Supporting Information

Synthesis and characterization of a butyltin Keggin ion with a rare 4-coordinate Ca center

Danielle C. Hutchison[a], Rebecca D. Stern[b], Lev N. Zakharov[a], Kristin A. Persson[b,c], May Nyman[a]*

[a]Department of Chemistry, Oregon State University, 153 Gilbert Hall, Corvallis, Oregon 97331 (USA)

[b]Department of Materials Science and Engineering, University of California Berkeley, Berkeley, California 94720 (USA)

[c]Lawrence Berkeley National Laboratory, Berkeley, CA 94720 (USA)

*Corresponding Author Email: may.nyman@oregonstate.edu

Table of Contents

Table S 1: Bond Valence Sum for β-$CaSn_{12}$

Assignment	Atom 1	Atom 2	d (Å)	BV	BVS
Ca^{2+}	Ca1	O1	2.288(19)	0.4	1.71
	Ca1	O3	2.263(16)	0.4	
	Ca1	O3	2.263(16)	0.4	
	Ca1	O2	2.31(2)	0.4	
O^{2-}	O1	Sn1	2.096(11)	0.6	2.16
	O1	Sn1	2.096(11)	0.6	
	O1	Sn2	2.129(19)	0.5	
	O1	Ca1	2.288(19)	0.4	
O^{2-}	O2	Sn3	2.097(13)	0.6	2.14
	O2	Sn3	2.097(13)	0.6	
	O2	Sn6	2.12(2)	0.6	
	O2	Ca1	2.31(2)	0.4	
O^{2-}	O3	Sn4	2.118(16)	0.6	2.16
	O3	Sn5	2.100(16)	0.6	
	O3	Sn4	2.118(16)	0.6	
	O3	Ca1	2.263(16)	0.4	
OH^-	O4	Sn1	2.075(16)	0.6	1.34
	O4	Sn5	2.031(17)	0.7	
OH^-	O5	Sn1	2.039(16)	0.7	1.35
	O5	Sn1	2.061(17)	0.7	
O^{2-}	O8	Sn2	2.039(17)	0.7	1.37
	O8	Sn3	2.050(16)	0.7	
OH^-	O11	Sn5	2.106(8)	0.6	1.16
	O11	Sn5	2.106(8)	0.6	
O^{2-}	O14	Sn6	2.02(2)	0.7	1.41
	O14	Sn7	2.047(19)	0.7	
OH^-	O15	Sn7	2.050(9)	0.7	1.35
	O15	Sn7	2.050(9)	0.7	
OH^-	O17	Sn3	2.071(19)	0.6	1.26
	O17	Sn4	2.08(2)	0.6	
OMe-	O6	Sn1	2.171(16)	0.5	2.15
	O6	Sn2	2.139(18)	0.5	
	O6	C52	1.34(3)	1.1	
OMe-	O7	Sn1	2.161(13)	0.5	1.74
	O7	Sn1	2.161(13)	0.5	
	O7	C51	1.50(4)	0.7	

OMe-	O9	Sn3	2.110(18)	0.6	1.99
	O9	Sn3	2.110(18)	0.6	
	O9	C54	1.45(5)	0.8	
OMe-	O10	Sn3	2.170(19)	0.5	1.74
	O10	Sn6	2.16(2)	0.5	
	O10	C53	1.49(4)	0.8	
OMe-	O12	Sn4	2.11(2)	0.6	1.90
	O12	Sn5	2.17(2)	0.5	
	O12	C50	1.45(4)	0.8	
OMe-	O13	Sn7	2.130(19)	0.5	1.76
	O13	Sn5	2.162(18)	0.5	
	O13	C56	1.51(3)	0.7	
OMe-	O16	Sn4	2.158(16)	0.5	1.92
	O16	Sn7	2.20(2)	0.4	
	O16	C55	1.40(3)	1.0	

Table S 2: Atomic percentages for selected elements in β-$CaSn_{12}$ determined by SEM-EDX

	Na At%	Cl At%	Sn At%	Ca At%	Sn:Ca
Area 1	2.40	1.35	78.81	17.44	4.5
Area 2	1.54	1.83	81.67	14.96	5.5
Area 3	2.44	3.02	77.89	16.65	4.7

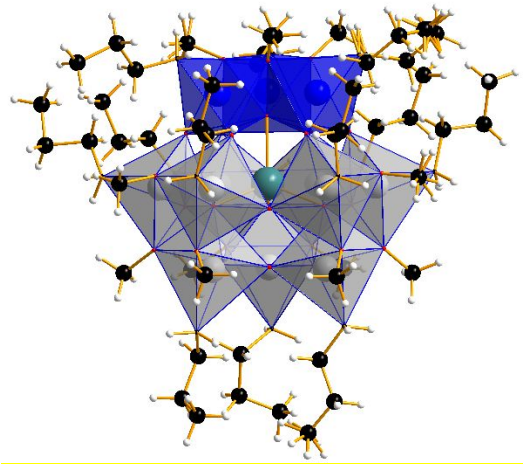

Figure S 1: Single crystal x-ray structure of the β-$CaSn_{12}$ $[(BuSn)_{12}(CaO_4)(OCH_3)_{12}(O)_4(OH)_8]^{2+}$ molecule with complete butyl ligands. Gray and blue polyhedra represent Sn; Ca is shown in teal, O in red, C in black, and H in white.

