

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

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Material and Methods

The compound, $[n\text{-Bu}_2\text{Sn}(\text{O}_2\text{P}(\text{OMe})\text{Me})_2]_n$ (**1**) was synthesized by following a procedure as reported earlier.^R The multinuclear [¹H, ¹³C{¹H}, ³¹P{¹H}, ¹¹⁹Sn{¹H}] NMR spectra were recorded on BRUKER DPX-300 spectrometer at 300, 75.47, 121.50 and 111.88 MHz, respectively. The ¹H and ¹³C NMR chemical shifts are quoted with respect to the residual protons of CDCl₃ while the ¹¹⁹Sn and ³¹P NMR data are referenced to Me₄Sn and 85% H₃PO₄ respectively. The solid state NMR spectrum was recorded on a Bruker Avance II+ 600 NMR spectrometer operating at 600.11 MHz proton frequency (223.67 MHz for ¹¹⁹Sn), using 4 mm solid state CP/MAS dual probe head. The samples were loaded in 4 mm zirconia rotors and spun at magic angle spinning (MAS) rates of 14 and 11 kHz to identify the isotropic chemical shift values. NMR spectra was measured with one-pulse sequence, 16K time domain data points, spectrum width of 2000 ppm, 6000 scans and a recycle delay of 5s. The spectrum was referenced with respect to Me₄Sn as well as SnCl₄ as a secondary reference (isotropic chemical shift -145 ppm). The IR spectra were recorded on Nicolet protege 460 E.S.P. spectrophotometer using KBr optics. The UV-Vis spectra were recorded on a Perkin-Elmer (Lambda Bio 20) spectrophotometer. Scanning electron microscope (SEM) EVO-50 from CARL Zeiss AG, Germany was used to take images of the spin coated samples on a glass surface. Tapping-mode atomic force microscopy (AFM) was carried out on Bruker Dimension icon AFM instrument. The images of the spin coated samples on glass surface

were acquired in air using MPP-11100-10 probe. The Bruker tip radius and resonance frequency are 8nm and 75 kHz, respectively. Energy-dispersive X-ray spectroscopy of the samples was performed on Rontac instrument. Spin coated sample on glass surface was analyzed for EDX studies. Optical Microscopy (OM) was carried out on Zeta 20. Images were captured at 10X and 20X zoom.

Spectroscopic characterization of the micro crystallites of 1

^1H NMR (CDCl_3): δ 3.53 (d, $^3J_{\text{P-H}} = 11.1$ Hz, 6H, P-O- CH_3), 1.69-1.58 (br, 4H, Sn CH_2), 1.45-1.42 (m, 4H, Sn CH_2CH_2), 1.31-1.21 (m, 10H, Sn(CH_2) $_2\text{CH}_2$ + P CH_3), 0.84 (t, $^3J_{\text{H-H}} = 7.5$ Hz, 6H, Sn(CH_2) $_3\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 51.8 (d, $^2J_{\text{P-C}} = 7.5$ Hz, P-O- CH_3), 32.0 (s, $^1J_{\text{Sn-C}} = 1042$ Hz, Sn CH_2), 26.6 (s, $^2J_{\text{Sn-C}} = 147.8$ Hz, Sn CH_2CH_2), 27.5 (s, $^3J_{\text{Sn-C}} = 40.7$ Hz, Sn(CH_2) $_2\text{CH}_2$), 13.8 (s, Sn(CH_2) $_3\text{CH}_3$), 11.4 (d, $^1J_{\text{P-C}} = 143.2$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 23.0. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3): δ -398. IR (KBr, cm^{-1}): 1056 ($\nu_{\text{P-O}}$), 1157 ($\nu_{\text{C-O}}$), 514 ($\nu_{\text{Sn-C}}$).
Anal. Calcd for $\text{C}_{12}\text{H}_{30}\text{O}_6\text{P}_2\text{Sn}$ (452.05): C, 31.96; H, 6.70. Found: C, 31.90; H, 6.73.

