

## Supporting Information

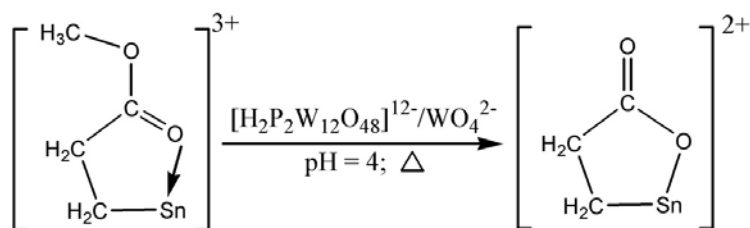
### New tetra(organotin)-decorated boat-like polyoxometalate

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#### 1. Synthetic discussion

Organotin groups tend to incorporate with various lacunary Keggin and Dawson-type polyoxoanions, but it is usually difficult to isolate the single crystals of these polyoxometalate (POM)-based hybrids from the aqueous reaction system, especially the estertin derivative of POMs. So far, quite a few of estertin-substituted POMs have been prepared by the routine aqueous solution method.<sup>1</sup> Considering that the highly lacunary polyoxoanion subunits have relatively stronger reactivity on their inner surfaces with various electrophilic metal ions and easily accept more extra W atoms, we attempt to prepare the estertin derivative of POMs by the use of the hexavacant Dawson-type unit  $\alpha$ -[P<sub>2</sub>W<sub>12</sub>O<sub>48</sub>]<sup>14-</sup> as the precursor. Compound **1** was prepared by the reaction mixture of K<sub>12</sub>H<sub>2</sub>P<sub>2</sub>W<sub>12</sub>O<sub>48</sub>·24H<sub>2</sub>O,<sup>2</sup> Cl<sub>3</sub>Sn(CH<sub>2</sub>)<sub>2</sub>COOCH<sub>3</sub>,<sup>3</sup> and NaWO<sub>4</sub>·2H<sub>2</sub>O in pH = 4 NaOAc-HAC buffer solution at 80 °C. During the preparation of **1**, it has been found that the pH value and reaction time of the synthetic system play important roles in the isolation of single crystals of **1**. The pH value should be controlled in the range of 4.0 ~5.0, while the stirring time of the solution should keep more than one hour. Furthermore, the molar ratio of {P<sub>2</sub>W<sub>12</sub>}/NaWO<sub>4</sub> should keep the ratio of ca. 1:1, otherwise, only the wheel-type polyoxoanion {P<sub>8</sub>W<sub>48</sub>} is obtained. Single crystal X-ray diffraction analysis indicates that {P<sub>2</sub>W<sub>12</sub>} precursors convert into  $\alpha_1, \beta_1, \beta_2$ -{P<sub>2</sub>W<sub>15</sub>} subunits in the synthetic process, and dimerize a new boat-like lacunary polyoxoanion. Furthermore, the losing of -CH<sub>3</sub> group of acrylate in compound **1** indicates that [Sn(CH<sub>2</sub>)<sub>2</sub>COOCH<sub>3</sub>]<sup>3+</sup> should hydrolyze into [Sn(CH<sub>2</sub>)<sub>2</sub>COO]<sup>2+</sup> during the reaction process. Such a phenomenon has never been observed in earlier