Complete ESI-MS Peak Assignments

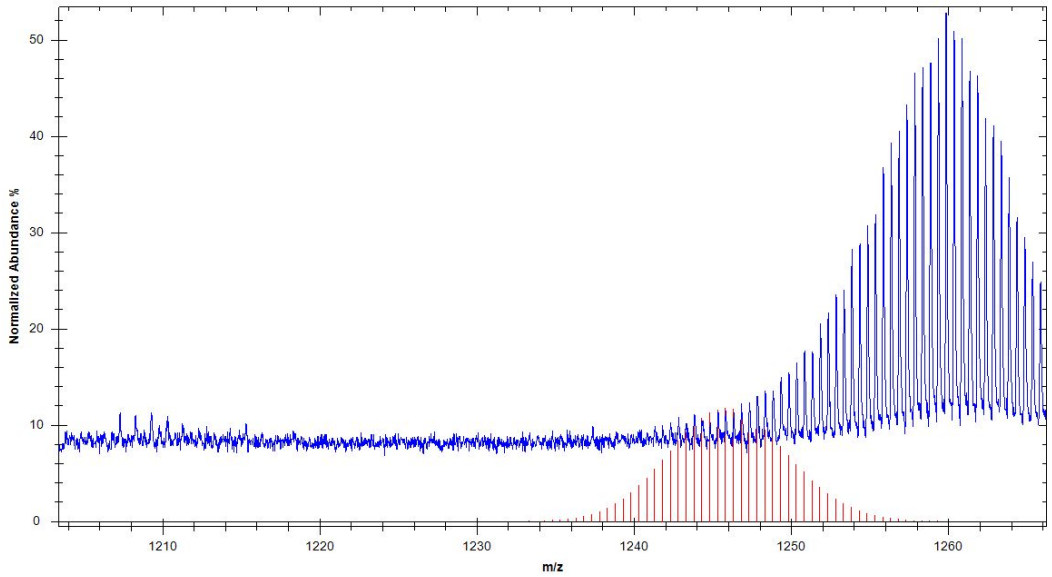

Figure S 2: Experimental ESI MS (+, blue spectrum) and calculated peak positions (red) for $[(BuSn)_{12}(CaO_4)(O)_{11}(OH)_6]^{2+}$. One component of overlapping peak centered at 1259.85 m/z.

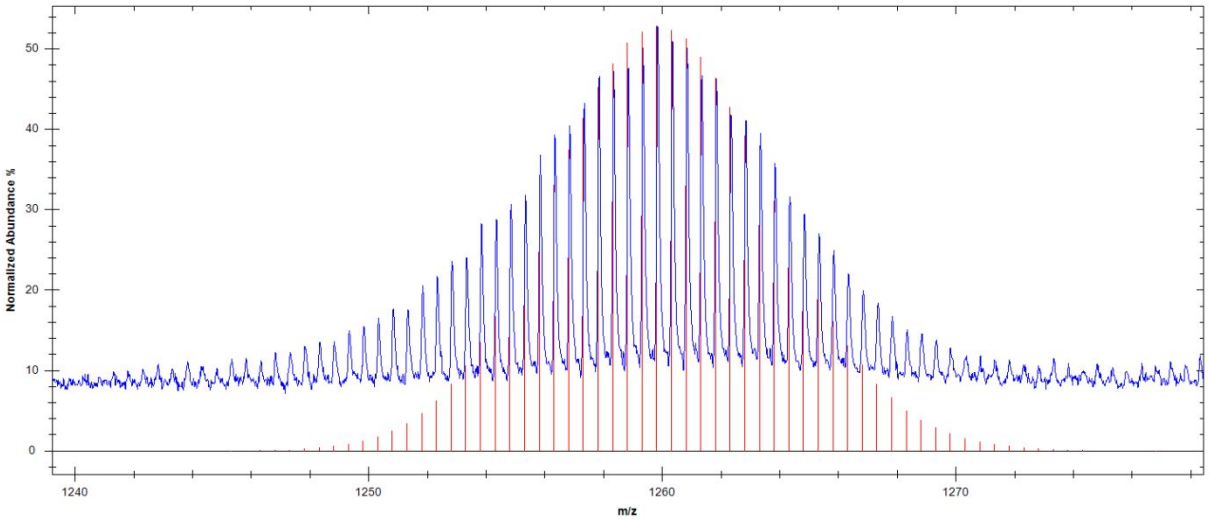

Figure S 3: Experimental ESI MS (+, blue spectrum) and calculated peak positions (red) for $[(BuSn)_{12}(CaO_4)(O)_{10}(OH)_8]^{2+}$. One component of overlapping peak centered at 1259.85 m/z.