Figure S1. Powder X-ray diffraction pattern of (a) simulated obtained from single crystals (b) micro crystallites of 1.

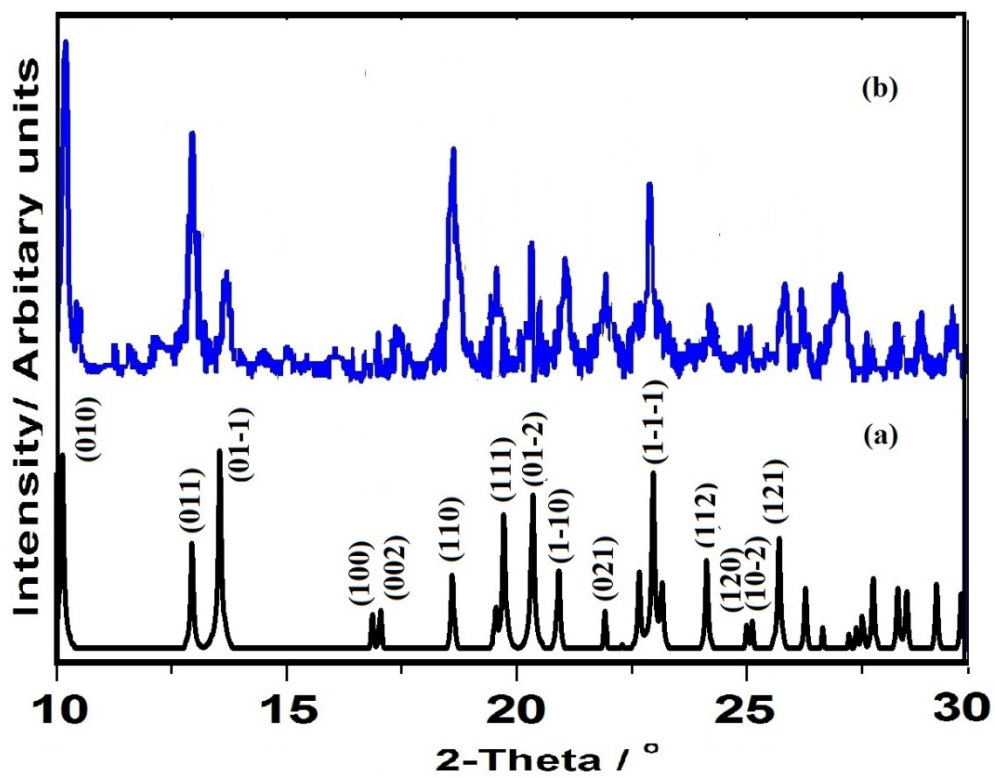


Figure S2. ^{119}Sn solid state NMR spectra of 1 at 14 kHz and 11 kHz.

