Trimeric, hexa-dimethyltin-functionalized selenotungstate $[{Sn(CH_3)_2(CH_3COO)}_3{Sn(CH_3)_2}_3{Se_2W_{18}O_{62}(OH)(H_2O)}_3]^{18-}$

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	Table S1. A detailed survey of dimethyltin-containing POMs				
Year	Formula	Basic Building Blocks	Number of Sn Centers	Dimension	Ref.
2004	$(CsNa_{2}[{Sn(CH_{3})_{2}}_{3}(H_{2}O)_{4}(\beta-XW_{9}O_{33})]\cdot7H_{2}O)_{\infty}(X = As, Sb)$	Keggin-type $\{XW_9O_{33}\}$ (X = As, Sb)	3	2D lattice	1
2005	$[\{Sn(CH_3)_2(H_2O)\}_2\{Sn(CH_3)_2\}As_3(\alpha-AsW_9O_{33})_4]^{21-1}$	Keggin-type {AsW ₉ O ₃₃ }	3	nanocluster	2
2005	$[\{SnCH_3\}_2(H_2O)\}_{24}\{Sn(CH_3)_2\}_{12}(A-XW_9O_{34})_{12}]^{36-}(X = P, As)$	Keggin-type {XW ₉ O ₃₄ } (X = P, As)	36	nanocluster	3
2006	$[\{Sn(CH_3)_2\}_4(H_2P_4W_{24}O_{92})_2]^{28-}$	$Dawson-type \\ \{H_2P_4W_{24}O_{92}\}$	4	nanocluster	4
	$[{(CH_3)_2Sn}(MoO_4)](1)$	{MoO ₄ }	1	3D network	
2006	$[((CH_{1}), Sn_{1}), O, (M_{2}O_{1}),](2)$	$\{MoO_4\}$	4	2D layer	5
	$[\{(CH_3)_2Sn\}\{Mo_2O_7(H_2O)_2\}] \cdot H_2O(3)$	$\{Mo_2O_7(H_2O)_2\}$	1	2D layer	
2006	$[\{(CH_3)_2Sn\}_2(W_6O_{22})]^{4-}$	$\{W_6O_{22}\}$	2	1D chain	6
2007	$[{(Sn(CH_3)_2)(Sn(CH_3)_2O)(A-PW_9O_{34})}_3]^{21-}$	Keggin-type {PW ₉ O ₃₄ }	6	nanocluster	7
2007	$[\{(CH_3)_2Sn\}_6(OH)_2O_2(H_2BW_{13}O_{46})_2]^{12-}$	Keggin-type { H ₂ BW ₁₃ O ₄₆ }	6	nanocluster	8
2008	$[\{(CH_3)_2Sn(H_2O)\}_4\{(CH_3)_2Sn\}(B-\beta-XW_9O_{33})_2]^{8-}(X = As, Sb)$	Keggin-type $\{XW_9O_{33}\}$ (X = As, Sb)	5	2D assemblies	9
2009	$\begin{split} Na[C(NH_2)_3]_2[\{(CH_3)_2Sn(H_2O)\}_3(A-\alpha-\\ PW_9O_{34})]\cdot 9H_2O\ (1)\\ Na[C(NH_2)_3]_2[\{(CH_3)_2Sn(H_2O)\}_{3}-\\ (A-\alpha-AsW_9O_{34})]\cdot 8H_2O\ (2)\\ Na_2[C(NH_2)_3]_2[\{(CH_3)_2Sn(H_2O)\}_3(A-\alpha-\\ SiW_9O_{34})]\cdot 10H_2O\ (3) \end{split}$	Keggin-type {XW ₉ O ₃₄ } (X = P, As, Si)	3	3D networks	10
2010	$\label{eq:charge} \begin{split} & [\{(CH_3)_2Sn(H_2O)\}\{(CH_3)_2Sn\}(A-\alpha-PW_9O_{34})]^{5-}(\textbf{1}) \\ & [\{(CH_3)_2Sn(H_2O)_2\}\{(CH_3)_2Sn(H_2O)\}_2(A-\alpha-PW_9O_{34})]^{3-}(\textbf{2}) \end{split}$	$\begin{array}{l} Keggin-type\\ \{PW_9O_{34}\}\end{array}$	2 3	1D chain 2D assembly	11