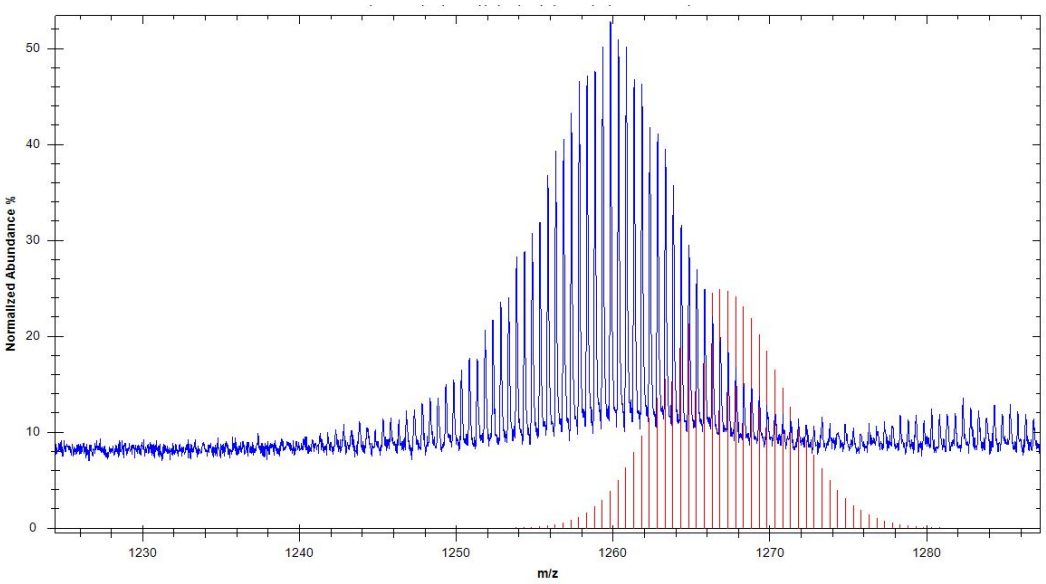

Figure S 4: Experimental ESI MS (+, blue spectrum) and calculated peak positions (red) for $[(BuSn)_{12}(CaO_4)(O)_{11}(OH)_4(OCH_3)_2]^{2+}$. One component of overlapping peak centered at 1259.85 m/z.

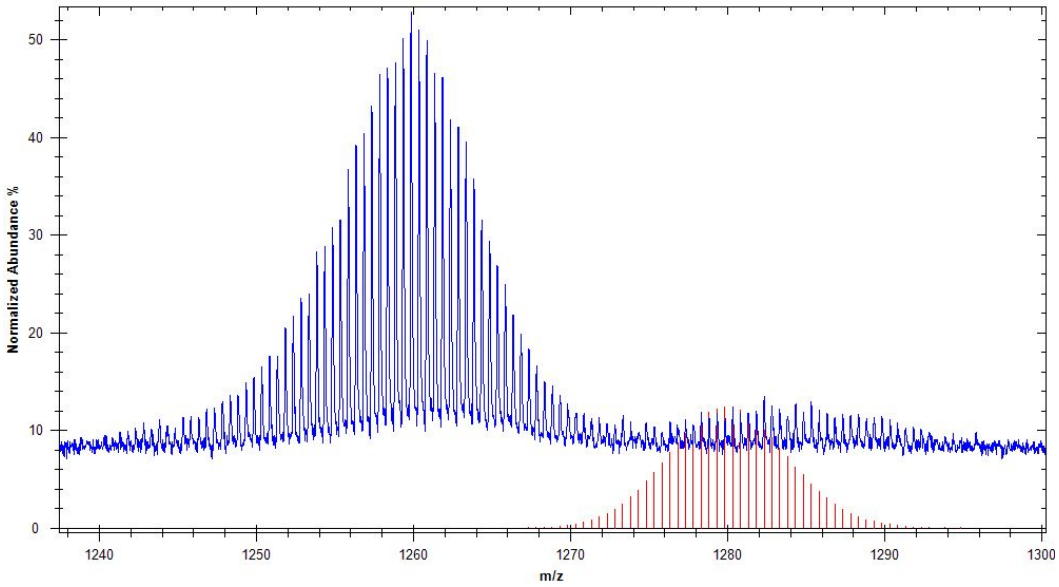

Figure S 5: Experimental ESI MS (+, blue spectrum) and calculated peak positions (red) for $[(BuSn)_{12}(CaO_4)(O)_{11}(OH)_3(OCH_3)_3]^{2+}$. One component of overlapping peak centered at 1259.85 m/z.

