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Growth modulation of bent micro crystals to single crystals in a one-dimensional coordination framework

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The growth of bent micro crystallites of several microns in length is achieved during evaporation-assisted crystallization of di-*n*-butyltinbis(*O*-methylmethylphosphonate), 1 from a solution in chloroform. The induction of charge transfer interactions between 1 and iodine facilitates the isolation of cubic shaped single crystals. The structure of 1 adopts a one-dimensional motif featuring an infinite array of [-Sn-O-P-O-]$_2$ cyclic rings while CH---O hydrogen bonds are oriented orthogonal to the inorganic chain. The bonding attributes provide a rationale to the bending phenomenon of the slender crystallites.

The crystalline materials with twisted habits or curved morphologies as found in nature[1] have triggered a spur of intense activities with the realization of similar structural effects in synthetic organic molecules and polymeric frameworks. The examples of organic crystals that exhibit such behaviour upon external stimuli, including mechanical stress,[2] light[3] and heat[4] have shown an exponential increase recently. It has been recognized that elastic or non-elastic deformation in organic crystals has a correlation with the anisotropic crystal packing that arises due to the presence of strong as well as weak bonding interactions. The weak interactions (van der-Waals, H-bonding and π-π) allow the external stress to propagate in the lattice structure and facilitate deformation of the primitive shape of the crystals.[5] Studies are also aimed at deriving practical applications of these materials in the field of actuators and biomimetic materials.[6]

Recent advances in synthetic chemistry of metal organic frameworks (MOFs)/infinite coordination polymers (ICPs) have provided a great deal of insight into nucleation and crystal growth phenomena. This has led to the development of new protocols to control the size, shape and morphology of the crystals in bulk as well as nano/colloidal regimes.[7] In this context, the choice of organic solvents (e.g. CH$_3$CN, EtOH, THF, DMSO, DMF) of varying nucleophilicity and donor strength is also known to play a crucial role in modulating the crystal growth phenomena, as exemplified in carboxylate-based coordination polymers.[8] These studies have offered promise to the construction/design of innovative materials with a wide ranging applications.[7-9] In a seminal study, the associated property of hybrid inorganic-organic framework to exhibit anisotropic deformation under mechanical stress has been demonstrated by Cheetham *et al*. in the polymorphs of Cu$_{1.5}$(H$_2$O)(O$_3$PCH$_2$CO$_2$) featuring three-dimensional coordination polymer and a layered structure.[10] Similar to organic crystals, the authors suggested a qualitative correlation between the observed structural deformation and chemical bonding within the crystal lattice. Also relevant to these studies is the description of soft nature of the crystals of one-dimensional coordination polymer, Zn{O$_2$P(OEt)$_2$}$_2$.[11]

In continuation of our recent studies on the synthesis and structural aspects of diorganotin(IV) phosphonate esters, R$_2$Sn{OP(O)(OMe)Me}$_2$ (R = Me, Et), we have drawn our attention to a unique crystal growth behaviour of *n*-Bu$_2$Sn{OP(O)(OMe)Me}$_2$ (1) which has been previously characterized by spectroscopic methods.[12] Upon evaporation induced crystallization of 1 from a solution in chloroform, fibre-like crystallites of several microns in length were obtained. The phenomenon has also been observed in chloroform-acetonitrile and chloroform-ether solvent mixtures. Although the influence of solvent-surface interaction on the crystal growth and morphology has remained the subject of interest in a few earlier reports,[13] a detailed study of

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the unidirectional growth of **1** is warranted. An examination of these crystallites under optical microscopy (OM) and scanning electron microscopy (SEM) (Figure 1) reveals several significantly bent crystallites from the isolated crop. The
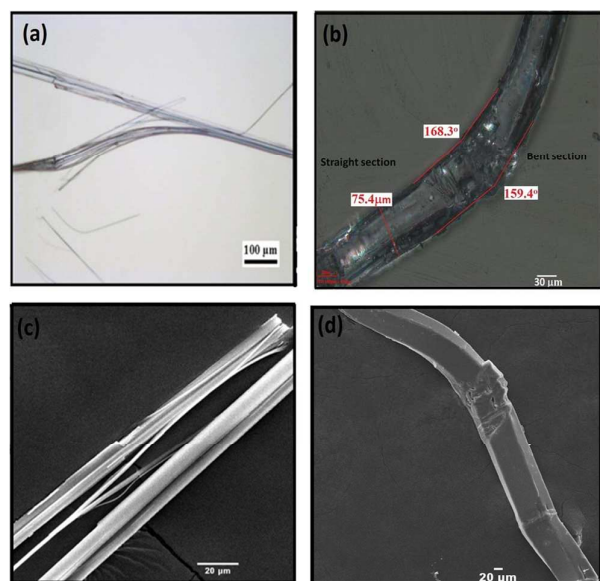