Section 1 A Detailed Survey of Dimethyltin-Containing POMs

	$[\{(CH_3)_2Sn(H_2O)\}_3(A-\alpha-PW_9O_{34})]^{3-}(3)$		3	3D network	
2015	$ \begin{array}{l} (C_{2}H_{8}N)_{7}Na_{12}[\{Sn(CH_{3})_{2}\}_{4}\{Sn(CH_{3})_{2}(H_{2}O)\}_{2}\{Sn(CH_{3})_{2}(H_{2}O)_{2}\}Se_{8}W_{54}O_{191}(OH)_{7}(H_{2}O)_{2}]\cdot 64H_{2}O\ (1)\\ (C_{2}H_{8}N)_{8}Na_{10}[\{Sn(CH_{3})_{2}\}_{10}\{Sn(CH_{3})_{2}(H_{2}O)\}_{6}Se_{11}W_{5}\\ & \ \ \ \ \ \ \ \ \ \ \ \ \$	$ \{Se_4W_{27}\} \& \\ Dawson-type \\ \{Se_2W_{12}\} and \\ \{\beta - Se_2W_{15}\} \\ Dawson-type \\ \{\gamma - Se_2W_{14}\} $	7 16	nanocluster chain	12
2016	$[\{Sn(CH_3)_2(CH_3COO)\}_3\{Sn(CH_3)_2\}_3\{Se_2W_{18}O_{62}(OH) \\ (H_2O)\}_3]^{18-}$	$\begin{array}{l} Dawson-type \\ \{Se_2W_{18}\}\end{array}$	6	nanocluster	this work

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Section 2 Synthesis, Crystal Data, and Structures of 1

2.1 Synthesis

Materials: All chemicals and solvents were commercially purchased and used without further purification.

Synthesis of 1: Na₂WO₄·2H₂O (3.40 g, 10.24 mmol) and Na₂SeO₃ (0.20 g, 1.14 mmol) were dissolved in 50 mL water. The pH value of the solution was adjusted to 4.5 by acetic acid solution. After the solution was stirred for around 30 min, solid (CH₃)₂SnCl₂ (0.25 g, 1.14 mmol) and dimethylamine hydrochloride (0.50 g, 6.13 mmol) were successively added. The final pH was kept at 3.2 by 4 M HCl. This solution was stirred for another 30 min, then filtered and left to evaporate slowly. Colorless block–shaped crystals were obtained after five weeks, which were then collected by filtration and air–dried. Yield: 0.46 g, (15.4 %, based on W). IR (in cm⁻¹): 3422 (w), 3107 (w), 2779 (w), 1628 (w), 1464 (s), 1410 (m), 1194 (m), 946 (s), 842 (w), 806 (w), 740 (w). Elemental analysis, calc. for $C_{36}H_{176}N_9Na_9O_{223}Se_6Sn_6W_{54}$: C 2.77, N 0.81, Na 1.32, Sn 4.56, Se 3.03, W 63.5 %; Found C 2.56, N 0.94, Na 1.41, Sn 4.71, Se 2.87, W 64.4 %.

2.2 Synthesis Discussion

The precise control of the one–pot reaction conditions of combining $(CH_3)_2Sn^{2+}$ groups with the SeO₃^{2–} anion templates at proper pH was employed for the assembly of **1**. The SeO₃^{2–} anion templates have a lone pair of electrons and only form three bonds through oxygen atoms in trigonal configurations owing to the inducing effect of the lone pair of electrons.¹ Moreover, the electrophile $(CH_3)_2Sn^{2+}$ groups possess the stability of the Sn–C bond in aqueous media and also the fact that Sn^{IV} can substitute for addenda metals in POM skeletons². Significantly, diverse $(CH_3)_2Sn^{2+}$ moieties realize that dimethyltin–containing POMs develop abundant architectures². Therefore, a synergistic effect between $(CH_3)_2Sn^{2+}$ groups and the anion template effect of SeO₃^{2–} may guide the construction of unprecedented dimethyltin–functionalized selenotungstates.

