Thin films of metal-organic compounds and metal nanoparticle-embedded polymers for nonlinear optical applications

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Abstract. Thin films based on two very different metal-organic systems are developed and some nonlinear optical applications are explored. A family of zinc complexes which form perfectly polar assemblies in their crystalline state are found to organize as uniaxially oriented crystallites in vapor deposited thin films on glass substrate. Optical second harmonic generation from these films is investigated. A simple protocol is developed for the *in-situ* fabrication of highly monodisperse silver nanoparticles in a polymer film matrix. The methodology can be used to produce free-standing films. Optical limiting capability of the nanoparticle-embedded polymer film is demonstrated.

Keywords. Polar crystal; uniaxial orientational order; thin film; second harmonic generation; silver nanoparticle; polyvinyl alcohol; free-standing film; optical limiter.

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1. Introduction

The flexibility inherent in the design and fabrication of molecular materials, in terms of fine-tuning the molecular structure and molecular assembly, make these systems promising candidates for a wide range of electronic, magnetic and optical applications. However, molecular materials are yet to find extensive application and their full potential is still not realized. This may be attributed to a number of technical limitations including low thermal and mechanical stability, difficulties of fabricating high-quality single crystals or thin films and poor transparency in the relevant spectral regions in the case of optical and nonlinear optical (NLO) applications. Suitable design of the molecular building blocks and incorporation of judiciously chosen metal ions can circumvent some of the problems such as those related to thermal stability and optical transparency; metal-organic compounds are also amenable to fabrication as thin films which offer advantages like high purity due to the vacuum conditions, large area coverage and the facility for application of external fields on the material. We are interested in developing novel metal-organic

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compounds and their thin films and demonstrating molecular assemblies from which quadratic NLO responses such as second harmonic generation (SHG) can be elicited. π-conjugated molecules with a 'push–pull' electronic structure generally possess large hyperpolarizability [1], and if assembled in optimal lattices, produce strong SHG; metal ion coordination can lead to enhanced molecular hyperpolarizability.

Metal nanoparticles are highly promising candidates for nonlinear optical applications such as optical limiting [2]. Most of the earlier studies in this area have focused on colloidal formulations of metal nanoparticles [3]. Thin films with a tunable content of metal nanoparticles would be of considerable value from an application perspective. We have addressed this question also, by invoking an approach based on metal-organic materials. Unlike the case above, in which molecular building blocks of metal ion coordinated organic ligands are used, here we utilize metal nanoparticle-embedded organic polymer thin films. Such an approach should prove quite versatile since a wide range of metals and polymers can be combined and the methodology can be extended even to semiconductor nanoparticles.

We describe in this paper, representative example of a class of zinc complexes we have developed [4,5] which show single component perfectly polar molecular assembly in the crystalline state. Thin films of these materials have been fabricated through physical vapor deposition [6]. Uniaxial orientational ordering of the perfectly polar crystallites in the thin film, achieved under optimal sublimation conditions, is demonstrated by X-ray diffraction and morphology studies on the films. Polarization dependence of the optical SHG from these films corroborates the orientational ordering in these films. We present also, a simple protocol for the *in-situ* generation of silver nanoparticles in a polyvinyl alcohol (PVA) film [7]. The procedure allows the fabrication of free-standing films which can be directly examined in a transmission electron microscope. The thermal treatment for the nanoparticle generation can be fine-tuned to obtain highly monodisperse silver nanoparticles in the 2–3 nm range. Z-scan measurements have indicated appreciable reverse saturable absorption in these films. The optical limiting characteristics of the $\sim$5 μm thick Ag–PVA films are discussed; they are comparable to that of 1–2 mm path length silver colloidal samples reported earlier [8].