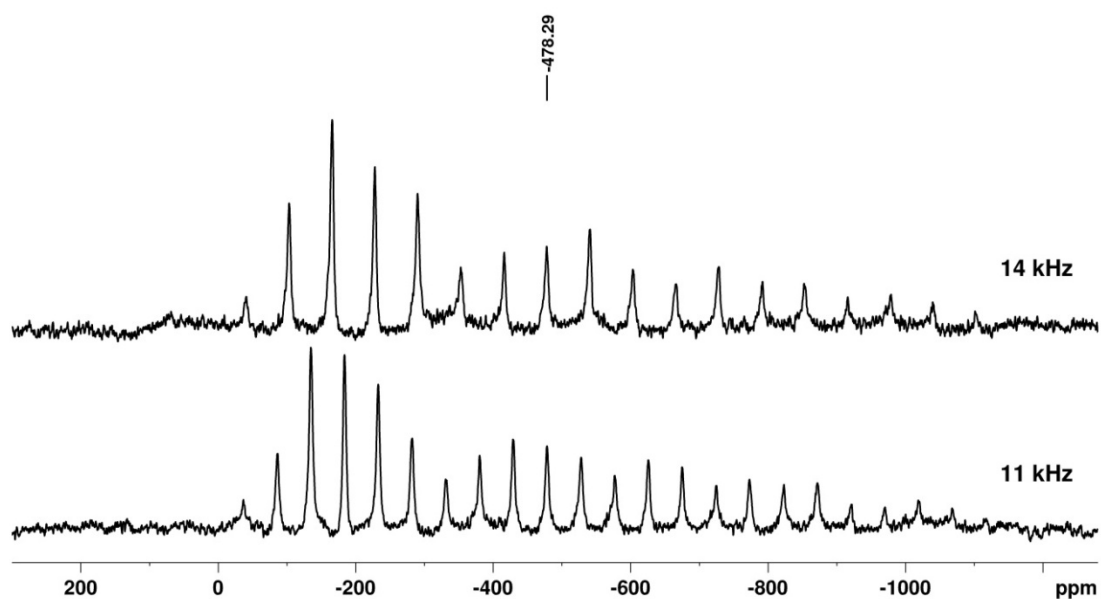
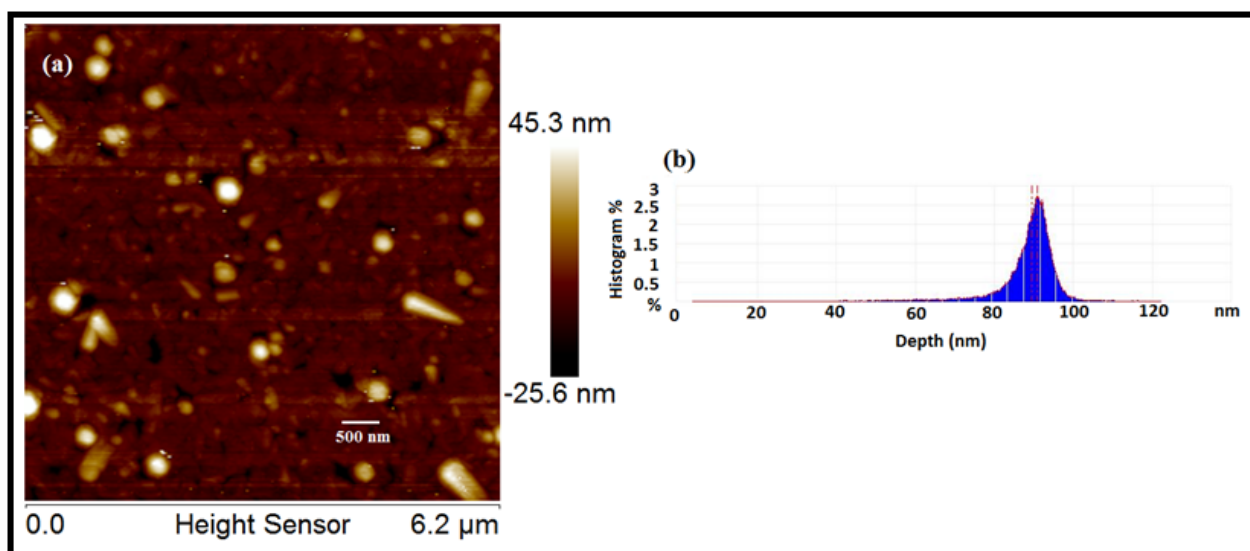
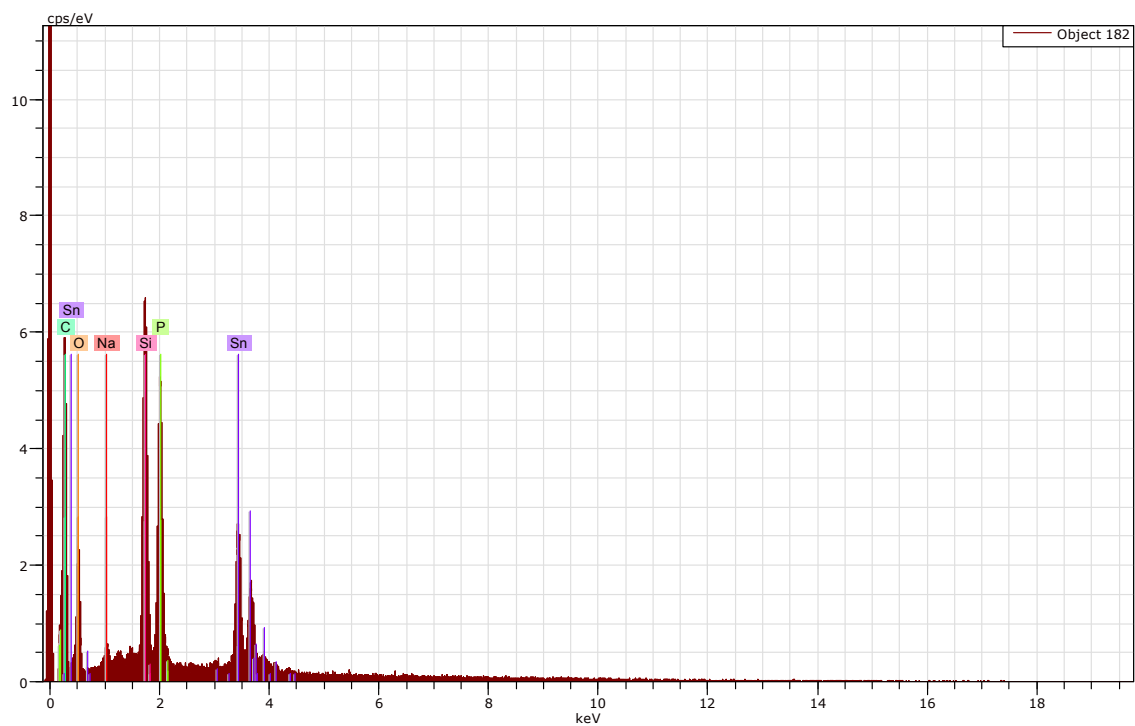