First, we chose Na₂WO₄ and Na₂SeO₃ as the W– & Se–sources. The acidification of them (W/Se molar ratio 9:1) by acetic acid was necessary.¹ Acetic acid has already been proven to be a suitable reagent for acidifying Se–based POTs clusters^{1b,1i}, and furthermore, one highlight of **1a** seems to be it possesses first reported carboxyl– modified dimethyltin moieties, so the function of acetic acid here could also described as small ligands for stabilizing the (CH₃)₂Sn²⁺ moieties besides a suitable reagent. Moreover, the molar ratio also plays an important role that is in accordance with the final structures: the { α -Se₂W₁₈} fragments in **1**.

Subsequently, dimethyltin species ((CH₃)₂Sn²⁺) and organic amine salts were introduced to the acid solution. Among several factors (e.g., reaction solvents etc.) during the synthesis, the features of the countercation constitute a key factor in the formation of several POMs, and therefore, choosing desirable counteraction may allow for a rational design of tailored POM assemblies^{2a}. Recently, Kortz et al. demonstrated that the $[C(NH_2)_3]^+$ cation can be used as a structure–directing agent to construct supramolecular arrangements, especially for dimethyltin–containing POMs^{2j,2k}, as a result of its rigid and planar geometry and its hydrogen bonding capability over a wide pH range. In this context, Cronin et al. has also investigated the templating effect of some organo–ammonium cations, such as $[C_2H_8N]^+$, in the construction of novel POM frameworks³ and in particular in Se–templated {W₁₈} cage¹ⁱ. Thus, dimethylamine hydrochloride was used during the combination of $(CH_3)_2Sn^{2+}$ groups with the SeO₃^{2–} anion templates which was employed to restrict the aggregation of more highly symmetrical architectures during the assembly process. 1 cannot be isolated by only using other cations (e.g., alkali ions).

Finally, different pH value leads to the formation of 1 thus the impact of the pH should be considered during the one-pot syntheses. From the previously reported studies, the pH value is a known crucial parameter in POT chemistry: a series of available building units toward the formation of the final structures are driven by it^{1i,4}. More importantly, the Wells–Dawson–type { α –Se₂W₁₈} clusters are usually obtained with the pH value range from 3.0^{1j} to 3.6¹ⁱ. Thus, we choose 3.2 as the suitable pH value for the formation of the Wells–Dawson–type { α –Se₂W₁₈} clusters and the carboxyl–modified dimethyltin groups, as well as the unprecedented, chiral cyclic–like assembly of 1.

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2.3 Crystal Data

	1
Empirical formula	$C_{36}H_{176}N_9Na_9O_{223}Se_6Sn_6W_{54}$
M	15624.56
λ/Å	0.71073
T/K	296(2)
Crystal system	Hexagonal
Space group	$P6_3$
a/Å	27.5538(5)
b/Å	27.5538(5)
$c/{ m \AA}$	22.0582(5)
$lpha/^{\circ}$	90
$eta / ^{\circ}$	90
$\gamma^{\prime \circ}$	120
V/Å ³	14503.2(6)
Ζ	2
D_c /Mg m ⁻³	3.578
μ/mm^{-1}	22.681
<i>F</i> (000)	13676
θ Range/°	1.707–24.997
Measured reflections	84243
Independent reflections	17012
<i>R_{int}</i> after SQUEEZE	0.0696
Goodness-of-fit on F^2	1.016
$R_1(I>2\sigma(I))^a$	0.0365
wR_2 (all data) ^b	0.0904
${}^{a}R_{1} = \sum F_{o} - F_{c} / \sum F_{o} . {}^{b}w$	$wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$

 Table S2. Crystal Data and Structure Refinements for 1.

Single-crystal X-ray diffraction: Single-crystal X-ray diffraction data for 1 was recorded on a Bruker Apex CCD II area-detector diffractometer with graphite-

monochromated Mo_{*K*α} radiation ($\lambda = 0.71073$ Å) at 296(2) K. Absorption corrections were applied using multiscan technique and performed by using the SADABS program¹. The structures of **1** were solved by direct methods and refined on *F*² by full-matrix leastsquares methods by using the SHELXTL package.² The numbers of lattice water molecules and counter cations for **1** was estimated by the results of elemental analyses, TG curves, and calculations of electron count in the voids with SQUEEZE³. Detailed interpretation for **1** was shown in CIF files. CCDC 1449917 contain the supplementary crystallographic data for this paper.

