



**A recipe for the synthesis of diorganotin(IV) phosphonates  
in colloidal regime by solution based approach**

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## COMMUNICATION

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## A recipe for the synthesis of diorganotin(IV) phosphonates in colloidal regime by solution based approach

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**The study presents synthesis of diorganotin(IV) phosphonates,  $R_2Sn\{O_3P(CH_2)_3SiR^1R^2\}_2$  [ $R = Et, n-Bu$ ;  $R^1 = R^2 = Me, Et$  or  $Ph$ ] and  $Sn\{O_3P(CH_2)_3SiR^1R^2\}_2$  featuring rod, rosette and spherical morphologies. The presence of silaalkylphosphonate ligands in the structural framework facilitates the transformation of bulk samples into nano/colloidal domain by a facile solution based approach. The colloidal particles show enhanced antimicrobial activity against *B. Subtilis* bacteria as compared to their bulk counterparts.**

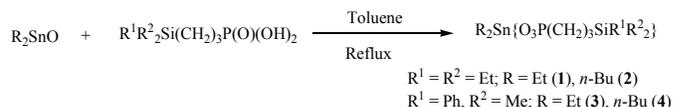
Nano/colloidal particles derived from infinite coordination polymers (ICPs) have vastly expanded the scope of coordination chemistry from mere academic curiosity to a wide range of applications in the field of gas sorption, catalysis, biomedical imaging, drug delivery, magnetic resonance imaging (MRI) contrast agents etc.<sup>1,2</sup> Extensive studies over the past decade have enriched our understanding of synthetic methods to construct particles of metal-coordination frameworks in nano/colloidal/submicrometer size regimes by a judicious combination of metal ion and organic based ligand sets. Mirkin *et al.* have demonstrated the application of solvent assisted precipitation approach to construct colloidal ICPs from crystalline, semicrystalline as well as amorphous coordination frameworks,<sup>2a, b</sup> while other widely used protocols involve microemulsion, sonochemical and solvothermal techniques.<sup>3</sup> Notable success has also been achieved in controlling the morphology of nano-/micro crystallites through the addition of a modulator, which provides the potential to trap particles of a particular size formed *in situ* under competing “coordination equilibrium” conditions and thus different aspects of crystallization can be studied by real time growth process.<sup>4</sup>

Metal-phosphonates constitute an interesting class of coordination polymers with rich structural chemistry by virtue of variable bonding attributes of monoanionic and dianionic phosphonate ligands.<sup>5</sup> Among this family, those derived from tetravalent Sn(IV) and Zr(IV) metal ions have been extensively studied in the past. Early developments in this area have established that these polymeric frameworks are layered materials with good thermal and chemical stability and are potential candidates as materials for acid catalysts, ion exchangers, proton conductors and intercalating agents. Recent

studies on morphological attributes of tin(IV) phosphonates<sup>6</sup>,  $Sn(O_3PR)_2$  ( $R = Me, Ph$ ) featuring spherical and rosette-like aggregates are particularly noteworthy. It has been shown that modulation in size of these aggregates largely depends upon the time and temperature of hydrothermal treatment. A related example is the representation of  $\alpha$ -Zirconium phosphate with nanoplatelet-like structures which exhibit iridescent properties.<sup>7</sup>

An important offshoot among metal(IV) phosphonates are the organotin based coordination frameworks.<sup>8</sup> Our recent contribution in this area has demonstrated that incorporation of silaalkylphosphonate groups in  $Et_2Sn(O_3PCH_2SiMe_3)$  endows this polymer with unusual solubility in hydrocarbon, aromatic and ether solvents and thus offer a simple solution based approach to transform the rod like aggregates of the bulk samples into colloidal particles by ultrasonication.<sup>9</sup> These results have prompted us to explore possibilities to construct new nano structured materials derived from analogous tin-based coordination polymers. Herein, we wish to report the synthesis of a series of isostructural diorganotin-phosphonates of compositions,  $R_2Sn\{O_3P(CH_2)_3SiR^1R^2\}_2$  as well as  $Sn\{O_3P(CH_2)_3SiR^1R^2\}_2$  [ $R = Et, n-Bu$ ;  $R^1, R^2 = Me, Et$  or  $Ph$ ] and their morphological behavior as a function of varying alkyl/aryl substituents on the metal and/or ligand. The results provide a unique insight into the formation of rod, rosette and spherical attributes of these coordination driven assemblies. The particle size can be readily modulated into nano/colloidal domains by a solution based approach.