Figure S3. (a) AFM image of a growth solution of 1 in presence of iodine. (b) Depth histogram.



It is important to mention the AFM image often does not provide a proper resolution of the image in x and y axes.⁵ This difference is evident upon comparing the results with SEM micrographs.

Figure S4. EDX data of the colloidal particles obtained from growth solution of 1 in presence of iodine



El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
O	8	K-series	37.54	40.77	48.95	8.4
C	6	K-series	21.06	22.87	36.58	6.5
Sn	50	L-series	17.57	19.08	3.09	0.6
P	15	K-series	7.98	8.66	5.37	0.4
Si	14	K-series	7.24	7.86	5.38	0.4
Na	11	K-series	0.69	0.75	0.63	0.1
Total:			92.09	100.00	100.00	

X-ray crystal structure of 1

The intensity data of **1** was collected on Nonius Kappa CCD diffractometer equipped with molybdenum sealed tube and highly oriented graphite monochromator at 150(2) K by ω , ϕ and 2θ -rotation at 10s per frame. Cell parameters, data reduction and absorption corrections were performed with Nonius software (*DENZO* and *SCALEPACK*).¹ The structure was solved by direct methods using *SIR-97*² and refined by full matrix least-square method on F^2 using *SHELXL-2013*.³ All calculations and graphics were performed using *WinGx*.⁴ All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions by using a riding model. Images were created with the Diamond program.