During the refinement, all the Sn, W, and Se atoms were refined anisotropically, while the rest of the cations and all of the solvent water molecules were just refined isotropically because of their unusual anisotropic thermal parameters and obvious disorder problems. As for all the H atoms in the methyl groups were all directly added to the final molecular formula due to the two tips: 1) the diffraction intensity for all the C atoms is very weak; 2) most C atoms on the tin atoms or $\{C_2H_8N\}$ units exhibit obvious ADP and NPD problems with the anisotropic parameters, they are just refined isotropically. H atoms on lattice water molecules cannot be found from the residual peaks and were directly included in the final molecular formula.

The 'omit -350' command was used to omit the weak reflections above 50 degree.

In the final refinement, sixteen unnormal reflections are directly omitted from the crystal data with "OMIT" commands, due to their unusual high "Delta(F^2)/esd" values and their resolution (A) values are larger than 4. The omitted reflections are as follows:

OMIT	0	1	0
OMIT	0	1	1
OMIT	0	1	-1
OMIT	-1	2	0
OMIT	-1	3	0
OMIT	0	1	-2
OMIT	0	1	2
OMIT	0	0	-2
OMIT	0	1	3
OMIT	0	1	-3

OMIT -2	3	0
OMIT -3	5	1
OMIT -2	3	-1
OMIT -3	5	-1
OMIT -2	3	1
OMIT 0	3	0

The highest residual peak, 1.882 eA³. The deepest hole is -2.318 eA³.

About 24 solvent water molecules, 3 Na⁺ cations and 9 $\{C_2H_8N\}^+$ cations were found from the Fourier maps, however, there are still a very large accessible solvent voids in the crystal structure caculated by SQUEEZE subroutine of PLATON software, indicating that some more water molecules and cations should exist in the structure, but cannot be found from the weak residual electron peaks. Based on the TGA curve, bond valence sum calculations and elemental analyses, another 1 water molecules, 6 Na⁺ cations and 9 H⁺ were included into the molecular formula directly.

SQUEEZE RESULTS (APPEND TO CIF)

loop_

_platon_squeeze_void_nr

_platon_squeeze_void_average_x

_platon_squeeze_void_average_y

_platon_squeeze_void_average_z

_platon_squeeze_void_volume

_platon_squeeze_void_count_electrons

1	0.000	0.000	0.004	958.0	485.8
2	0.133	0.754	0.338	163.3	92.7
3	0.246	0.379	0.338	164.0	89.4
4	0.333	0.667	0.304	113.5	186.8
5	0.379	0.133	0.838	163.1	96.0
6	0.621	0.867	0.338	162.7	92.6
7	0.667	0.333	0.804	113.5	197.6
8	0.754	0.621	0.838	163.4	100.2
9	0.867	0.246	0.838	163.7	97.1

_platon_squeeze_details

;

;

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2.4 Structures of 1



Fig. S1. Structure of $[\{Sn(CH_3)_2\}_3\{Se_2W_{18}O_{62}(OH)(H_2O)\}_3]^{21-}$ in 1a.



Fig. S2. Different protonations in the $\{\alpha$ -Se₂W₁₈ $\}$. Symmetry codes: #1 (-x, y, 0.5-z).

Tab	Table S3. The BVS calculation results of all the oxygen atoms in 1.					
Oxygen	Bond	Oxygen	Bond	Oxygen	Bond	
Code	Valence	Code	Valence	Code	Valence	
O1	1.366	O ₂₃	2.015	O ₄₅	1.842	
O_2	2.086	O ₂₄	1.558	O_{46}	1.890	
O_3	1.968	O ₂₅	2.020	O ₄₇	1.736	
O_4	1.974	O ₂₆	2.007	O_{48}	2.106	
O_5	2.006	O ₂₇	2.064	O ₄₉	2.017	
O_6	2.064	O ₂₈	2.021	O_{50}	1.793	
O_7	1.977	O ₂₉	2.092	O ₅₁	1.966	
O_8	2.147	O ₃₀	1.736	O ₅₂	1.965	
O_9	1.875	O ₃₁	1.703	O ₅₃	1.973	
O_{10}	1.925	O ₃₂	2.144	O ₅₄	2.194	
O ₁₁	1.806	O ₃₃	1.844	O ₅₅	1.644	
O ₁₂	1.918	O ₃₄	1.973	O ₅₆	1.852	
O ₁₃	2.169	O ₃₅	1.866	O ₅₇	1.948	
O ₁₄	2.020	O ₃₆	2.257	O ₅₈	1.745	
O ₁₅	1.990	O ₃₇	0.428	O ₅₉	2.049	
O ₁₆	2.200	O ₃₈	2.071	O_{60}	1.622	
O ₁₇	1.850	O ₃₉	1.609	O ₆₁	1.879	
O ₁₈	1.881	O_{40}	1.698	O ₆₂	1.685	
O ₁₉	2.074	O_{41}	1.827	O ₆₃	1.918	
O_{20}	2.100	O_{42}	1.965	O ₆₄	1.817	
O ₂₁	2.030	O ₄₃	2.070	O ₆₅	1.925	
O ₂₂	2.036	O ₄₄	1.583	O ₆₆	1.897	
Total 9 protons per cluster						