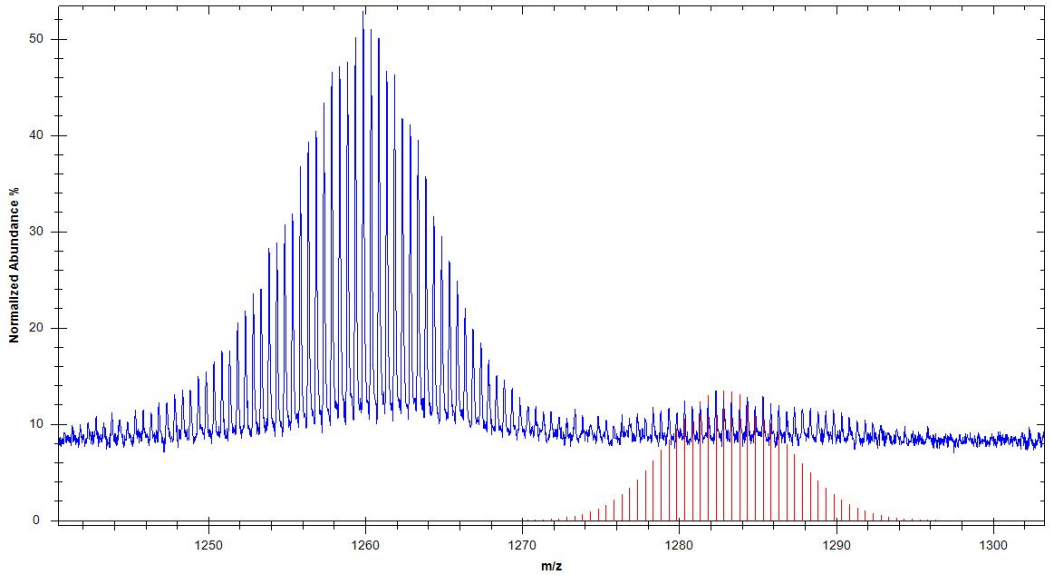

Figure S 6: Experimental ESI MS (+, blue spectrum) and calculated peak positions (red) for $[(BuSn)_{12}(CaO_4)(O)_8(OH)_4(OCH_3)]^{2+}$. One component of overlapping peak centered at 1282.83 m/z.

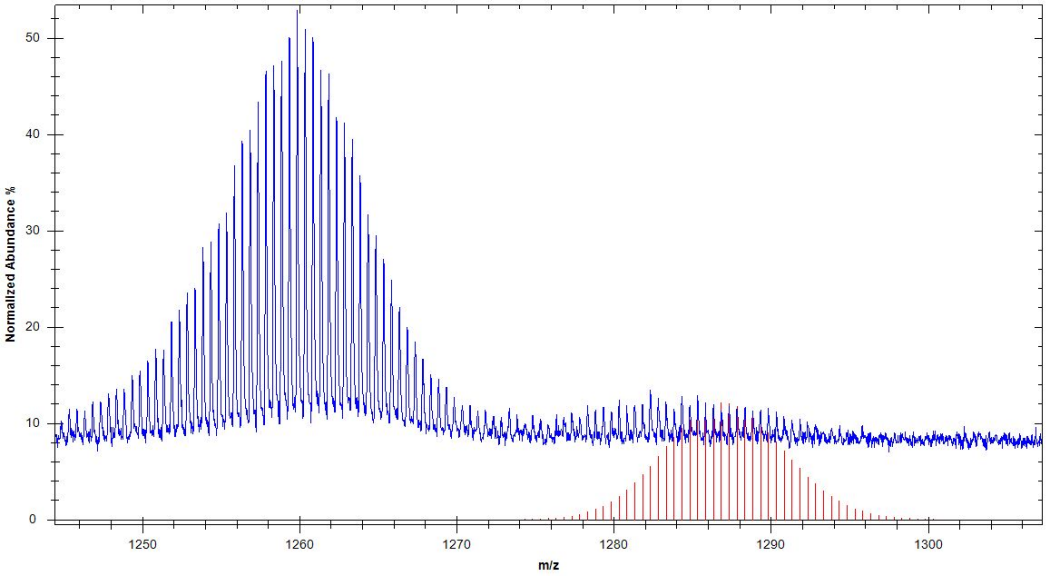

Figure S 7: Experimental ESI MS (+, blue spectrum) and calculated peak positions (red) for $[(BuSn)_{12}(CaO_4)(O)_{10}(OH)_4(OCH_3)_4]^{2+}$. One component of overlapping peak centered at 1282.83 m/z.