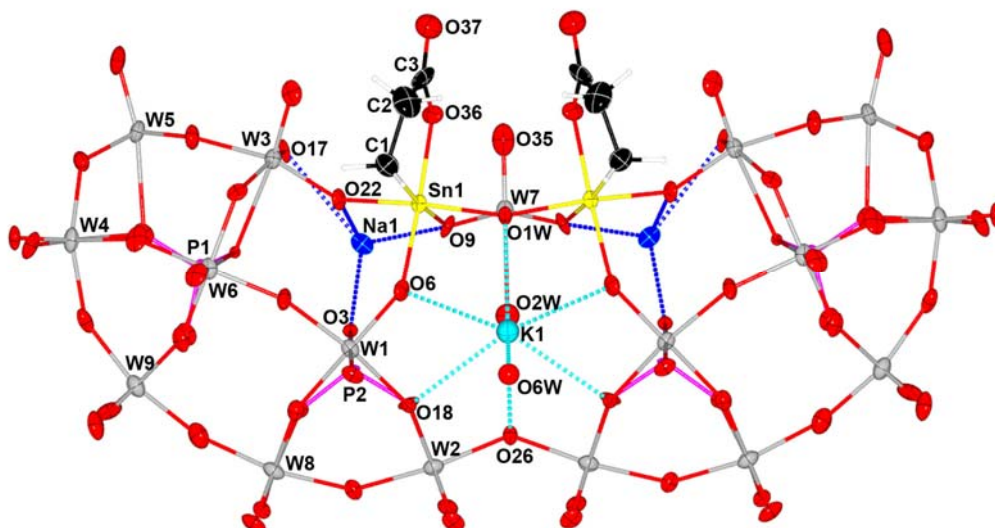
reports.<sup>1</sup>



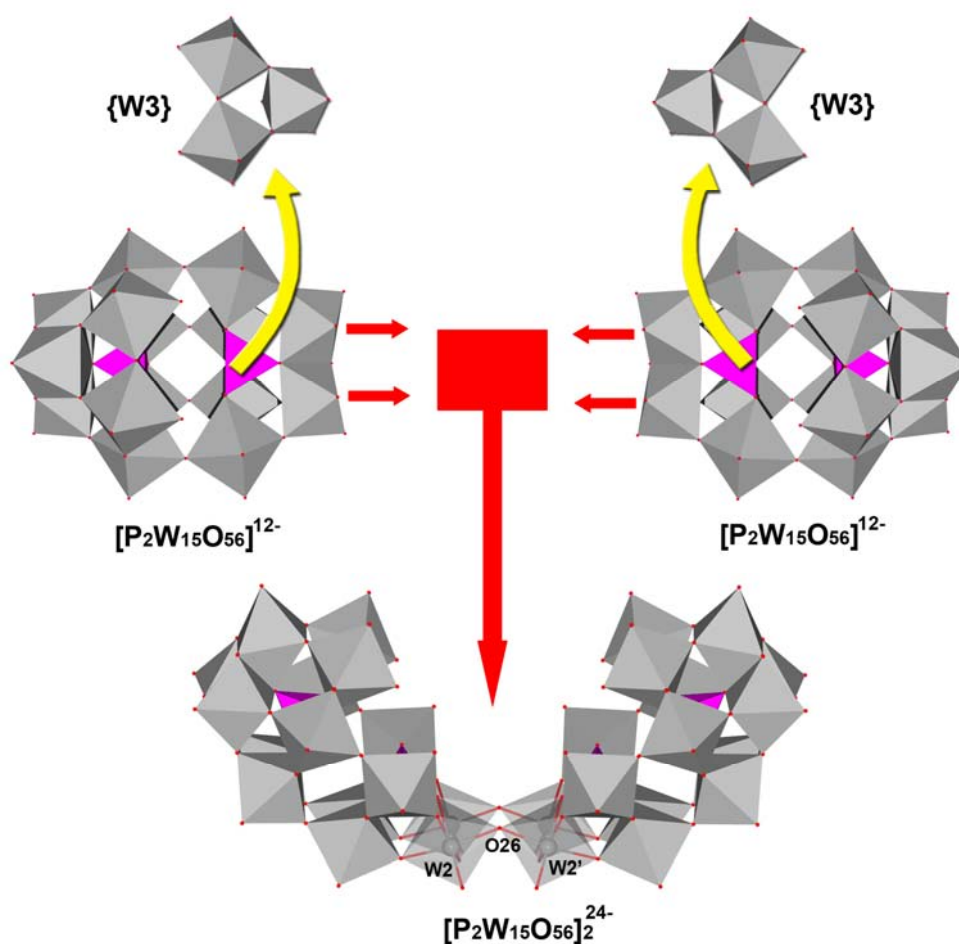
## References

- (a) X. H. Wang, H. C. Dai and J. F. Liu, *Polyhedron* 1999, **18**, 2293-2300; (b) G. Sazani and M. T. Pope, *Dalton Trans.* 2004, 1989-1994; (c) S. Bareyt, S. Piligkos, B. Hasenknopf, P. Gouzerh, E. Lacte, S. Thorimbert and M. Malacria, *Angew. Chem. Int. Ed.* 2003, **42**, 3404-3406.
- R. Contant; A. Tézé, *Inorg. Chem.* 1985, **24**, 4610-4614.
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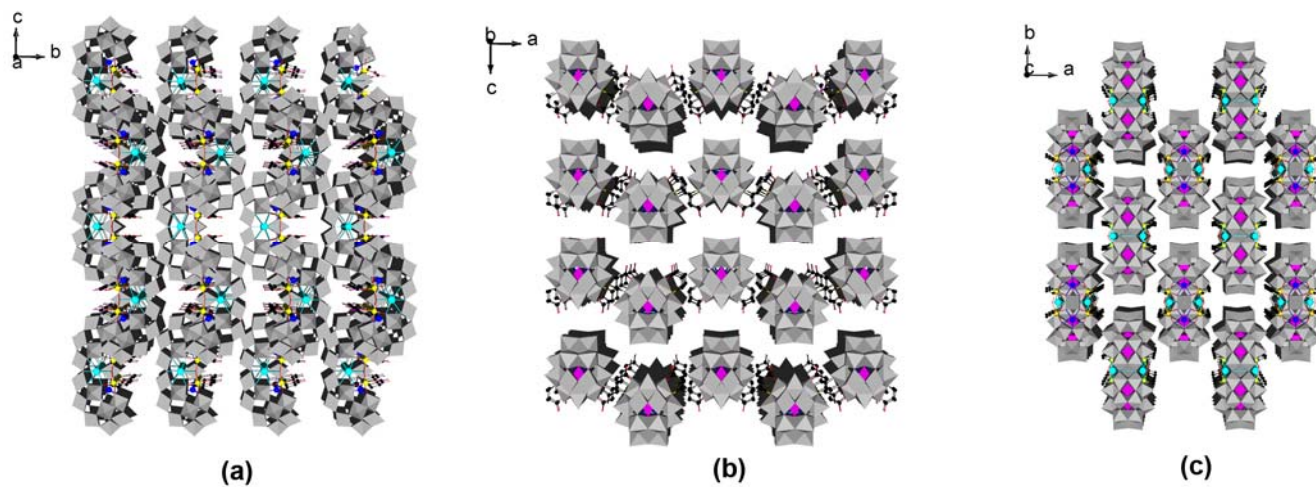
## 2. Crystal Structures