Figure 1. (a, b) Optical (c, d) Scanning electron micrographs of micro crystallites of *n*-Bu$_2$Sn{OP(O)(OMe)Me}$_2$ (**1**)

micrographs of a few selected crystallites under high resolution reveals that a continuum morphology is observed incorporating straight and the bent portions. The kink at the bent section subtends an angle of 160-170° (figure 1b). Based on a recent report,[14] we surmise that collision of the growing crystallites with the walls of the container imposes external constraints and the resulting mechanical stress may contribute to the bending phenomenon. These crystallites diffract poorly due to low mass thus limiting structural elucidation by X-ray crystallography. Nevertheless, the spectroscopic data of the crystallites are consistent with the expected composition, while the powder X-ray diffraction pattern reveals identical 2θ values (10-30° range) with that of simulated pattern obtained from single crystal analysis, suggesting phase purity of the micro crystallites (Figure S1).

The single crystals of **1** were successfully achieved by the addition of trace amount of iodine (iodine: polymer= 1:20) into the growth solution in chloroform after several days. The ratio of iodine to polymer concentration was optimized by a visual colour change of the solution from violet to orange and finally to yellowish-brown upon increasing the concentration of the polymer. Further increase in the polymer concentration into the solution results in the appearance of undesired turbidity. A perspective view of the structure shown in figure 2 reveals the formation of one-dimensional coordination polymer by virtue of bridging bidentate mode of the phosphonate ester ligands. The tin atoms in the polymeric chains adopt a distorted octahedral geometry with equatorial SnO$_4$ core [∑360±0°] and
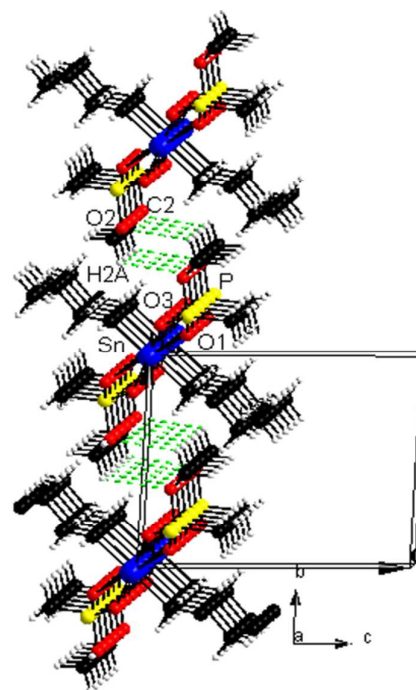

Figure 2. 2D structure of **1** viewed along *a*-axis showing 1D chains running along *a*-axis and C-H---O hydrogen bonding interactions along *c*-axis.

trans *n*-butyl groups [∠C-Sn-C = 180.0(0)°] while other metrical parameters resemble closely with those reported earlier for analogous dialkyltinbis(*O*-methylmethylphosphonate).[12] The inorganic chains comprising of [-Sn-O-P-O-]$_2$ rings run along crystallographic *a*-axis while the presence of weak C-H---O hydrogen bonds is discernable along the crystallographic *c*-axis. The orientation of secondary interactions approximately orthogonal to the linear inorganic chains provides anisotropy in the crystals and finds a close analogy with several reported examples of organic molecules exhibiting bent phenomenon.[5] The metrical parameters associated with these hydrogen bonds are as follows: [H2A---O2 = 2.700(21), C2---O2 = 3.2347(44) Å; ∠C2-H2A---O2 = 114.718(234)].