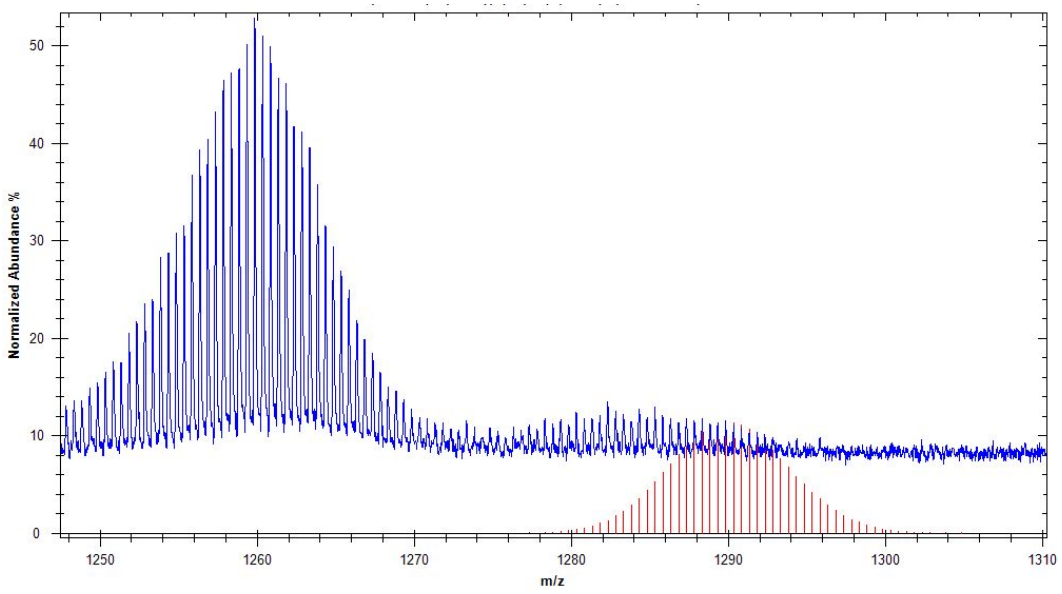

Figure S 8: Experimental ESI MS (+, blue spectrum) and calculated peak positions (red) for $[(BuSn)_{12}(CaO_4)(O)_8(OH)_{10}(OCH_3)_2]^{2+}$. One component of overlapping peak centered at 1282.83 m/z.

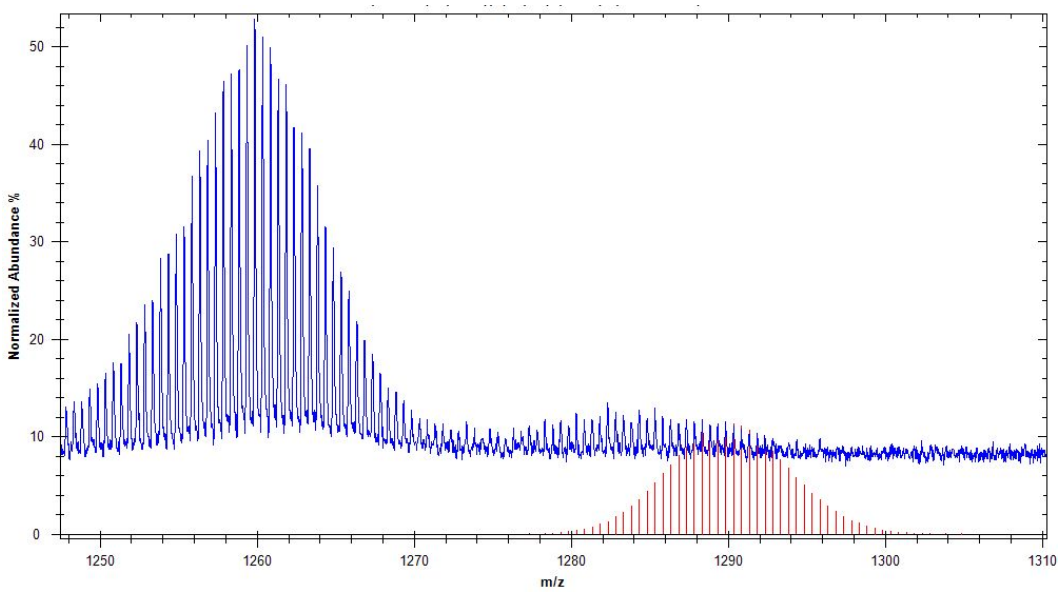

Figure S 9: Experimental ESI MS (+, blue spectrum) and calculated peak positions (red) for $[(BuSn)_{12}(CaO_4)(O)_{10}(OH)_3(OCH_3)_5]^{2+}$. One component of overlapping peak centered at 1282.83 m/z.

