Thin films of perfectly polar crystallites with uniaxial orientational ordering†

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Received 12th November 2004, Accepted 4th January 2005
First published as an Advance Article on the web 17th January 2005
DOI: 10.1039/b417323f

The family of metal–organic complexes, (4-dialkylaminopyridyl)bis(acetylacetonato)zinc(II) which show perfectly polar assembly in the crystalline state are found to grow as orientationally ordered crystallites in vapor deposited thin films on glass substrates. A unique crystallographic axis of the crystallites, the longest unit cell axis in most cases, is oriented perpendicular to the substrate plane. The fact that the current observations cover a family of compounds is novel and of general significance for oriented thin film growth on amorphous substrates. Crystal structure, thin film morphology and second harmonic generation of a representative system are presented; the crystallites in the thin films do not show azimuthal orientational ordering.

Spontaneous organization of dipolar molecules into perfectly polar bulk materials is not common. Such assemblies are of fundamental interest in electro-optic, ferroelectric, and piezoelectric applications.[1] Polar organization of molecules may be achieved in doped polymer films through electric field poling[2] and in Langmuir–Blodgett films, through X or Z type multilayer deposition.[3] Polar molecular crystals have been realized through cocrystallization or salt formation,[4] and host–guest complexation[5,6] approaches. The dilution of the active molecule in these materials due to the presence of a second component required to induce the polar assembly, has been effectively circumvented in the single component, perfectly polar crystals of metal–organic compounds we have reported.[7,8] High quality crystalline thin films are required for many opto-electronic applications. Thin films with oriented crystallites have been fabricated by sublimation onto oriented PTFE[9] and cleaved single crystals[10] and by mechanical dragging procedures.[11] Günter and coworkers have used an organic molecular beam deposition process to grow films of H-bonded molecules with preferred orientations.[12,13] Oriented crystallites and films of NLO-phores have been fabricated through vapor phase assembly on functionalized substrates.[14] The vapor deposition technique is a convenient route to highly pure materials in the form of thin films, amenable to large area applications. 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. We envisaged that the metal–organic complexes noted above, would be ideal candidates for thin film assembly through vapor deposition on glass substrates. Examination of the family of compounds, (4-dimethylaminopyridyl)bis(acetylacetonato)zinc(II) (ZNDA),[7] (4-pyrrolidinopyridyl)bis(acetylacetonato)zinc(II) (ZNPPA)[8] and (4-morpholinopyridyl)bis(acetylacetonato)zinc(II) (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. We report the fabrication of the films by physical vapor deposition and direct demonstration of uniaxial orientational ordering by X-ray diffraction. Crystal structure, scanning electron microscopy (SEM) and optical second harmonic generation (SHG) of ZNMPA films are presented; SEM and SHG studies suggest random in-plane orientation of the crystallites.

All the compounds are stable to sublimation under vacuum and possess good optical transparency ($\lambda_{\text{cut-off}} < 330$ nm). The films were grown on glass substrates, under 10^{-6} mbar pressure. Different positions of the substrate, on and away from the normal to the sublimation boat were explored;[12] 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 crystallite orientation. X-Ray diffractograms of the films of ZNDA, ZNPPA and ZNMPA are presented in Fig. 1a, 1b and 1c respectively; the variations with the position of the substrate are shown. The peaks are indexed[15] using the single crystal structures of ZNDA and ZNPPA reported earlier[7,8] and that of ZNMPA presented below. The optimal distance was found to be 5 cm in the case of ZNDA film (Fig. 1a); the corresponding film shows only (h 0 0) peaks suggesting a preferential $\boldsymbol{a}$ axis orientation normal to the substrate ($h = 4n$ is imposed by the *Fdd*2 space group). At other distances, (1 1 1) and (2 2 0) peaks are also observed. Crystals of ZNPPA have been shown to form dimorphic structures with extreme dipole orientations.[8] At non-optimal distances, both the centrosymmetric (C) and noncentrosymmetric (N) structures are obtained in the films (Fig. 1b); interestingly, both show preferred orientations. When the substrate is at 5 cm, the centrosymmetric structure is exclusively formed, with the $\boldsymbol{c}$ axis oriented normal to the substrate. 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 (unit cell lengths—ZNDA : $a = 28.057$, $b = 11.363$, $c = 11.3253$ Å; ZNPPA (C): $a = 10.994$, $b = 12.322$, $c = 15.365$ Å; ZNPPA (N): $a = 11.1810$, $b = 28.583$, $c = 12.3090$ Å). Films of 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. These observations demonstrate the uniaxial orientational ordering of the polar crystallites with respect to the substrate normal, in the