### Equation 1



The synthetic details and characterization of silaalkylphosphonic acid,  $R^1R^2Si(CH_2)_3P(O)(OH)_2$  [ $R^1 = R^2 = Et$  (**1a**);  $R^1 = Ph, R^2 = Me$  (**2a**)] are described in the supplementary section. The reaction of these ligands with equimolar quantities of diethyl-/di-*n*-butyl tin oxide in refluxing toluene under classical azeotropic dehydration conditions affords the isolation of desired diorganotin phosphonates **1-4**, as shown in equation 1. However, dimethyltin oxide reacts with two-equivalents of **1a** or **2a** under identical conditions to afford the coordination polymers,  $Sn\{O_3P(CH_2)_3SiR^1R^2\}_2$  [ $R^1 = R^2 = Et$  (**5**);

$R^1 = \text{Ph}$ ,  $R^2 = \text{Me}$  (**6**)] via cleavage of both Sn-C bonds. It is notable that complete demethylation as observed herein is a scarce phenomenon in organotin chemistry and requires harsh reaction conditions and strongly acidic carboxylate/phosphinate/phosphonate ligands.<sup>10</sup>

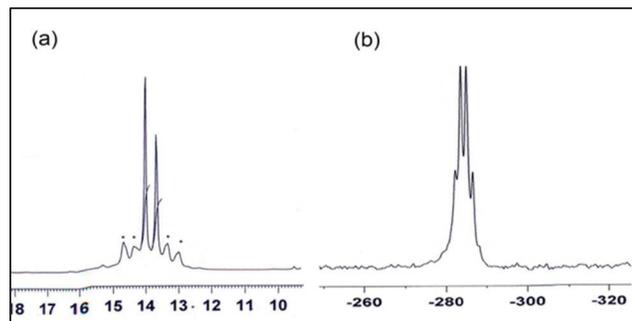


Figure 1. (a)  $^{31}\text{P}$  and (b)  $^{119}\text{Sn}$  NMR spectra of **1** (asterisks represents tin satellites).

All attempts to grow single crystals of these polymers invariably resulted in slow precipitation of microcrystallites which are not suitable for X-ray crystallography. However, IR and multinuclear ( $^1\text{H}$ ,  $^{31}\text{P}$ ,  $^{13}\text{C}$ ,  $^{119}\text{Sn}$ ) NMR spectral data are quite useful to establish their structural motifs in solid as well as in solution (ESI S2). As shown in Figure 1, the  $^{31}\text{P}$  NMR spectra of **1-4** reveal two distinct resonances between  $\delta$  13.6-14.0 with each signal being flanked by tin satellites, thus enabling an estimate of two distinct  $^2J_{\text{Sn-O-P}}$  coupling (145, 160 Hz) values. The results are attributed to different environment of phosphorus nuclei arising from tridentate coordination mode of the phosphonate dianion.<sup>11</sup> The  $^{119}\text{Sn}$  NMR spectrum of each polymer shows a quartet like resonance centred at  $\delta$  -283 due to coupling with three adjacent phosphorus nuclei. It is noteworthy that solid state  $^{119}\text{Sn}$  [magic angle spinning (MAS)] NMR spectra exhibit isotropic chemical shift of  $\delta$  283.4 and 283.0 for **1** and **4** respectively and suggest the structural similarity of these compounds in both solid state and in solution. Nevertheless, the  $^2J_{\text{Sn-O-P}}$  coupling is not observed in the solid state NMR spectra due to larger line width of the signal as compared to the line width in solution. The spectral data are in conformity with those of an analogous diethyltin phosphonate,  $\text{Et}_2\text{Sn}(\text{O}_3\text{PCH}_2\text{SiMe}_3)$  reported recently by our group<sup>9</sup> and suggest the formation of one-dimensional ladder-like structural motif. The stability of these polymers under hydrolytic conditions is evident from a close resemblance of  $^{31}\text{P}$  NMR spectra of the assynthesized samples and those after keeping in contact with de-ionized water. Nevertheless, X-ray powder diffraction (PXRD) pattern of the exposed samples reveal a strong increase in the background intensity and broadening of the diffraction peaks, suggesting partial amorphization (ESI S3). The  $^1\text{H}$  and  $^{13}\text{C}$  (DEPT-135) NMR spectra of **5** and **6** in  $\text{CDCl}_3$  solution separately identify characteristic signals due to the phosphonate ligand only. A comparative study of  $^{119}\text{Sn}$  NMR spectra in the solid state ( $\delta$  -680) as well as in solution ( $\delta$  -601) reveals a discernable difference in the chemical shifts ( $\Delta\delta = 80$  ppm). These results along with absence of  $J$ -coupling information are suggestive of fluxional nature of these polymers in solution. The  $^{31}\text{P}$  NMR spectra exhibit two non-equivalent phosphorus atoms with chemical shift at  $\delta$  25.4 and 18.2. Thermogravimetric analysis (TGA) of **1-6** reveals that these are thermally stable upto 200 °C and subsequent weight loss follows in a single step up to 500 °C (ESI S4).