Table S1. Summary of crystallographic data

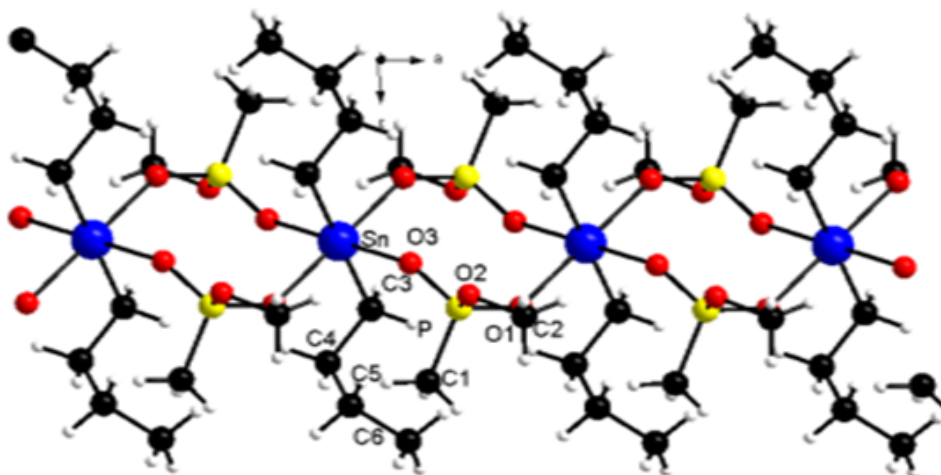
Crystal data	1
Empirical formula	C ₁₂ H ₃₀ O ₆ P ₂ Sn
Fw	450.99
λ , Å	0.71073
Crystal system	Triclinic
Space group	P -1
a, Å	5.2504(4)
b, Å	8.6355(7)
c, Å	10.3202(8)
α , deg.	86.763(5)
β , deg.	85.077(5)
γ , deg.	82.392(4)
V, Å ³	461.60(6)
Z	1
ρ_{calcd} , Mg m ⁻³	1.622
μ (mm ⁻¹)	1.577
F(000)	230
Crystal size (mm)	0.60 x 0.30 x 0.20
θ (°)	3.968 to 30.013
Limiting indices	-7 \leq h \leq 7, -12 \leq k \leq 11, -3 \leq l \leq 14
Reflections collected	8779
Independent reflections	2603
Data completeness	0.981
Max. and Min. transmission	0.745 and 0.553
R(int)	0.0848
Goodness-of-fit on F ²	1.036
Data/restraints/parameters	2603 / 0 / 100
Final R indices (I $>$ 2 σ (I))	R \sim 1 = 0.0410, wR \sim 2 = 0.0782
R indices (all data)	R \sim 1 = 0.0612, wR \sim 2 = 0.0844
Largest diff. peak and hole eÅ ⁻³	0.659 and -1.982

Table S2. Selected Bond lengths (Å) and Bond angles (deg) for *n*-Bu₂Sn{OP(O)(OMe)Me}₂ (1)

Sn-C(3)	2.136(3)	Sn-O(1)	2.201(2)
Sn-O(3) ⁱⁱ	2.204(2)	P-O(3)	1.499(2)
P-O(1)	1.500(2)	P-O(2)	1.589(2)
P-C(1)	1.779(3)	O(2)-C(2)	1.441(4)
C(3)-Sn-C(3) ⁱ	180.00(13)	O(1)-Sn-O(3) ⁱⁱ	89.33(8)
O(1) ⁱ -Sn-O(3) ⁱⁱ	90.67(8)	O(3)-P-O(1)	117.48(13)
O(3)-P-O(2)	104.34(12)	O(1)-P-O(2)	110.43(12)
O(3)-P-C(1)	110.55(15)	O(1)-P-C(1)	107.55(15)
O(2)-P-C(1)	105.93(15)		

Symmetry transformations used to generate equivalent atoms: (i) $-x, -y+2, -z$ (ii) $x-1, y, z$
(iii) $-x+1, -y+2, -z$ (iv) $x+1, y, z$

Figure S5. 1D structure of $n\text{-Bu}_2\text{Sn}\{\text{OP}(\text{O})(\text{OMe})\text{Me}\}_2$ (1) viewed along b -axis.



References

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2. A. Altomare, M. C. Burla, M. Carnalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagan, *J. Appl. Cryst.*, 1999, **32**, 115.
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