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† Electronic supplementary information (ESI) available: synthesis and characterization, thin film fabrication and characterization and crystallographic details. See http://www.rsc.org/suppdata/jm/b4/b417323f/
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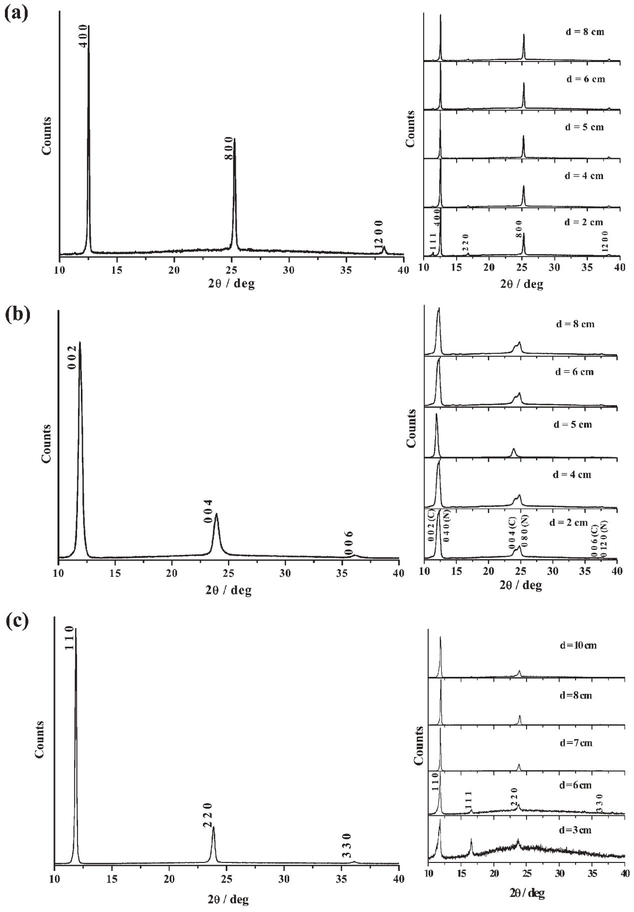

Fig. 1 X-Ray diffractograms of (a) ZNDA, (b) ZNPPA and (c) ZNMPA thin films. *Right*: diffractograms of films formed at different distances, *d*, between the sublimation boat and the substrate, *Left*: enlarged view of the diffractogram for the optimal distance case. N and C in (b) refer to the dimorphic forms of ZNPPA.