**Fig. S1.** ORTEP drawing of the polyoxoanion of **1** with thermal ellipsoids at 50 % probability.

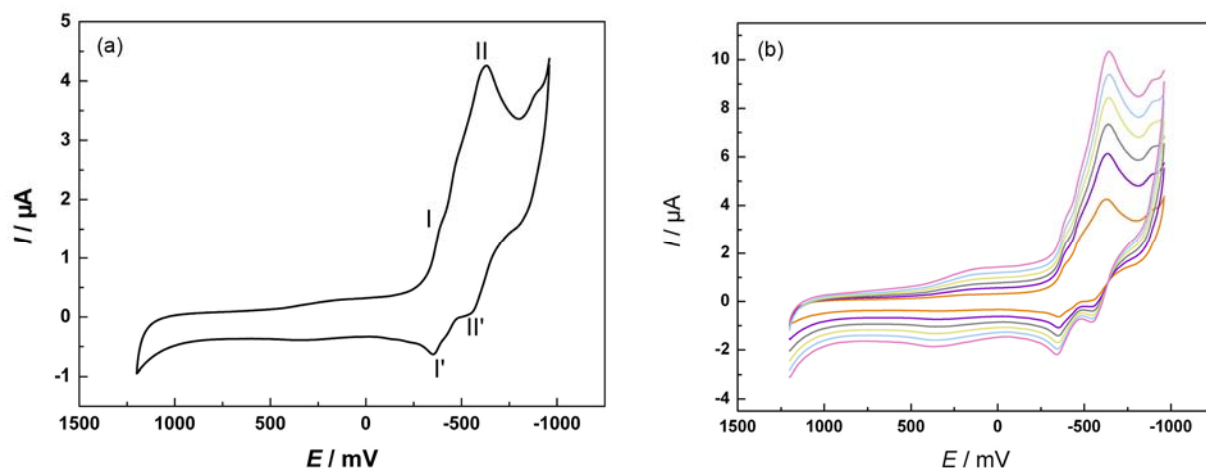


**Fig. S2.** Schematic view of the basic building block ( [P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>]<sup>12-</sup> ) and the connection modes of the boat-like polyoxoanion matrix ( [P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>]<sub>2</sub><sup>24-</sup> ) in **1**.

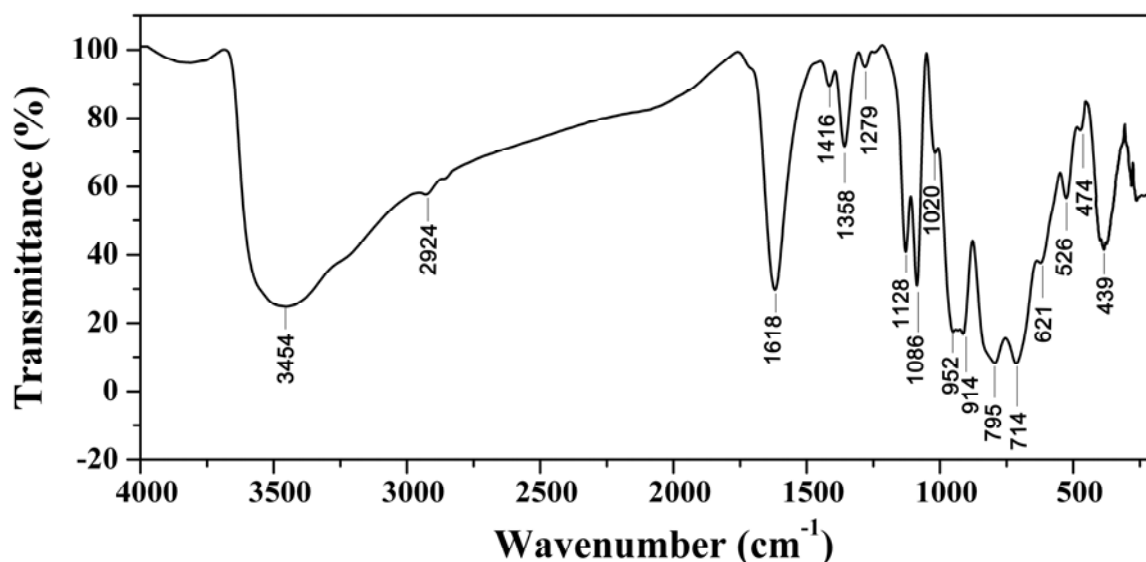


**Fig. S3.** The packing arrangement of the polyoxoanion in **1** viewed along (a) *a* axis; (b) *b* axis; (c) *c* axis. The counter cations and the solvent water molecules reside in the interspaces of the adjacent polyoxoanions and are omitted for clarity.

