Supporting Information

Temperature-Resolved Assembly of a Series of the Largest Scandium-Substituted Polyoxometalates

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Section S1 Synthesis and Methods

Synthesis of 1

$Na_9[SbW_9O_{33}]\cdot 19.5H_2O$ (0.300 g，0.10 mmol) and $ScCl_3\cdot 6H_2O$（0.050 g，0.19 mmol）were added into 5 mL of NaAc buffer solution (pH = 4.8). And then, KCl (0.100 g, 1.34 mmol) was added into the mixture with vigorous stirring for about 30 min. This mixture was sealed in a Teflon-lined autoclave (25 mL) and heated at 100 ℃ for 5 days. After cooled to room temperature, colorless crystals **1** were obtained. The pH value after reaction is about 4.1. Yield: 43 mg (14.3 %, based on Sb). ICP Anal. Calcd (%) for K5 $H_{88}Na_4O_{254}Sb_6Sc_{11}W_{60}$: Na, 0.55; K, 1.17; Sc, 2.96; Sb, 4.38; W, 66.07; found: Na, 0.62; K, 1.35; Sc, 2.82; Sb, 4.42; W, 63.17. IR (4000-400 cm^{-1}, KBr pellet): 3401 (s), 952 (s), 886 (m), 755 (w), and 669m^{-1} (w).

Synthesis of 2

$Na_9[SbW_9O_{33}]\cdot 19.5H_2O$ (0.300 g，0.10 mmol) and $ScCl_3\cdot 6H_2O$（0.050 g，0.19 mmol）were added into 5 mL of NaAc buffer solution (pH = 4.8). And then, KCl (0.100 g, 1.34 mmol) was added into the mixture with vigorous stirring for about 30 min. This mixture was filtrated and filtrate was kept at room temperature (about 30 ^{o}C) for 3 hours, colorless needle-like crystals **2** were obtained. The pH value after reaction is about 4.4. Yield: 67 mg (22.3 %, based on Sb). ICP Anal. Calcd (%) for $H_{71}K_2Na_6O_{242}Sb_8Sc_7W_{60}$: Na, 0.84; K, 0.47; Sc, 1.91; Sb, 5.91; Found (%): Na, 0.93; K, 0.58; Sc, 1.81; Sb, 5.67; W, 65.46. W, 66.94. IR (4000-400 cm^{-1}, KBr pellet): 3402 (s), 948 (s), 885(w) , 756 (w), and 672m^{-1} (w).

Synthesis of 3

$Na_9[SbW_9O_{33}]\cdot 19.5H_2O$ (0.300 g，0.10 mmol) and $ScCl_3\cdot 6H_2O$（0.050 g，0.19 mmol）were added into 5 mL of NaAc buffer solution (pH = 4.8). And then, KCl (0.100 g, 1.34 mmol) was added into the mixture with vigorous stirring for about 30 min. This mixture was sealed in a Teflon-lined autoclave (25 mL) and heated at 180 ℃ for 5 days. After cooled to room temperature, colorless crystals **3** were obtained. The pH value after reaction is about 4.6. Yield: 22 mg (7.3 %, based on Sb). ICP Anal. Calcd (%) for $H_{125}K_{10}Na_5O_{271}Sb_8Sc_6W_{60}$: Na, 0.67; K, 2.27; Sc, 1.56; Sb, 5.65; W, 63.97; found (%): Na, 0.78; K, 2.13; Sc, 1.36; Sb, 5.99; W, 60.39. IR (4000-400 cm^{-1}, KBr pellet): 3406 (s), 949 (s), 889 (w), 754 (w), and 667cm^{-1} (w).

Catalytic oxidation of thioethers.

The catalytic oxidation of various thioethers was carried out in 25 mL glass vessel under vigorous agitation with a magnetic stirring bar at temperature (80 °C) at reflux. A desired amount of solid catalyst was placed into the glass vessel, then a solution containing thioether, acetonitrile, and dodecane (an internal standard for GC-analysis) was added. The reaction vessel was sealed and stirred at thermostated oil-bath (80 °C). After the reaction, the vessel was cooled to room temperature and diluted with acetonitrile for GC analysis. The thioether oxidation products (sulfoxide and sulfone) were identified with GC−MS and quantified using gas chromatography with internal standard techniques.

Recyclability of the catalyst: the oxidation of methyl 4-methoxyphenyl sulfide (entry 6 in Table 1) was selected as a probe reaction. At first, 0.5 mmol of methyl 4-methoxyphenyl sulfide, 1.1 mmol of H_2O_2, and 0.5×10^{-2} mmol of compound **3** were added into 10 mL MeCN. The mixture was stirred for 3 h at 80 °C. Upon the completion of the reaction, another 0.5 mmol of methyl 4- methoxyphenyl sulfide and 1.1 mmol of H_2O_2 were added. After that, the mixture was stirred for 3 h at 80 °C again. The process was repeatedly carried out.

Single-crystal X-ray diffraction: Crystals **1-3** were collected on a Bruker APEX II CCD area diffractometer equipped with a fine focus, 2.0 kW sealed tube X-ray source (MoK radiation, λ = 0.71073 Å) operating at 293(2) K. The empirical absorption correction was based on equivalent reflections. Structures were solved by direct methods followed by successive difference Fourier methods. Computations were performed using SHELXTL and final full-matrix refinements were against F^2. ICSD-432579-432581 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the ICSD database via http://www.fiz-karlsruhe.de/request.