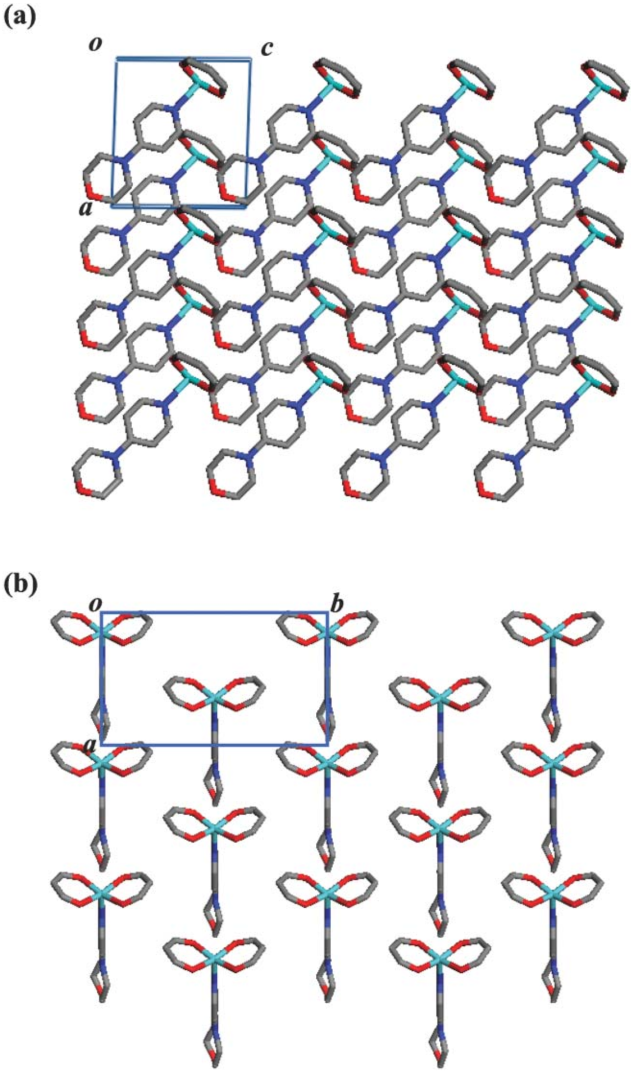

Fig. 2 The perfectly polar assembly of molecules in crystals of ZNMPA: (a) view along ***b*** axis, (b) view along ***c*** axis. C (grey), N (blue), O (red) and Zn (cyan) atoms are indicated; H-atoms, the methyl C atoms of the acac ligand and the disordered positions of two C atoms in the morpholine group are omitted for clarity.

thin films of this family of complexes. The structural and morphological aspects and SHG of ZNMPA presented below as a representative case, provide further insight into the crystallite organization in these thin films.

Crystals of ZNMPA grown from methanol are found to belong to the polar monoclinic space group, *Cm* with half the molecule as the asymmetric unit.[16] Two carbon atoms of the morpholine ring show disorder due to ring flipping; this appears to lead to large thermal parameters for the aromatic ring carbons as well. The molecules assemble into a perfect polar lattice with the molecular dipoles parallel to the [1 0 $\bar{1}$] direction (Fig. 2a). The lattice can be visualized in terms of the stacking of these polar sheets. The mirror plane (***ac***) ensures that the sheets are oriented in the same direction as can be inferred from Fig. 2b. The 'self-poled' assembly is similar to that in ZNDA[7] and in the polar form of ZNPPA.[8] As discussed earlier,[7] the stochastic model for polarity generation developed by Hulliger and coworkers[6,17] in terms of hierarchical intermolecular interactions, could provide a basis for understanding the perfect polar assembly of these screw-shaped molecules. From the X-ray diffraction data (Fig. 1c) and the single crystal structure it can be shown that the molecular dipoles are oriented at 50.8° with respect to the substrate in the thin films of ZNMPA. The films we have fabricated have thicknesses in the range 0.3–2 μm. The scanning electron micrograph in Fig. 3 shows that the film consists of well-packed, flat, micron-sized crystallites, resulting in a smooth surface. The crystallites exhibit a clear orientational preference with their flat face parallel to the substrate. The X-ray diffraction indicates that this face is the (1 1 0) plane. The SEM image reveals no ordering of crystallite orientation within the plane.

The ZNMPA molecule possesses a 'push–pull' electronic system with the morpholino group as the donor and the pyridinium unit involving the electropositive metal as the acceptor. Kurtz–Perry[18] measurements on the microcrystalline powder using a 1064 nm laser beam indicated an SHG of $\sim$1.0 U (U = SHG of urea). We have examined the SHG from the thin films; the quadratic variation with thickness (Fig. 4a) indicates homogeneous growth of these films. Following the procedure developed by Zyss and coworkers,[9] the SHG was measured in p and s- polarizations, in the so-called q–p and q–s geometries, when the plane of

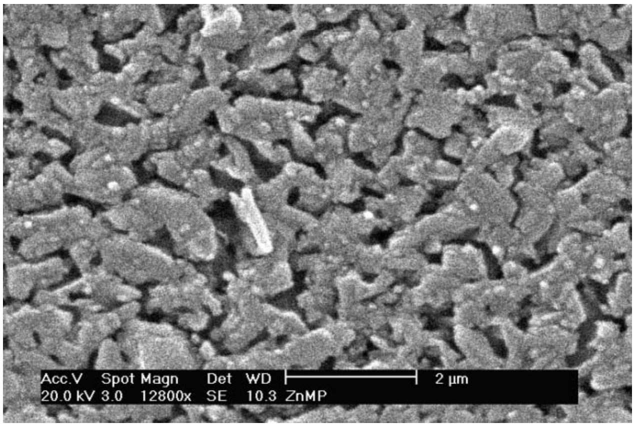

Fig. 3 SEM image of ZNMPA thin film on glass substrate.