The role of molecular iodine during the growth of single crystals of **1** has been examined in detail. In this respect, a freshly prepared solution of the polymer and iodine (iodine: polymer = 1:20) was subjected to the UV-Vis spectral studies at different time intervals and the results are shown in Figure 3. The spectra reveals the appearance of characteristic bands due to I$_3^-$ species at 294 and 364 nm suggesting charge transfer interactions between **1** and iodine.[15] The intensity of these bands increases with time in lieu of the band due to iodine (510 nm). These changes are accompanied by a visual colour change of the solution from violet to orange and finally to yellowish-brown within two hours (inset, figure 3). The results are consistent with the affinity of phosphonate esters to undergo charge transfer interactions with iodine *via* a series of complex equilibria.[15] It is worthy to mention that the kinetic studies of charge transfer interactions in the present case are
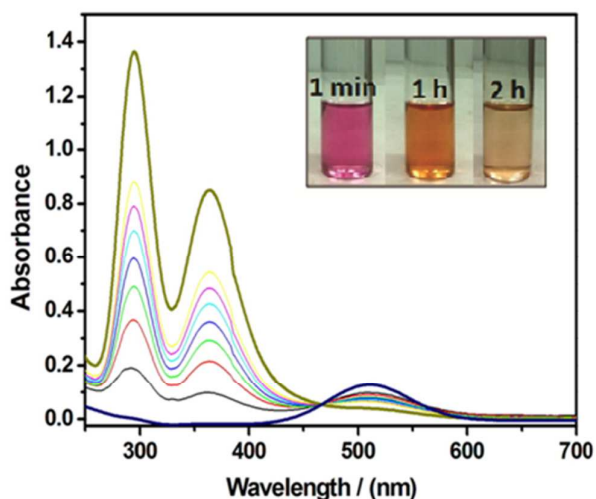
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Figure 3. UV-Vis spectra of a solution of (a) I_2 in chloroform (blue), (b) **1** (3.0 mM) and I_2 (0.15 mM) in chloroform within an interval of 20 min (grey-yellow) and (c) after 24h (green). Inset shows visual colour change of the chloroform solution.

precluded in view of the fluxional nature of **1** in solution as evident from a large upfield isotropic chemical shift value (δ − 478) in the solid-state ^{119}Sn NMR spectrum (figure S2) as compared to that observed in solution (δ -398).

To map the particle growth process leading to single crystals, the solution of **1** in chloroform containing iodine was examined by SEM and AFM studies. The SEM micrographs of the solution after 2 h reveals non-uniform, irregular-shaped nanoplatelets (figure 4a) which undergo transformation to large cubic shaped crystallites (figure 4b) after 24 h. In addition, small nano crystals of 40-60 nm size are also discernable suggesting the onset of morphological changes during the growth phenomenon. The AFM images of the large crystallites reveal the height profile of about 90 nm (figure S3).
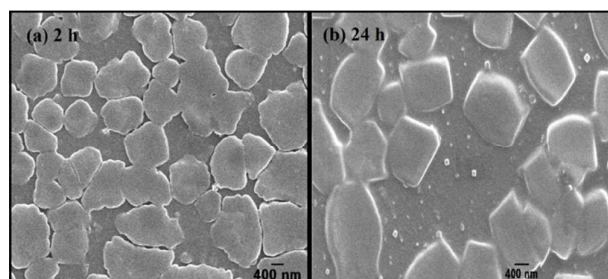

Figure 4. SEM images of n-Bu$_2$Sn{OP(O)(OMe)Me}$_2$ (**1**) after (a) 2 h (b) 24 h.

The Energy-Dispersive X-ray (EDX-SEM) studies confirm the ratio of Sn:P as 1:2 (figure S4), consistent with that of the as-synthesized polymer. The control over the morphology of **1** as observed herein, utilizing iodine-induced charge transfer interactions, is unique when compared with a variety of established protocols.[7]

Conclusions

The results reported herein describes the crystallization behaviour of di-n-butyltinbis(O-methylmethylphosphonate), **1** in absence and presence of iodine as a modulator. Of particular relevance is the isolation of bent microcrystallites of several microns in length from a growth solution of **1** in chloroform. The role of iodine in facilitating the growth of single crystals has been established for the first time and a plausible rationale is invoked by considering donor-acceptor charge transfer complexation, [P-I]$^+$I$_3^-$ (P = polymer) with the polymeric framework. The structure and bonding attributes, featuring weak CH---O hydrogen bonds which are oriented orthogonal to the inorganic chain, provide a qualitative rationale to understand the bending phenomenon of slender crystallites of **1**.

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