2. Thin films of perfectly polar crystallites with uniaxial orientational ordering

The molecular structure of the zinc complexes we have developed, which show perfectly polar organization in the crystalline state is shown in figure 1; we describe the studies on (4-dimethylaminopyridyl)bis(acetylacetonato)zinc(II) (ZNDA) as a representative example. ZNDA crystallizes in the orthorhombic space group, F $d\,d\,2$ with half of the C_2-symmetric screw-shaped molecule (figure 2a) in the asymmetric unit [4]. The assembly of the molecules, with all the dipoles in the crystal lattice oriented parallel to the c-axis is revealed by the unit cell shown in figure 2b. A molecular design strategy for the formation of a polar lattice proposed earlier [9], involves a dipolar backbone with an optimal decoration that ensures weak or negligible lateral recognition and a hierarchy of intermolecular interactions along the polar chain and perpendicular to it [10]. The molecules that we have developed
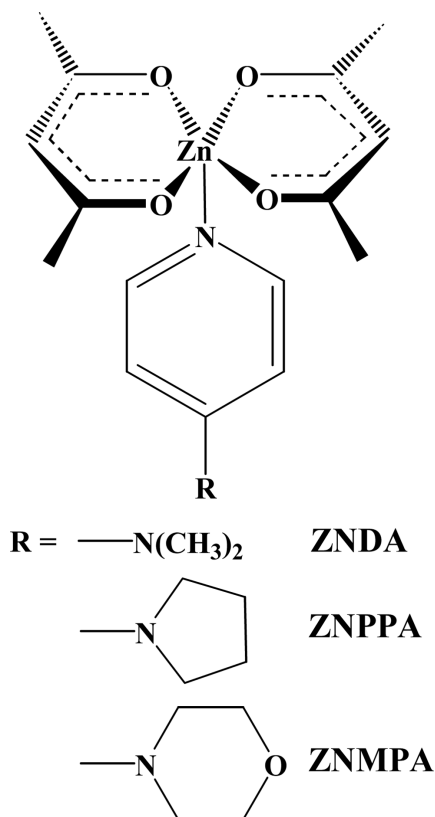
Figure 1. Molecular structure of the zinc(II) complexes which show perfectly polar assembly in crystals.

have a dipolar axis and a head group that curtails lateral close contacts without obstructing the head-to-tail Coulombic interactions. The intermolecular interactions in ZNDA crystals, along the a and b directions are weak or negligible. The model noted above provides some insight into the formation of the perfectly polar lattices in our systems.

Thin films of ZNDA were grown on glass substrates under 10^{-6} mbar pressure, by subliming the solid material. The substrate was placed vertically above the sublimation boat; variation of the distance between the two was found to have a profound influence on the crystallite organization in the thin film. X-ray diffractograms of the thin films fabricated at different distances are shown in figure 3. It is found that the peaks can be indexed [11] using the single crystal structure of ZNDA. Notably, the film obtained at the optimal distance of 5 cm shows only $(h\,0\,0)$ peaks indicating a preferential a-axis orientation normal to the substrate ($h = 4n$ is imposed by the $\mathrm{F}\,d\,d\,2$ space group) [6]. At other distances, $(1\,1\,1)$ and $(2\,2\,0)$ peaks are observed suggesting the occurrence of crystallites in different orientations. It is interesting to note that, in the orientationally ordered films, the longest crystallographic axis is normal to the substrate; similar observations have
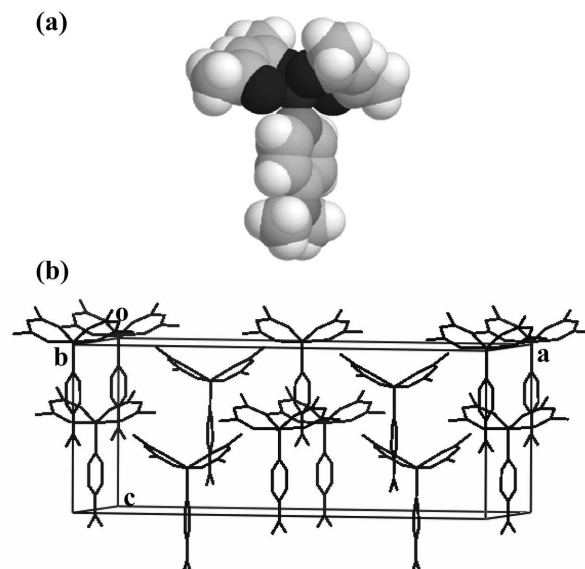
(a)

(b)

Figure 2. (**a**) Molecular and (**b**) crystal structure of ZNDA from single crystal X-ray analysis; H atoms are omitted for clarity.

been made with other compounds as well [6]. The scanning electron micrograph of the thin film (figure 4) shows crystallites with dimensions in the range of 60–200 nm. The organized disposition of the crystallites is clearly observed.