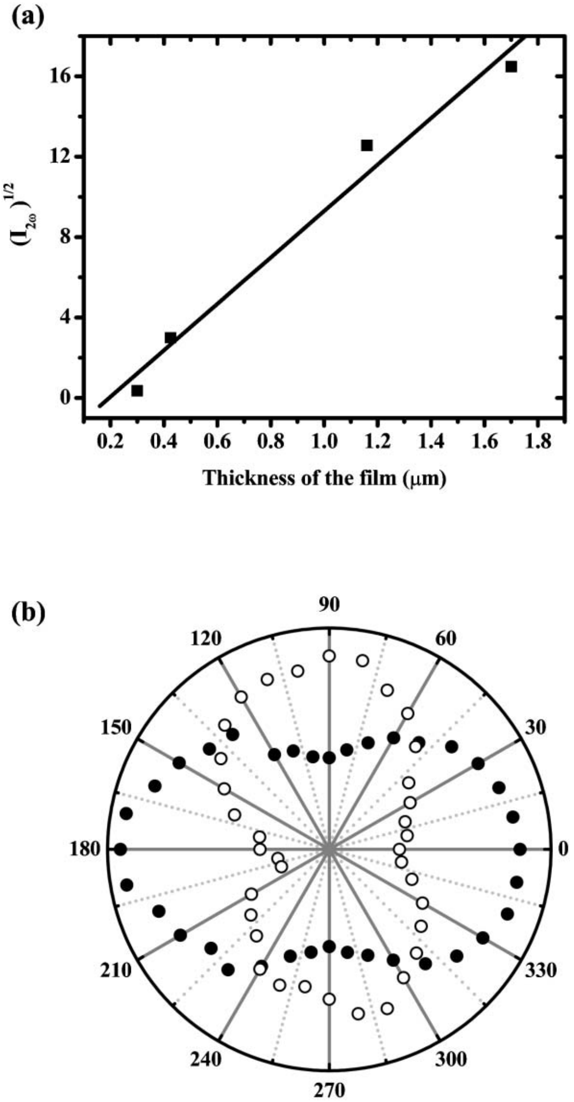

Fig. 4 (a) Dependence of the SHG of ZNMPA films on the thickness; (b) polar plots of the SHG of ZNMPA film in q–p (●) and q–s (○) geometries (see text for details) as a function of the angle of rotation of the plane of polarization of the fundamental wave; the zero of the scale is chosen to coincide with one of the maxima in the q–p geometry.

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 (as in ref. 9) or by the fabrication protocol (as in ref. 12). The similar SHG variation in the two geometries with a 90° phase shift (Fig. 4b) follows the pattern predicted for a collection of crystallites with uniaxial orientational ordering but random orientations within the plane.[9] This inference is consistent with the SEM observation.

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.

Acknowledgements

Financial support from the DST (NSTI program), New Delhi, use of the National Single Crystal X-ray Diffractometer Facility at the School of Chemistry, University of Hyderabad and the University with Potential for Excellence program of the UGC, New Delhi are gratefully acknowledged. SPA thanks the CSIR, New Delhi for a Senior Research Fellowship.

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16 Crystal data for ZNMPA: empirical formula = $C_{9.50}H_{13}NO_{2.50}Zn_{0.5}$, monoclinic, space group *Cm*, a = 8.601(9), b = 14.833(12), c = 7.782(8) Å, β = 91.57(8)°, Z = 4, $\rho_{\text{calc.}}$ = 1.432 g cm^{-3}, μ (MoK_α) = 1.27 mm^{-1}, reflections with $I \geqslant 2\sigma_I$ = 1113, parameters = 159, absorption correction (empirical, ψ–scan) $T_{\min}$ = 0.7896, $T_{\max}$ = 0.9739, R [for $I \geqslant 2\sigma_I$] = 0.0501, wR^2 = 0.1189, Flack parameter = 0.04(3) largest difference peak and hole = 0.58/−0.79 eÅ^{-3}. CCDC reference number 253976. See http://www.rsc.org/suppdata/jm/b4/b417323f/ for crystallographic data in .cif or other electronic format.

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