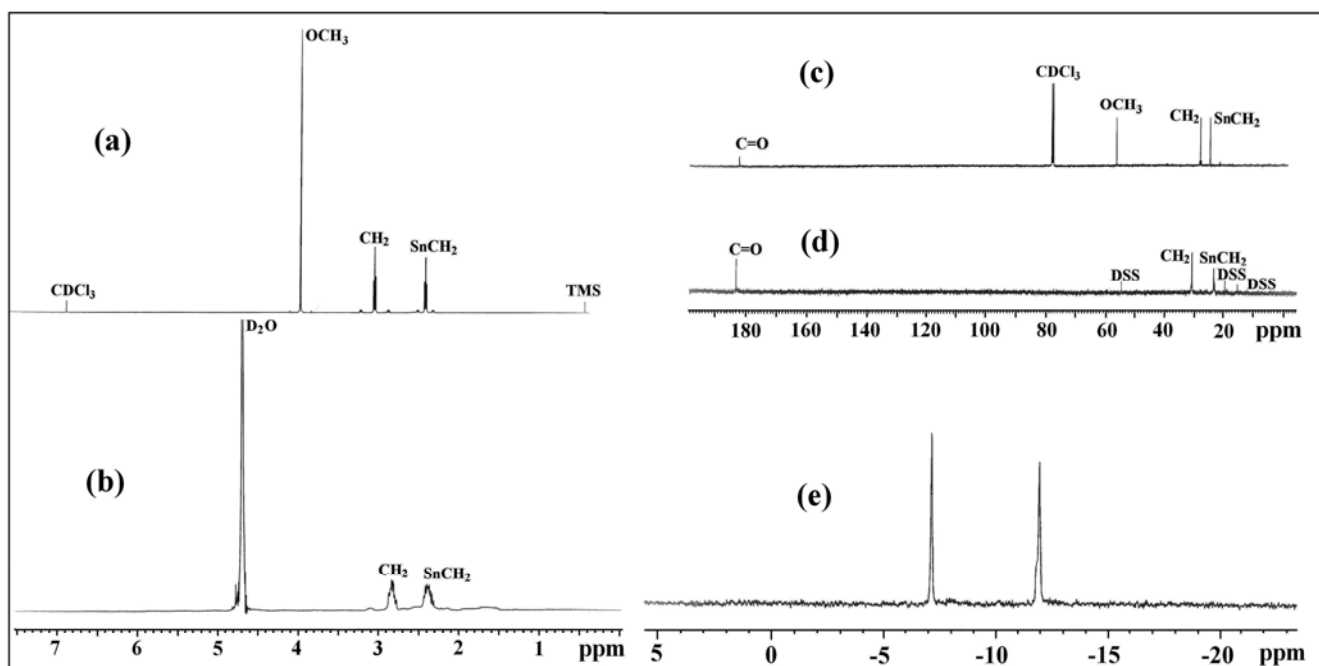
### 3. Characterizations



**Fig. S4.** (a) Cyclic voltammogram (CV) of  $1.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$  of **1** in  $0.4 \text{ mol}\cdot\text{L}^{-1}$  NaOAc-HAc (pH 4) medium. Working electrode: glassy carbon; Reference electrode: Ag/AgCl; The scan rate was  $10 \text{ mV}\cdot\text{s}^{-1}$ ; (b) Cyclic voltammograms behavior of **1** in pH 4 ( $0.4 \text{ mol}\cdot\text{L}^{-1}$  NaOAc-HAc) buffer solution at different scan rates (from inner to outer: 10, 20, 30, 40, 50,  $60 \text{ mV}\cdot\text{s}^{-1}$ ).