The morphological attributes of **1**, **2** and **5** have been examined by scanning electron microscopy (SEM). As shown in figures 2 and 3, the SEM micrographs identify rod-like and rosette-like motifs for **1** and **2** respectively, while the formation of spherical particles of

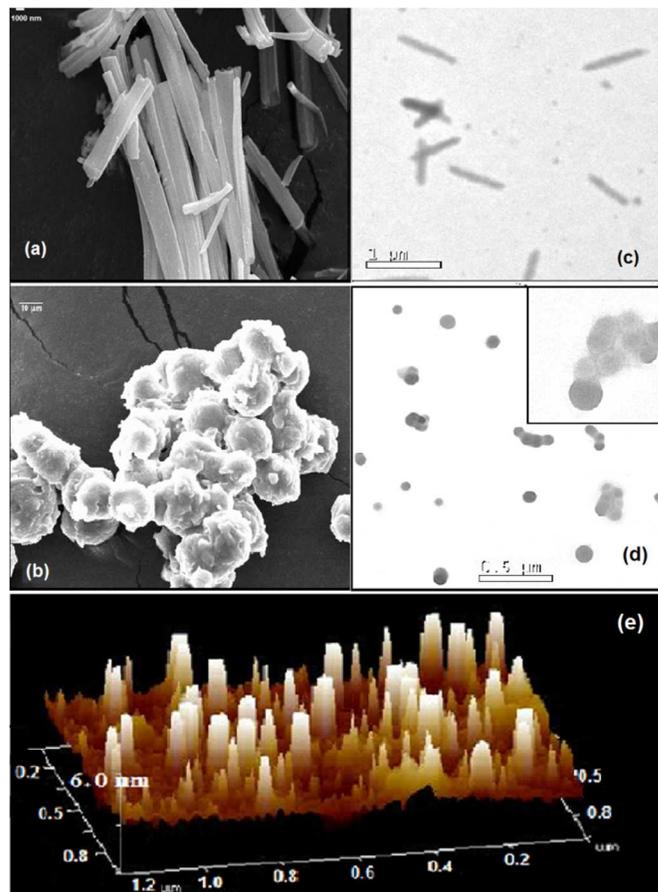


Figure 2. (a, b): SEM micrographs of **1** and **2**; (c, d): HR-TEM micrographs of colloidal particles derived from **1** and **2** respectively; (e) AFM image showing height profile of disk shaped particles.