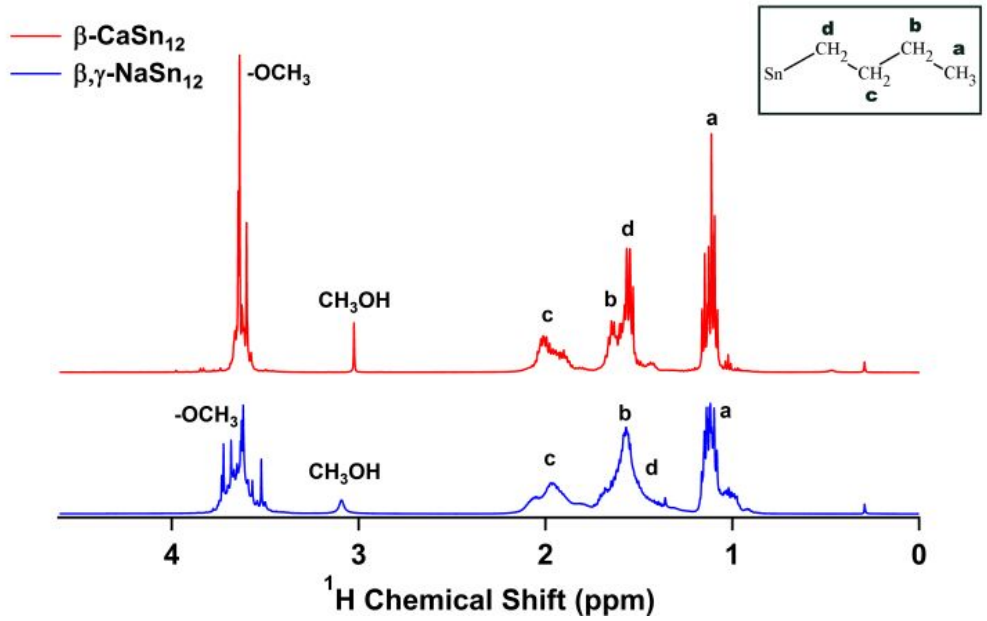

Figure S 10: Full ^{1}H NMR spectrum of β-$CaSn_{12}$ in C_6D_6 (red) and β,γ-$NaSn_{12}$ (blue) in C_6D_6.

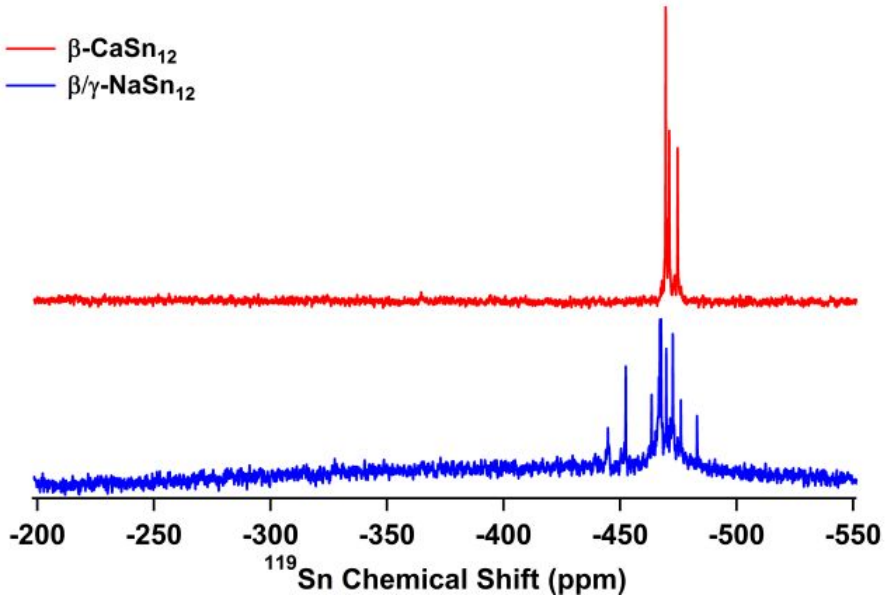

Figure S 11: Full ^{119}Sn NMR spectrum of β-$CaSn_{12}$ (red) and β,γ-$NaSn_{12}$ (blue) in C_6D_6.