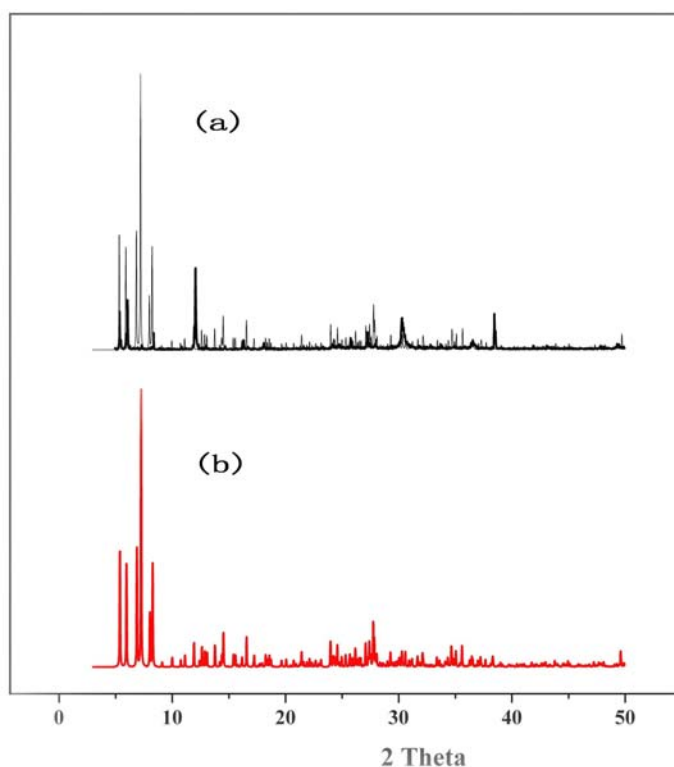


**Fig. S5.** The IR spectrum of **1**. The broad band at  $3454 \text{ cm}^{-1}$  corresponds to the O–H stretching vibrations of the lattice and coordinated water molecules. The characteristic peaks at 1128(m), 1086(s), 1020(w), 951-914(s), 795(s), 714(s),  $621 \text{ (m)} \text{ cm}^{-1}$  are attributed to  $\nu(\text{P-O})$ ,  $\nu(\text{W=O}_d)$ ,  $\nu(\text{W-O}_a)$ ,  $\nu(\text{W-O}_b)$  and  $\nu(\text{W-O}_c)$  of the polyoxoanion, respectively. The  $\nu_{\text{as}}(\text{COO}^-)$  vibration appears at  $1618 \text{ cm}^{-1}$ , while the  $\nu_{\text{s}}(\text{COO}^-)$  appears at  $1358 \text{ cm}^{-1}$ . Further, the peaks at 2924 and  $1416 \text{ cm}^{-1}$  are assigned to  $\nu(\text{CH}_2)$  and  $\delta(\text{CH}_2)$ , respectively. These peaks indicate that  $-\text{CH}_3$  is lost and the intramolecular Sn–O bond remains in the structure. The band at  $439 \text{ cm}^{-1}$  is assigned to the stretching vibration of Sn–O bond. Bands at 474 and  $526 \text{ cm}^{-1}$  are attributed to the antisymmetric and symmetric vibrations of Sn–C bonds.<sup>1</sup> (ref: Rauf, M.K.; Saeed, M.A. *J. Organomet. Chem.* 2008, **693**, 3043.)