Second harmonic generation from the thin films was measured using the fundamental beam of an Nd:YAG laser (1064 nm, 6 ns, 10 Hz). The quadratic dependence of the SHG on the film thickness (figure 5a) suggests homogeneous growth of the films in the range of 0.1–1.0 μm. The SHG was measured in p and s polarizations (designated as q–p and q–s geometries respectively, since there is no special axis in the film imposed either by the substrate or by the method of film fabrication) by rotating the plane of polarization of the fundamental beam. Similar variations with only a 90° phase shift (figure 5b) follows the pattern expected of a collection of crystallites with uniaxial orientational ordering perpendicular to the substrate and random orientation within the substrate plane [12]. This inference is consistent with the crystallite organization observed in the SEM image of the film.

3. Silver nanoparticle-embedded polyvinyl alcohol film and optical limiting

We have combined the advantages of the chemical reduction route to metal nanoparticles, environmentally benign reagents and the stabilization of nanoparticles in a polymer matrix, in the *in-situ* generation of silver nanoparticles in polyvinyl alcohol (PVA) film through mild thermal treatment [7]. Utilization of a sacrificial polystyrene film facilitated the formation of free-standing films of Ag–PVA. Aqueous solutions of silver nitrate and polyvinyl alcohol (average MW = 15,000–20,000,
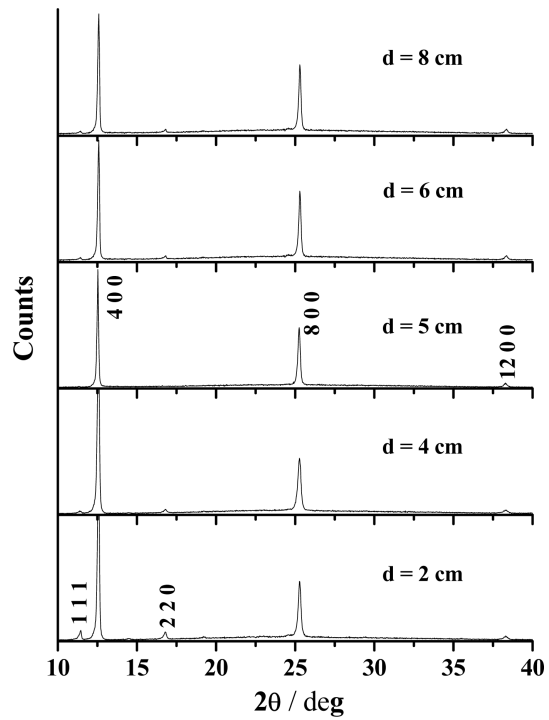
Figure 3. X-ray diffractograms of thin films of ZNDA formed at different distances, d, between the sublimation boat and the substrate.
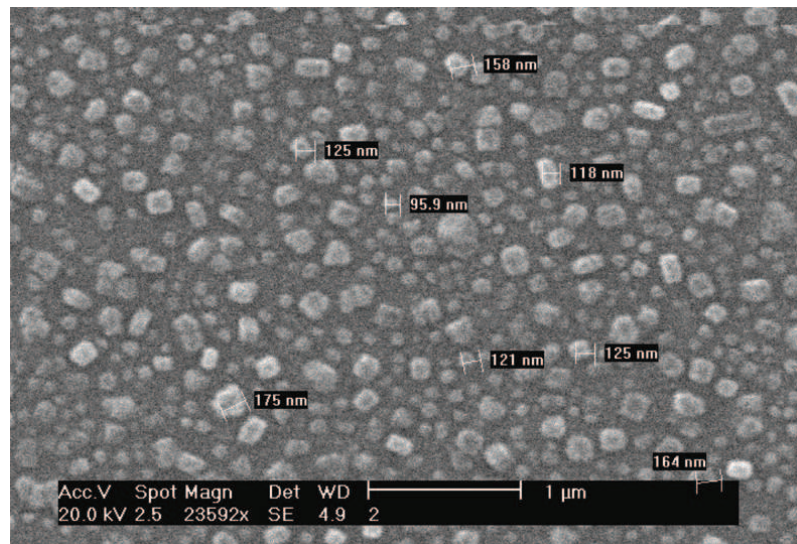