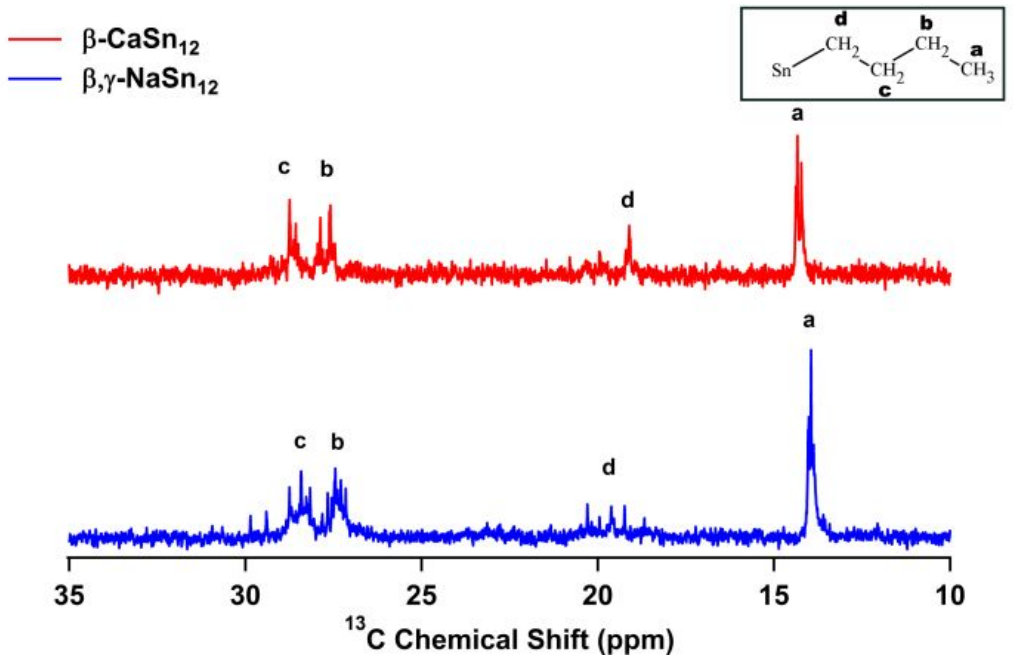

Figure S 12: ^{13}C NMR spectrum of β-$CaSn_{12}$ (red) and β,γ-$NaSn_{12}$ (blue) in C_6D_6.

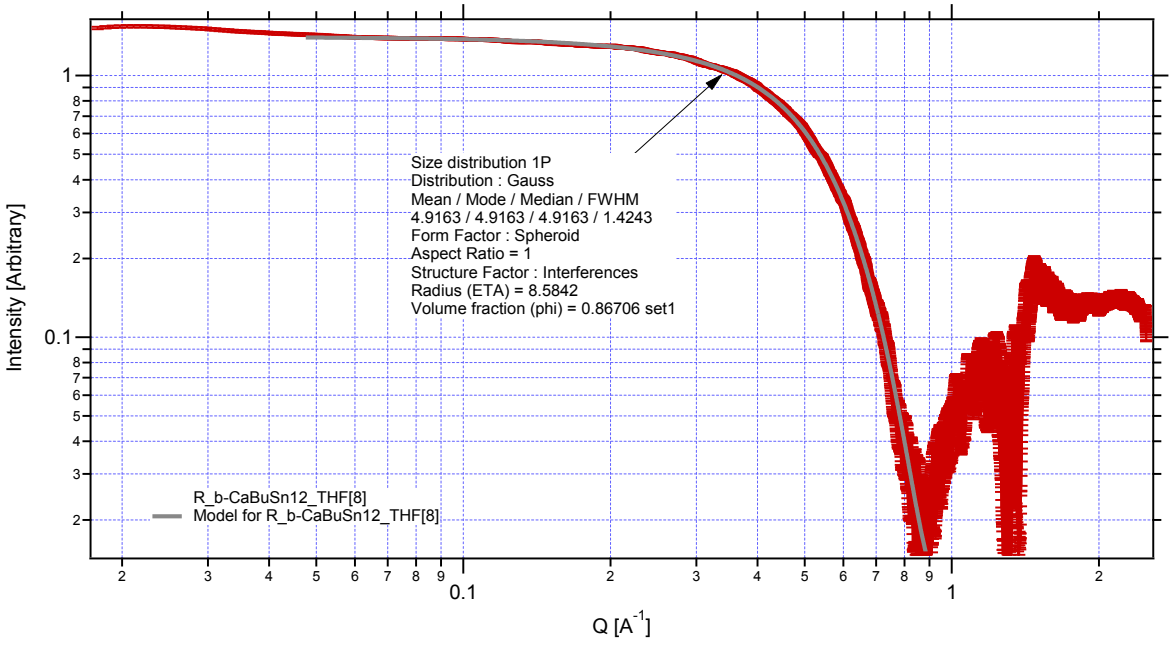

Figure S 13: Scattering curve of β-$CaSn_{12}$ in THF (red) and spherical model of the data (gray). The model gives a cluster radius of 4.9Å, a center-to-center distance between clusters of 8.6Å, and 0.87 nearest neighbors.