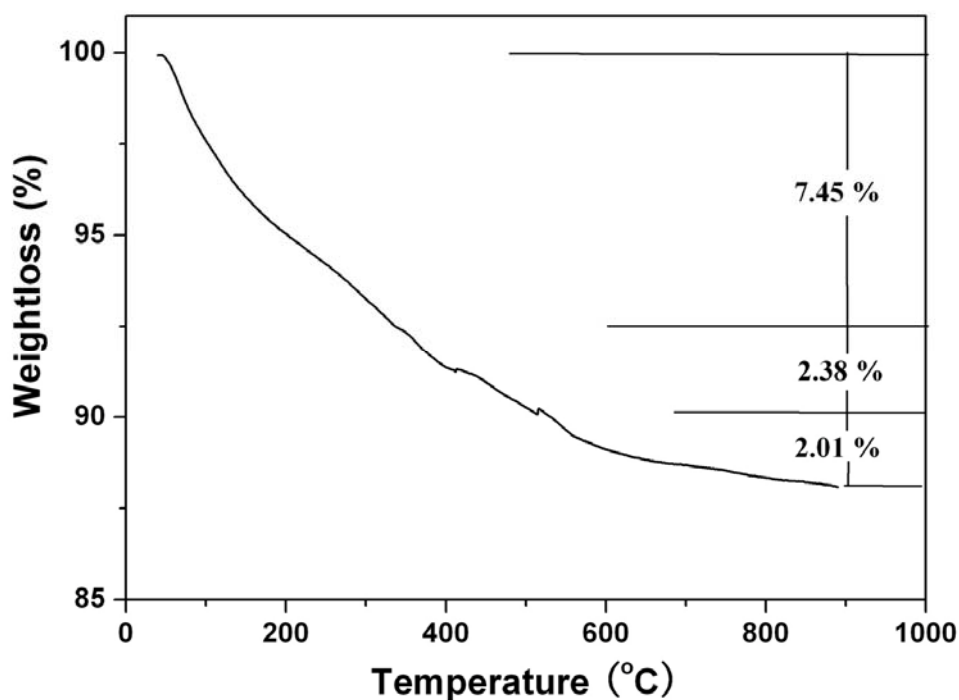


**Fig. S6.** NMR spectra were recorded at room temperature with a 500 MHz Bruker AVANCE 500 spectrometer. (a)  $^1\text{H}$  NMR (CDCl<sub>3</sub>/TMS) of the starting material Cl<sub>3</sub>SnCH<sub>2</sub>CH<sub>2</sub>COOCH<sub>3</sub>: 3.99 (s, 3 H, -OCH<sub>3</sub>), 2.96 (t, *J* = 7.6 Hz, 2 H, -CH<sub>2</sub>) and 2.24 (t, *J* = 7.6 Hz, 2 H, SnCH<sub>2</sub>) ppm. (b)  $^1\text{H}$  NMR (D<sub>2</sub>O) of compound **1**: 2.83 (m, 2 H, -CH<sub>2</sub>) and 2.39 (m, 2 H, SnCH<sub>2</sub>) ppm. (c)  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>/TMS) of the starting material Cl<sub>3</sub>SnCH<sub>2</sub>CH<sub>2</sub>COOCH<sub>3</sub>: 181.26 (C=O), 55.76 (OCH<sub>3</sub>), 27.80 (CH<sub>2</sub>) and 24.50 (SnCH<sub>2</sub>) ppm. (d)  $^{13}\text{C}$  NMR (D<sub>2</sub>O/DSS) of compound **1**: 183.34 (C=O), 31.21 (CH<sub>2</sub>) and 23.91 (SnCH<sub>2</sub>) ppm. (e)  $^{31}\text{P}$  NMR (D<sub>2</sub>O/PO<sub>4</sub><sup>3-</sup>): -7.06 (2P) and -11.85 (2P) ppm.

As shown in Fig. S6b and 6d, there are no signals of -OCH<sub>3</sub> group in  $^1\text{H}$  and  $^{13}\text{C}$  NMR of compound **1** in comparison with the relevant NMR of the starting material Cl<sub>3</sub>SnCH<sub>2</sub>CH<sub>2</sub>COOCH<sub>3</sub> (see Fig. S6a and 6c), which further confirms the hydrolysis of [Sn(CH<sub>2</sub>)<sub>2</sub>COOCH<sub>3</sub>]<sup>3+</sup> into [Sn(CH<sub>2</sub>)<sub>2</sub>COO]<sup>2+</sup> during the reaction process. Furthermore,  $^{31}\text{P}$  NMR shows two peaks, which is consistent with the structural feature of compound **1**, indicating that the polyoxoanion should be stable in aqueous solution.



**Fig. S7** (a) The experimental (black and thick line) and (b) simulated XRPD patterns of compound **1**. Their peak positions are in good agreement with each other, indicating the phase purity of the products. The differences in intensity may be ascribed to the preferred orientation of the powder samples.



**Fig. S8.** TG curve of **1**. In the temperature range of 44 - 900 °C, the TG curve shows three continuous weight losses. The first weight loss is 7.45 % in the temperature range of 44 ~ 340 °C, corresponding to the loss of all lattice and coordinated water molecules in **1** (ca. 40 H<sub>2</sub>O). The second and third weight loss steps of 2.38 % in the temperature range of 342 ~ 512 °C correspond to the loss of organotin groups (calc. value 2.32 %). The fourth weight loss of ca. 2.01 % in the range of 514 ~ 900 °C is attributed to partial loss of phosphorus oxide.

## 5. Crystal data, bond length and angle, BVS calculation

**Table S1** Crystal Data and Structure Refinement for **1**

	<b>1</b>
Empirical formula	C <sub>12</sub> H <sub>96</sub> K <sub>2</sub> Na <sub>18</sub> O <sub>165</sub> P <sub>4</sub> Sn <sub>4</sub> W <sub>31</sub>
<i>M</i>	9670.67
$\lambda/\text{\AA}$	0.71073\AA
<i>T</i> /K	150(2)
Crystal dimensions/mm	0.16 × 0.12 × 0.10
Crystal system	Orthorhombic
Space group	<i>Pmmn</i>
<i>a</i> /\AA	21.393(4)
<i>b</i> /\AA	25.702(5)
<i>c</i> /\AA	14.846(3)
$\alpha/^\circ$	90.0
$\beta/^\circ$	90.0
$\gamma/^\circ$	90.0
<i>V</i> /\AA <sup>3</sup>	8163(3)
<i>Z</i>	2
<i>D<sub>c</sub></i> /Mg m <sup>-3</sup>	3.934
$\mu/\text{mm}^{-1}$	22.600
<i>F</i> (000)	8552
$\theta$ Range/ $^\circ$	3.01–25.00
Measured reflections	55619
Independent reflections	7544
Data/restraints/parameters	7544/127/512
<i>R<sub>int</sub></i>	0.1851
<i>R</i> <sub>1</sub> ( <i>I</i> > 2σ( <i>I</i> )) <sup>a</sup>	0.0575
<i>wR</i> <sub>2</sub> (all data) <sup>a</sup>	0.1280
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.011
$\Delta\rho_{\text{max, min}}/ \text{e \AA}^{-3}$	3.076, -2.715

<sup>a</sup> $R_1 = \sum ||F_0| - |F_C|| / \sum |F_0|$ ;  $wR_2 = \sum [w(F_0^2 - F_C^2)^2] / \sum [w(F_0^2)^2]^{1/2}$