300 nm to several micrometers in size are discernable in case of **5**. Interestingly, these polymers form colloidal dispersion upon sonication of a solution in ethanol-chloroform mixture (5:1), capable of scattering an incident laser light beam (Tyndall effect, ESI S5). An examination of these colloidal particles by SEM, HR-TEM and AFM reveals rod-like structures for **1** with largest dimension being of the order of 600-700 nm in length and 100 nm in width, while disk-shape particles of average diameter of  $80 \pm 10$  nm and height profile of 8-10 nm are discernable for **2** (Figure 2).

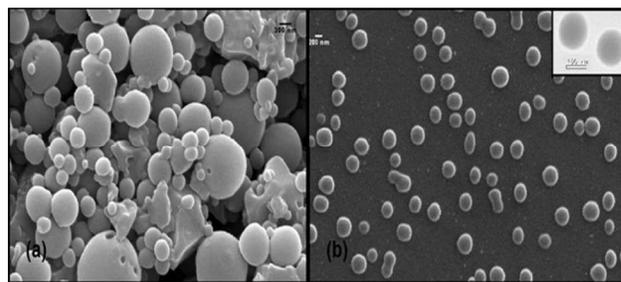


Figure 3. SEM images of (a) bulk and (b) spherical nano particles of **5** (Inset: HR-TEM with 100 nm scale bar).

For **5**, the colloidal dispersion shows nanospheres of nearly uniform size ( $310 \pm 10$  nm) particles suggesting their effective separation from the bulk (Figure 3). The results are quite significant in view of the application of ICPs with high degree of monodispersity in a number of applications in the field of biosensors, photonic crystals, porous membranes and hydrogen storage etc.<sup>12</sup> On the contrary, the

polymers **3**, **4** and **6** comprising of phenyldimethylsilyl-substituted phosphonate ligands exist as dense solid phases (ESI S6). It is noteworthy to mention that ultrasonication of a solution of these polymers in varying solvents, such as ethanol-chloroform, methanol-chloroform, *n*-propanol-chloroform and methanol-hexane do not show affinity to form colloidal dispersion presumably due to secondary interactions arising from the phenyl groups. These results provide a basis to infer that the influence of alkyl/aryl substituents on tin and phosphonate ligand is quite pronounced in modulating the morphological attributes of polymeric frameworks among the family.

Potential applications of organotin(IV) complexes as biocides and metal-based drugs have been studied extensively in the past.<sup>13,14</sup> Related studies on organotin(IV) compounds derived from oxyphosphorus based ligands are however scanty and primarily remain the subject of patented literature.<sup>15</sup> The results obtained from preliminary screening of the complexes, **1-6** for their antibacterial activity against Gram-positive bacteria, *Bacillus Subtilis* are intriguing. The activity was observed only for the complexes **1** and **2** in the colloidal domain while no inhibition zone was observed for their bulk counterparts. Further, the di-*n*-butyltin analog, **2** exhibit superior activity with the diameter of inhibition zone being of the order of 4 mm (Figure 4). The results are comparable to those reported earlier for other organotin(IV) complexes.<sup>13</sup> However, these complexes remain inactive against Gram-negative bacteria, *Pseudomonas aeruginosa*. The screening of solvents (CHCl<sub>3</sub>, EtOH) as well as phosphonic acids, **1a** and **2a** against their antibacterial activity (ESI S7) reveals that they play no role in the growth inhibition.



Figure 4. Inhibition zones for **1**, **2** and **5**; (a) colloidal particles; (b) bulk sample; (c) ethanol-chloroform (5:1) and (d) chloroform

In conclusion, the study presents the synthesis, characterization and morphological behavior of a series of diorganotin phosphonates. The observed modulations in rod, rosette and spherical morphologies in **1**, **2** and **5** and their miniaturization into colloidal particles by a facile solution based approach offer a gateway to expand the scope of organotin phosphonates as a new class of ICPs in nano/colloidal regime.

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#### Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details and characterization of the samples.

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## Table of Content

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The tin(IV) based coordination polymers bearing silaalkyl substituted phosphonate ligands adopt rod, rosette and spherical-shaped morphologies. The particle size can be modulated into nano/colloidal regime by a solution based approach.