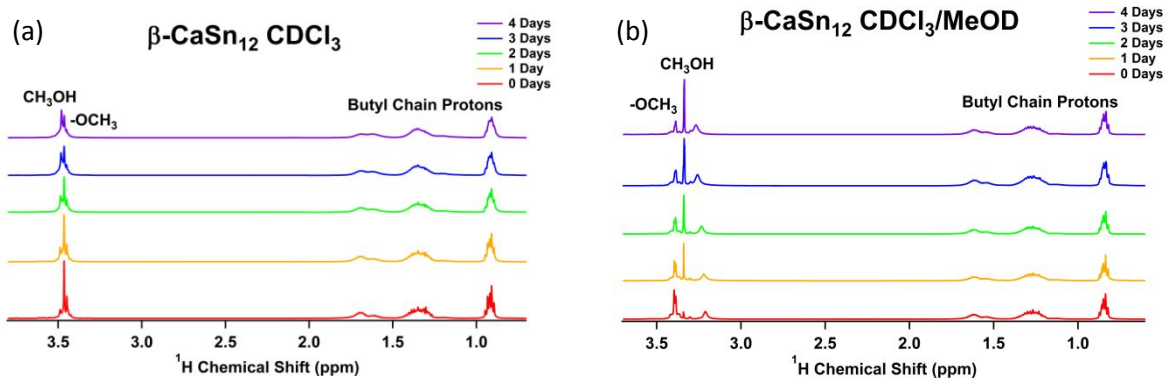

Figure S 14: (a) Aging of β-$CaSn_{12}$ in $CDCl_3$ monitored by ^1H NMR. (b) Aging of β-$CaSn_{12}$ in 90% $CDCl_3$/10% MeOD monitored by ^1H NMR.

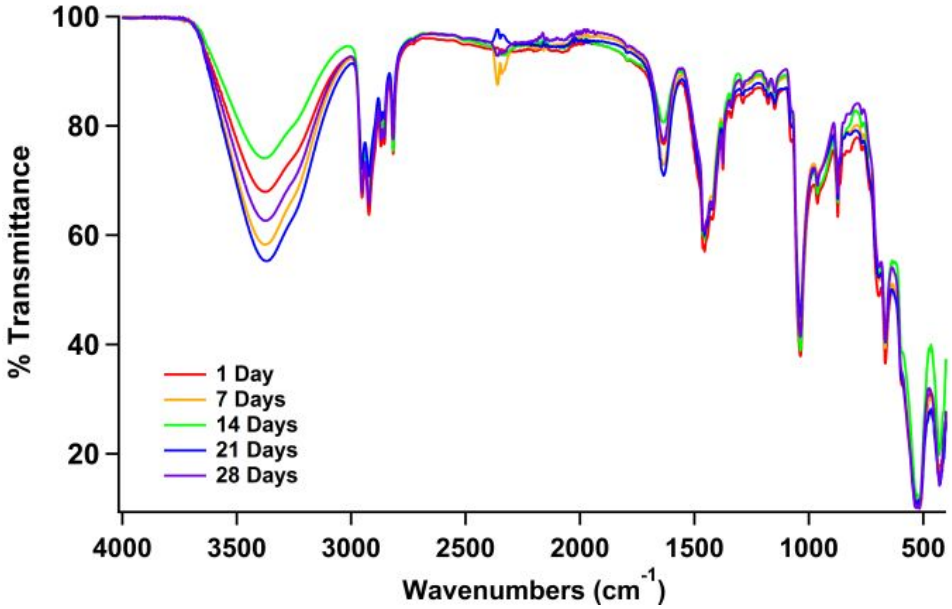

Figure S 15: Full FT-IR spectra of β-$CaSn_{12}$ from 1 to 28 days after isolation.

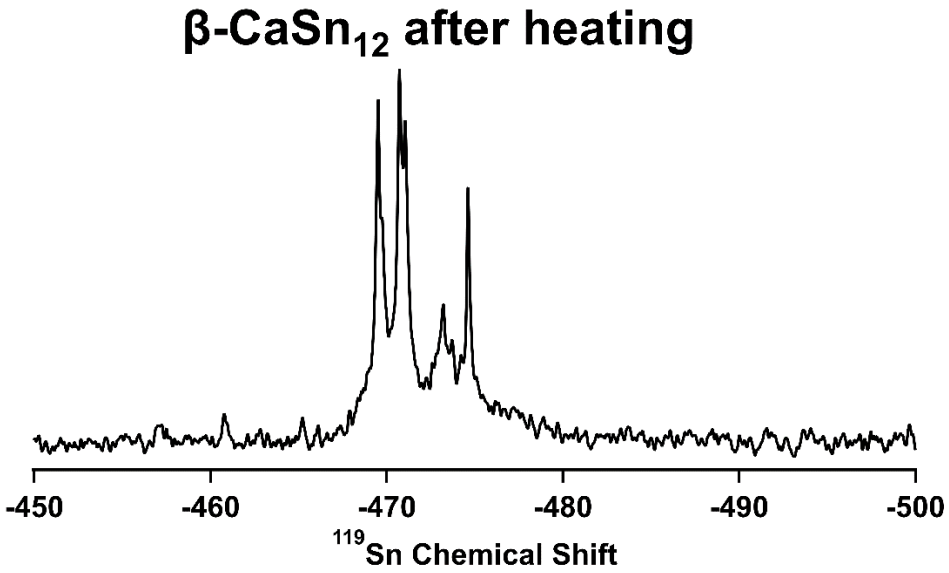

Figure S 16: ^{119}Sn NMR spectrum of cooled β-$CaSn_{12}$ solution after heating.