**Table S2.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **1**.  
 U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
W(1)	922(1)	1074(1)	7385(1)	15(1)
W(2)	3288(1)	1800(1)	5511(1)	18(1)
W(3)	1625(1)	417(1)	10386(1)	17(1)
W(4)	3293(1)	-1420(1)	9191(1)	22(1)
W(5)	2500	-802(1)	10860(1)	20(1)
W(6)	876(1)	-185(1)	8692(1)	18(1)
W(7)	2500	2500	9488(1)	18(1)
W(8)	1718(1)	359(1)	5513(1)	20(1)
W(9)	1718(1)	-868(1)	6882(1)	22(1)
P(1)	2500	-263(3)	8694(6)	17(2)
P(2)	2500	1084(3)	7069(5)	12(2)
O(1)	2500	-401(8)	7670(14)	20(5)
O(2)	2500	1590(8)	6515(12)	16(5)
O(3)	1930(6)	1079(5)	7668(9)	12(3)
O(4)	865(8)	488(5)	8179(10)	24(4)
O(5)	2500	-763(8)	9262(13)	20(5)
O(6)	843(7)	1550(5)	8276(10)	20(3)
O(7)	3223(6)	1073(5)	5189(9)	17(3)
O(8)	1916(6)	54(5)	8941(8)	8(3)
O(9)	1885(7)	1979(5)	9265(10)	20(4)
O(10)	1205(7)	570(5)	6445(10)	20(4)
O(11)	3235(7)	-1310(5)	7917(11)	22(4)
O(12)	1800(8)	-313(6)	6087(11)	31(4)
O(13)	163(6)	1090(5)	6978(9)	17(3)
O(14)	2500	1920(8)	4881(13)	20(5)
O(15)	3794(7)	-1931(5)	9245(10)	23(4)
O(16)	2500	-1786(8)	9120(15)	27(5)
O(17)	2500	524(7)	10502(14)	17(5)
O(18)	1215(6)	1593(5)	6479(9)	12(3)
O(19)	1227(7)	168(6)	4693(10)	26(4)
O(20)	1896(8)	-307(5)	10755(11)	26(4)
O(21)	106(7)	-299(6)	8595(11)	27(4)
O(22)	1532(7)	1003(5)	9727(10)	19(3)
O(23)	1163(7)	-454(5)	7581(10)	20(3)
O(24)	2500	614(7)	6459(13)	14(4)
O(25)	2500	-963(8)	11979(16)	36(6)
O(26)	3231(9)	2500	5980(14)	18(5)
O(27)	2500	243(7)	4907(13)	16(5)

O(28)	3788(7)	1968(6)	4654(10)	21(4)
O(29)	1214(8)	-1238(6)	6282(11)	31(4)
O(30)	3105(8)	-1312(5)	10418(10)	23(4)
O(31)	2500	-1117(9)	6502(14)	32(6)
O(32)	3833(7)	-833(6)	9184(11)	28(4)
O(33)	1352(7)	600(6)	11403(11)	26(4)
O(34)	895(7)	88(5)	9878(9)	17(3)
O(35)	2500	2500	10600(20)	38(9)
O(36)	1307(8)	1868(6)	11019(10)	25(4)
O(37)	940(10)	1852(7)	12397(12)	46(5)
O(1W)	702(10)	2500	9414(13)	19(5)
O(2W)	2500	2500	7842(7)	33(8)
Sn(1)	1058(1)	1726(1)	9631(1)	14(1)
C(1)	228(11)	1446(9)	10248(16)	30(6)
C(2)	244(13)	1633(11)	11220(19)	47(8)
C(3)	855(12)	1786(9)	11587(17)	31(6)
K(1)	1165(5)	2500	7598(6)	46(2)
Na(1)	2500	1204(5)	9027(8)	22(3)
Na(2)	4046(12)	2500	3441(16)	93(7)
Na(3)	2500	1634(11)	1841(18)	118(9)
Na(4)	599(11)	5720(9)	1306(15)	142(8)
Na(5)	1610(13)	1057(10)	3245(18)	66(7)
Na(6)	5531(13)	2500	9245(17)	114(9)
Na(7)	5063(17)	147(13)	3690(20)	95(10)
Na(8)	8980(30)	2500	2690(40)	150(20)
Na(9)	-120(50)	3160(30)	5380(60)	150(30)
O(3W)	7500	2500	2500(40)	120(20)
O(4W)	2500	2500	3250(40)	120(20)
O(5W)	759(18)	6709(13)	1920(20)	138(13)
O(6W)	-100(20)	2500	6930(30)	133(17)
O(7W)	824(18)	424(14)	2910(20)	55(10)
O(71W)	1100(20)	-109(17)	2800(30)	52(12)
O(8W)	4810(20)	-685(18)	4720(30)	79(15)
O(9W)	1940(40)	2500	1990(50)	90(20)
O(10W)	150(30)	1180(20)	3440(40)	91(17)
O(11W)	5070(40)	2500	3810(50)	100(30)
O(12W)	2500	-930(30)	4370(40)	80(20)
O(13W)	2500	833(10)	2363(18)	49(7)
O(14W)	2500	7500	830(40)	103(19)
O(15W)	2500	26(14)	3090(20)	91(12)