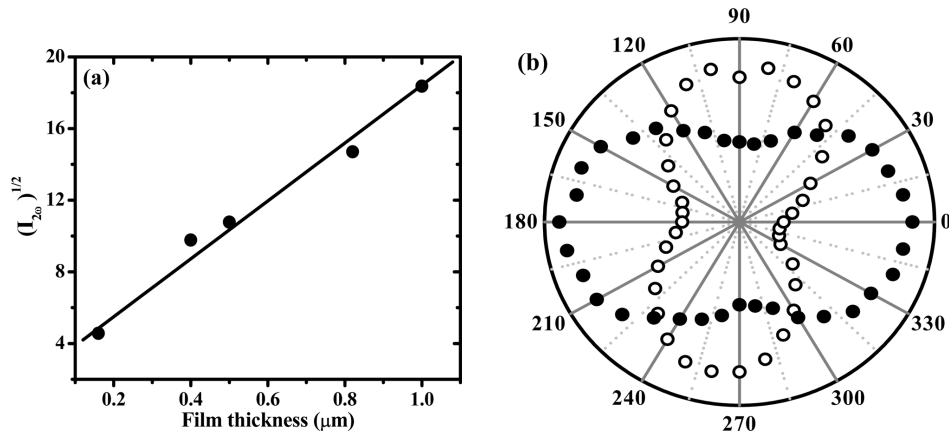**Figure 4.** SEM image of thin film of ZNDA on glass substrate.

Figure 5. (a) Dependence of the SHG of ZNDA film on the thickness; (b) polar plots of the SHG in q–p (•) and q–s (○) geometries 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.

% hydrolysis = 86) were mixed in different weight ratios. Films typically 0.5–0.6 μm thick were spin-coated on quartz substrates directly or on 3–6 μm thick polystyrene (PS) films pre-coated on glass substrates. These films were heated at 50–110°C for 5–60 min time periods which led to the generation of silver nanoparticles inside the PVA matrix. The PVA acts simultaneously as the reducing agent [13], stabilizer for the nanoparticles and the matrix for their homogeneous distribution and immobilization. The Ag–PVA on quartz was used for electronic absorption studies. The Ag–PVA/PS on glass could be immersed in toluene whereupon the PS layer dissolved, releasing the Ag–PVA thin film which was collected on a copper grid for direct TEM examination without any microtoming.

Electronic spectra of the Ag–PVA films clearly revealed the plasmon absorption band with a $\lambda_{max} \sim 420$ nm. Both temperature and time of the thermal treatment influence the nanoparticle generation as revealed by the changes in the spectrum. For a given composition and temperature, increase in the heating time leads to the increase of intensity, blue shift of the peak maximum and reduction of the linewidth (figure 6), suggesting increase in the nanoparticle production, decrease in their average size and enhancement in the monodispersity of the particle size. In general, increasing the temperature also leads to similar effects [7]. TEM images of the Ag–PVA films are in good agreement with these indications from the plasmon absorption studies. The micrograph shown in figure 7 illustrates the highly monodisperse and small nanoparticles (average particle size = 2.1 (0.2) nm) obtained in the films heated for 60 min at 110°C. The decrease of particle size and increase in monodispersity with the heat treatment is reminiscent of the digestive ripening reported for gold nanoparticles [14]. Increased heating time and temperature enhance the extent and rate of the reaction. Reduction in the polymer viscosity at higher temperatures possibly facilitates higher ion/atom mobility and homogeneous nucleation; the stabilization of the nanoparticles by the PVA matrix also effectively suppresses aggregation.
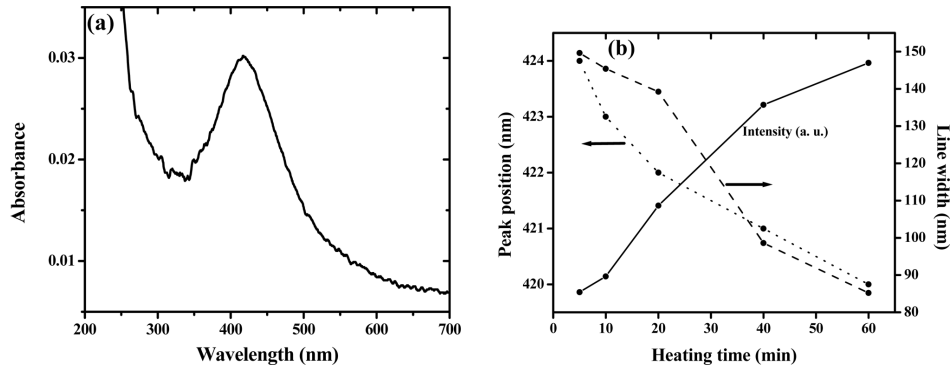
Figure 6. (**a**) Electronic absorption spectrum of Ag–PVA film (Ag/PVA = 0.042, thermal treatment time, temperature = 60 min, 90°C). (**b**) Variation of the intensity, peak maximum and peak width of the absorption of the Ag–PVA film with the time of thermal treatment.
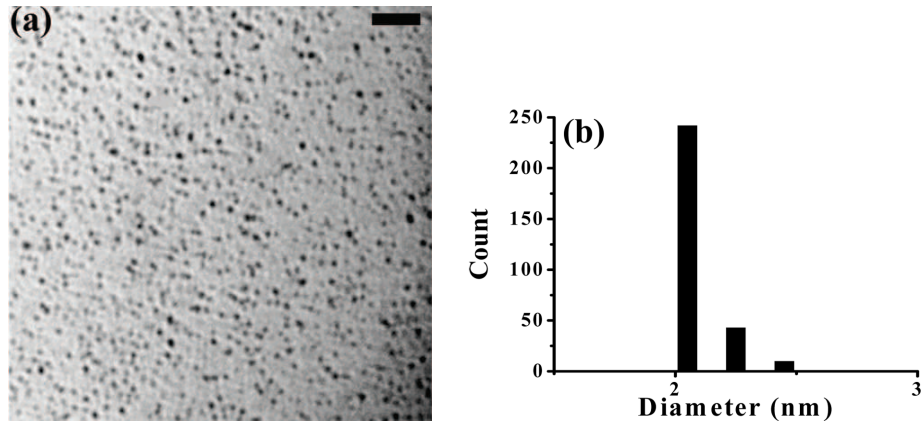