2.5 The BVS Calculation Result of All the Oxygen Atoms

Table S4. Selected bond lengths [Å] and the selected bond lengths [Å]	nd angles [°] for the tin atoms in 1 .
Sn(1)-C(4)	2.11(2)
Sn(1)-C(3)	2.11(2)
Sn(1)-O(19)#1	2.170(17)
Sn(1)-O(48)#1	2.185(16)
Sn(1)-O(10)	2.267(16)
Sn(1)-O(7)	2.311(16)
C(4)-Sn(1)-C(3)	164.5(8)
Sn(2)-O(1)	2.041(15)
Sn(2)-C(5)	2.10(2)
Sn(2)-C(6)	2.15(3)
Sn(2)-O(61)	2.197(17)
Sn(2)-O(7)	2.405(16)
C(5)-Sn(2)-C(6)	141.8(10)
Symmetry codes: #	#1: 1-y, x-y, z.

2.6 Selected Bond Lengths and Angles for the Tin Atoms in 1.

Section 3 Experimental Section

3.1 Materials and Physical Measurements

Characterization: Elemental analysis of Na, Sn, Se, and W were performed with a Leaman inductively coupled plasma (ICP) spectrometer; C and N were performed on a Perkin-Elmer 2400 CHN elemental analyzer. IR spectra were recorded on an Alpha Centauri FTIR spectrophotometer on pressed KBr pellets in the range 400~4000 cm⁻¹. Water contents were determined by TG analyses on a PerkinElmer TGA7 instrument in flowing N₂ with a heating rate of 10 °C min⁻¹. Electrospray ionization mass spectrometry was carried out on a Bruker Micro TOF-QII instrument (1 mg/mL).

Electrochemical experiments: Electrochemical measurements were carried out on a CHI 660 electrochemical workstation at room temperature. Thrice-distilled water was used throughout the experiments. All solutions were deaerated by bubbling pure argon prior to the experiments and the electrochemical cell was kept under an argon atmosphere throughout the experiment. A conventional three-electrode system was used with a 1.5 mm glassy carbon working electrode, an Ag/AgCl used as electrode, and a platinum wire counterelectrode. The glassy carbon working electrodes were polished with alumina on polishing pads, rinsed with distilled water, and sonicated in H₂O before each experiment. The scan rate was 50~500 mV s⁻¹. All potentials were measured and reported versus Ag/AgCl. Solutions **1** in 0.5 M H₂SO₄/Na₂SO₄ (pH = 2.50) were used. A pHS-25B pH meter was used for pH measurements.

Photocatalytic Measurements: Photocatalytic reactions were carried out in a Pyrex inner-irradiation-type reaction vessel with a magnetic stirrer at room temperature. The reactant solution was evacuated using N_2 several times to ensure complete air removal and then irradiated by using a 500 W mercury lamp. The produced H_2 was analyzed by a GC9800 instrument with a thermal conductivity detector and a 5 Å molecular sieve column (2 mm × 2 mm) using N_2 as carrier gas.

3.2 Cyclic Voltammetry



Fig. S3. Cyclic voltammograms of 1 (red) and $\{Se_2W_{18}\}$ (black) in 0.5 M H_2SO_4/Na_2SO_4 solution (pH = 2.50). The scan rate was 50 mV s⁻¹. The working electrode was glassy carbon, and the reference electrode was Ag/AgCl.