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**Table S3.** Selected bond lengths (Å) and bond angles (°) of **1**

W(7)-O(35)	1.66(4)	W(2)-O(28)	1.717(14)
W(7)-O(9)	1.908(14)	W(2)-O(18)#1	1.866(13)
W(7)-O(9)#1	1.908(14)	W(2)-O(26)	1.934(8)
W(7)-O(9)#2	1.908(14)	W(2)-O(7)	1.934(14)
W(7)-O(9)#3	1.908(14)	W(2)-O(14)	1.952(10)
W(7)-O(2W)	2.444(10)	W(2)-O(2)	2.314(13)
O(6)-Sn(1)	2.112(14)	Sn(1)-C(1)	2.12(2)
O(9)-Sn(1)	1.960(15)	O(36)-C(3)	1.30(3)
O(22)-Sn(1)	2.120(13)	O(37)-C(3)	1.23(3)
O(36)-Sn(1)	2.160(15)	C(1)-C(2)	1.52(3)
O(1W)-Sn(1)	2.156(8)	C(2)-C(3)	1.47(4)
P(1)-O(5)	1.54(2)	P(2)-O(3)	1.509(14)
P(1)-O(8)	1.536(13)	P(2)-O(3)#1	1.509(14)
P(1)-O(8)#1	1.536(13)	P(2)-O(24)	1.51(2)
P(1)-O(1)	1.56(2)	P(2)-O(2)	1.54(2)
K(1)-O(6)	2.730(15)	Na(1)-O(3)	2.379(17)
K(1)-O(6)#3	2.730(15)	Na(1)-O(3)#1	2.379(17)
K(1)-O(18)	2.864(14)	Na(1)-O(9)	2.414(17)
K(1)-O(18)#3	2.864(14)	Na(1)-O(9)#1	2.414(17)
K(1)-O(26)#2	2.73(2)	Na(1)-O(22)	2.373(16)
K(1)-O(1W)	2.87(2)	Na(1)-O(22)#1	2.373(16)
K(1)-O(2W)	2.879(11)	Na(1)-O(17)	2.80(2)
K(1)-O(6W)	2.87(5)	Na(2)-O(28)#3	2.33(2)
Na(2)-O(37)#4	2.28(2)	Na(2)-O(28)	2.33(2)
Na(2)-O(37)#5	2.28(2)	Na(2)-O(11W)	2.27(9)
O(35)-W(7)-O(9)	100.0(4)	O(28)-W(2)-O(18)#1	106.7(7)
O(35)-W(7)-O(9)#1	100.0(4)	O(28)-W(2)-O(26)	94.1(8)
O(35)-W(7)-O(9)#2	100.0(4)	O(28)-W(2)-O(7)	96.0(6)
O(35)-W(7)-O(9)#3	100.0(4)	O(28)-W(2)-O(14)	98.3(7)
O(35)-W(7)-O(2W)	180.000(9)	O(28)-W(2)-O(2)	171.8(6)
O(9)-Sn(1)-O(6)	90.2(6)	W(2)-O(26)-W(2)#2	137.1(11)
O(6)-Sn(1)-O(22)	88.9(5)	O(6)-Sn(1)-C(1)	99.0(7)
O(6)-Sn(1)-O(36)	177.0(6)	O(6)-Sn(1)-O(1W)	88.7(6)
O(37)-C(3)-C(2)	122(2)	C(3)-C(2)-C(1)	117.0(2)
C(2)-C(1)-Sn(1)	106.5(16)	O(36)-C(3)-C(2)	118.0(2)
O(37)-C(3)-O(36)	120.0(3)		
O(5)-P(1)-O(8)	108.2(7)	O(3)-P(2)-O(3)#1	107.8(11)
O(5)-P(1)-O(8)#1	108.2(7)	O(3)-P(2)-O(24)	110.2(7)
O(5)-P(1)-O(1)	110.2(12)	O(3)-P(2)-O(2)	108.8(7)

Symmetry transformations used to generate equivalent atoms: #1  $-x+1/2, y, z$ ; #2  $x, -y+1/2, z$ ; #3  $-x+1/2, -y+1/2, z$ ; #4  $-x+1/2, y, z-1$ ; #5  $-x+1/2, -y+1/2, z-1$ .



**Table S4.** Bond valence sum calculation<sup>1</sup> of selected non-H atoms in **1**

Atom center	BVS result	Atom center	BVS result
Sn1	2.046	W7	5.97
O1W	0.54	O2W	0.51
P1	4.96	P2	4.97

Ref: 1. (a) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244. (b) Trzesowska, A.; Kruszynski, R.; Bartczak, T. J. *Acta Cryst.* **2006**, *B62*, 745.