Figure 7. (**a**) TEM image of Ag–PVA film (Ag/PVA = 0.042, thermal treatment time, temperature = 60 min, 110°C). Scale bar = 20 nm. (**b**) Histogram of the particle size distribution in the image shown in (a).

Z-scan measurements were carried out on the Ag–PVA/PS films using the second harmonic (532 nm) from the Nd:YAG laser; f/24 geometry was employed [15]. Approximately 5 μm thick films with a linear transmission of 84% at low laser intensities, showed strong reverse saturable absorption at higher intensities [7]. The optical limiting behavior is revealed in the plot of the transmission vs. the input fluence (figure 8); the threshold value (defined [16] as the input fluence at which the transmittance reduces to half of the linear transmittance) is 0.83 J cm^{-2} and the output is clamped at 0.35 J cm^{-2}.

4. Conclusions

The fabrication of homogeneous thin films of perfectly polar crystallites with uniaxial orientational ordering, through physical vapor deposition of a family of
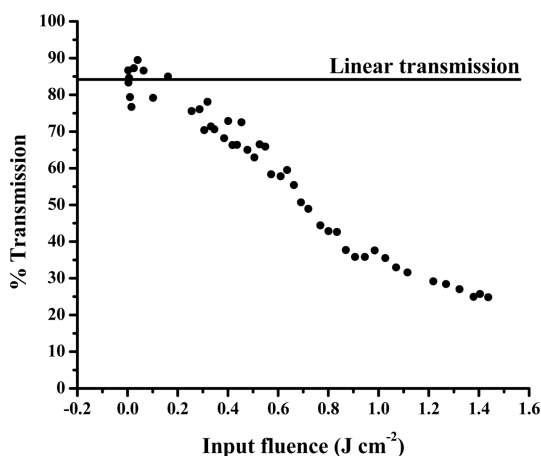
Figure 8. Optical limiting in Ag–PVA/PS film (Ag/PVA = 0.058, thermal treatment time, temperature = 60 min, 90°C) at 532 nm.

metal-organic compounds, demonstrates a convenient route to new molecular materials for quadratic nonlinear optical applications. The molecular assembly in the crystals and thin films is ideally suited for realizing electro-optic effects which remains to be investigated. The Ag–PVA system we have developed, illustrates a simple *in-situ* process for the fabrication of free-standing metal nanoparticle-embedded polymer film and the fine control achieved on the particle size selection. These films with immobilized and size-tuned metal nanoparticles appear to be promising candidates for optical limiting devices. Other metal/semiconductor–polymer systems fabricated recently in our laboratory point to the generality of the methodology described here and indicate that this protocol would facilitate the control of nanoparticle shape and morphology as well [17].

Acknowledgements

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