Table S5. Redox Peak Potentials for all the Tungsten Waves Determined by CyclicVoltammetry in 0.5 M H₂SO₄/Na₂SO₄ solution (pH = 2.50) for 1 and {Se₂W₁₈}.

	$E_{\rm pa}({ m V})$	$E_{\rm pc}\left({ m V} ight)$	$E_{1/2}(V)$	$\Delta E_p (\mathrm{mV})$
1	-0.118	-0.192	-0.155	74
1	-0.355	-0.446	-0.401	91
	-0.546	-0.600	-0.573	54
	-0.145	-0.243	-0.194	98
$\{Se_2W_{18}\}$	-0.417	-0.484	-0.451	67
	-0.600	-0.655	-0.628	55

3.3 UV-Vis spectra



Fig. S4. UV-Vis spectra of kept at room temperature for two weeks.



Fig. S5. $(\alpha hv)^{1/2}$ versus hv curve of **1** (a) and $\{Se_2W_{18}\}$ (b). The red dashed lines are the tangents of the curves. The intersection value is the band gap of **1**.

3.4 ESI-MS



Table S6. Assignment of peaks in negative mode Mass spectrum of 1.

Observed m/z	Calculated m/z	Charge	Molecular mass	Polyanion
2434 4	2434 3	6	1/605 8	$ \{ NaH_{11}[\{Sn(CH_3)_2\}_3\{Sn(CH_3)_2(CH_3COO)\}_3\{Se_2W_{18}O_{62}(OH) \} \} $
2434.4	2434.5	-0	14005.8	(H_2O) }3] (H_2O) } ⁶⁻
2456.9	5.9 2457.3	2457.3 -6	-6 14743.8	$\{(C_{2}H_{8}N)_{2}Na_{4}H_{6}[\{Sn(CH_{3})_{2}\}_{3}\{Sn(CH_{3})_{2}(CH_{3}COO)\}_{3}\{Se_{2}W_{1}$
				₈ O ₆₂ (OH)(H ₂ O)} ₃]} ⁶⁻
2508.4	4 2508 8) (15052	15052.9	${(C_{2}H_{8}N)_{5}Na_{7}[{Sn(CH_{3})_{2}}_{3}{Sn(CH_{3})_{2}(CH_{3}COO)}_{3}{Se_{2}W_{18}O}}$
2508.4	2508.8	-0	15052.8	₆₂ (OH)(H ₂ O)} ₃](H ₂ O) ₆ } ⁶⁻
2599.9	2500.2	6	15505.9	${(C_{2}H_{8}N)_{10}NaH[{Sn(CH_{3})_{2}}_{3}{Sn(CH_{3})_{2}(CH_{3}COO)}_{3}{Se_{2}W_{18}}}$
	2599.3	2599.3 -6	-6 15595.8	$O_{62}(OH)(H_2O)$ }3](H_2O)31} ⁶⁻

3.5 Photocatalytic Hydrogen Evolution



Fig. S7. Dependence of H_2 production on irradiation time with the use of 1 (black), $\{Se_2W_{18}\}$ (red), and $\{Se_4W_{36}\}$ (blue) as photocatalysts (50 mg). The experiments were performed under 125 W mercury lamp irradiation in methanol (10 mL) in 90 mL of water (9/1, v/v).

Section 4 Supplementary Physical Characterizations



Fig. S8. IR spectrum of **1**: The characteristic peaks at 946, 842, 806, and 740 cm⁻¹ are ascribed to vibrations of v(Se–O), v(W=Od), v(W–Ob), and v(W–Oc), respectively. The broad peak at 3422 cm⁻¹ and the strong peak at 1628 cm⁻¹ are attributed to the lattice water molecules and aqua ligands. The peaks at 3107, 2779, 1464, and 1410 cm⁻¹ are assigned to { C_2H_8N } organic molecules. The single peak of weak intensity around 1194 cm⁻¹, which is characteristic of methyltin(IV) derivatives and can be assigned to the symmetrical bending vibration of the methyl groups according to the previously reported dimethyltin-functionalized POM species.



Fig. S9. The XRPD patterns for simulated (a) and as-synthesized (b) of 1.



Fig. S10. TG/DTA curve of 1.