the *c*-axis. Zn(II) has distorted square-pyramidal coordination with normal bond parameters;<sup>13</sup> Fig. 1 shows clearly the ‘screw’-shaped structure. The molecules pack into a perfectly polar lattice with the dipoles aligned along the *c* axis (Fig. 2) by virtue of the special position of Zn and DMAP. 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<sup>14</sup> on the molecular geometry 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<sup>15</sup> between the carbon atoms of the dimethylamino groups of the DMAP ligand and oxygen atoms of the acac ligand of neighboring molecules (*r*<sub>C7...O12</sub> = 3.679 Å; *θ*<sub>C7–H7B...O12</sub> = 158.7°). A further network of weak intermolecular H-bonds (*r*<sub>C4...O8</sub> = 3.612 Å, *θ*<sub>C4–H4...O8</sub> = 139.6°; *r*<sub>C7...O8</sub> = 3.526 Å,

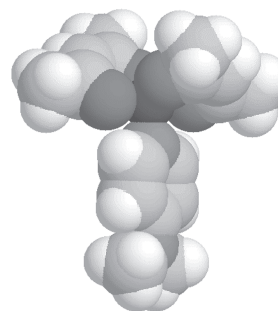


Fig. 1 Space-filling model of the molecular structure of ZNDA determined from single crystal X-ray analysis.

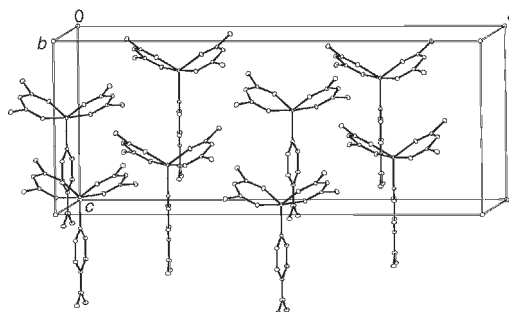
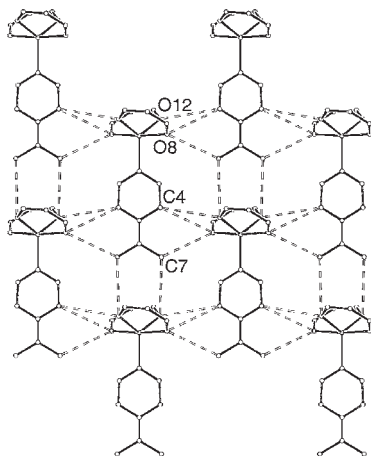
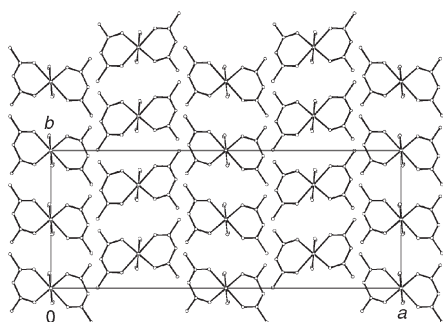


Fig. 2 View of the unit cell of ZNDA viewed approximately along the *b* axis; H atoms are omitted for clarity.

† Electronic supplementary information (ESI) available: synthesis characterization and crystal structure details of ZNDA and brief structural details of 4-morpholinopyridyl analog of ZNDA. Colour version of the space filling model of the structure of ZNDA. See <http://www.rsc.org/suppdata/cc/b1/b101248g/>



**Fig. 3** Non-covalent interactions (dashed bonds) in the sheets of ZNDA molecules in the *bc* plane; all H atoms and methyl carbon atoms of the acac ligand are omitted for clarity.



**Fig. 4** Projection of the crystal lattice of ZNDA onto the *ab* plane; H atoms are omitted for clarity.

$\theta_{C7-H7A...O8} = 155.6^\circ$ ;  $r_{C4...O12} = 3.585 \text{ \AA}$ ,  $\theta_{C4-H4...O12} = 151.0^\circ$ ) between DMAP and acac binds the ZNDA molecules into a sheet parallel to the *bc* plane (Fig. 3). The sheets are well separated in the *a*-direction with a distance of *ca.* 7 Å between adjacent DMAP planes (Fig. 4). Neither strong nor even the weak bonding interactions present within the sheets are observed between the sheets. Thus the 3-D lattice structure of ZNDA is built from electrostatic interactions along the *c* axis and weak non-covalent interactions within the *bc* plane leading to sheet structures with no bonding recognition between the sheets in the *a* direction. This bulk organization<sup>16</sup> is in perfect accord with the Hulliger model for the generation of polarity in supramolecular systems.

The polar arrangement in molecular lattices is of interest in NLO applications. We have measured the second harmonic generation (SHG) from microcrystalline powders of ZNDA using the Kurtz–Perry technique.<sup>17</sup> SHG comparable to that of urea is observed. The low SHG is due to the small hyperpolarizability (AM1/TDHF<sup>18</sup> calculation on the molecular geometry from crystal structure gives a static hyperpolarizability of  $4.4 \times 10^{-30}$  esu) and the non-optimal molecular orientation in the crystals, for phase-matched SHG.<sup>19</sup> Large single crystals or oriented crystalline films have to be fabricated to carry out EO studies. Our current efforts are directed towards these goals. The good thermal stability (mp = 240 °C) and damage-free sublimation coupled with the large transparency range ( $\lambda_{\text{max}} = 282 \text{ nm}$ ,  $\lambda_{\text{cut-off}} = 330 \text{ nm}$  for methanol

solutions) of ZNDA make it a promising candidate for further explorations.

In conclusion, the perfectly polar lattice of ZNDA, a case of self-poled assembly of molecular dipoles, reveals a hierarchy of intermolecular interactions in different directions in line with the requirements put forth in the stochastic model for the generation of polar supramolecular assemblies.

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