Crystal data: For **1**, Mr = 16639.52, triclinic, *P*-1, *a* = 22.1639(16), *b* = 23.9169(17), *c* = 30.203(2) Å, *α* = 99.428(1)°, *β* = 103.907(1)°, *γ* = 110.560(1)°, *V* = 13998.2(18) Å^3, *Z* = 2, *ρ*calcd = 3.948 g cm^{-3}, μ = 25.531 mm^{-1}, F(000) = 14328, GOF = 1.081. A total of 68758 reflections were collected, 35480 of which were unique (*R*(int) = 0.0306). R_1/wR_2 = 0.0851/0.2428 for 2921 parameters and 23668 reflections (I > 2σ(I)). For **2**, Mr = 16479.43, triclinic, *P*-1, *a* = 17.6677(13), *b* = 18.4206(14), *c* = 23.5822(18) Å, *α* = 71.357(2)°, *β* = 77.089(2)°, *γ* = 64.557(2)°, *V* = 6533.5(9) Å^3, *Z* = 1, *ρ*calcd = 4.170 g cm^{-3}, μ = 27.406 mm^{-1}, F(000) = 7035, GOF = 1.012. A total of 45000 reflections were collected, 22745 of which were unique (*R*(int) = 0.0589). R_1/wR_2 = 0.0853/0.2333 for 1492 parameters and 13215 reflections (I > 2σ(I)). For **3**, Mr = 17244.73, triclinic, *P*-1, *a* = 20.511(4), *b* = 23.388(5), *c* = 32.383(7) Å, *α* = 110.786(3)°, *β* = 95.640(3)°, *γ* = 94.999(3)°, *V* = 14328(5) Å^3, *Z* = 2, *ρ*calcd = 3.967 g cm^{-3}, μ = 25.100 mm^{-1}, F(000) = 14774, GOF = 1.058. A total of 89251 reflections were collected, 40518 of which were unique (*R*(int) = 0.0465). R_1/wR_2 = 0.0639/0.1715 for 3081 parameters and 29222 reflections (I > 2σ(I)).

Others: Powder XRD patterns were obtained using a Rigaku Ultima IV diffractometer，X'Pert PRO，MiniFlex II with Cu-$K\alpha$ radiation (λ = 1.54056 Å). IR spectra (KBr pellets) were recorded on a Nicolet iS50 FT-IR spectrometer. GC spectra were carried out with a Varian 430-GC gas chromatograph. GC−MS spectra were obtained from a Varian 450-GC/240-MS gas chromatograph−mass spectrometer.

Section S2 Additional Tables

Table S1. The impact of reaction temperature on the H_2O_2-based oxidation reaction of MSB.

Entry[a]	**Temp(℃)**	**Conv(%)**	**Selectivity(%)**

1	60	99	68
2	70	99	83
3[b]	80	100	87
4	90	100	87

a: Reaction conditions: substrate, 0.5 mmol; H_2O_2, 1.0 mmol; compound **3**, 0.25×10^{-2} mmol; time, 3 h; MeCN, 10 ml. b: Optimum reaction temperature: 80 °C.

Table S2. The impact of molar amount of catalyst **3** on the H_2O_2-based oxidation reaction of MSB.

Entry[a]	**n($\times10^{-2}$mmol)**	**Conv(%)**	**Selectivity(%)**
1	0	13	70
2	0.125	98	62
3[b]	0.25	100	87
4	0.375	100	86

a: Reaction conditions: substrate, 0.5 mmol; H_2O_2, 1.0 mmol; temperature, 80 °C; time, 3 h; MeCN, 10 ml. b: Optimum reaction amount of compound **3**: 0.25×10^{-2} mmol.

Table S3. The impact of reaction time on the H_2O_2-based oxidation reaction of MSB.

Entry[a]	**Time(h)**	**Conv(%)**	**Selectivity(%)**
1	1	95	57
2	2	98	65
3[b]	3	100	87
4	4	100	87

a: Reaction conditions: substrate, 0.5 mmol; H_2O_2, 1.0 mmol; compound **3**, 0.25×10^{-2} mmol; temperature, 80 °C; MeCN, 10 ml. b: Optimum reaction time: 3 h.

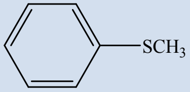
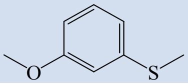
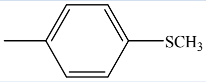
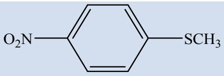
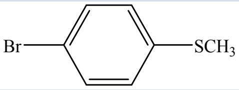
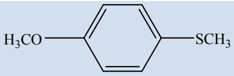
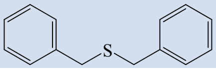
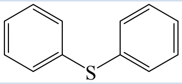
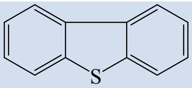
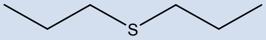
Table S4. The impact of molar amount of H_2O_2 on the H_2O_2-based oxidation reaction of MSB.

Entry[a]	**n(×mmol)**	**Conv(%)**	**Selectivity(%)**
1	1	100	87
2	1.05	100	93
3[b]	1.10	100	99
4	1.15	100	100

a: Reaction conditions: substrate, 0.5 mmol; time, 3 h; compound **3**, 0.25×10^{-2} mmol; temperature, 80 °C; MeCN, 10 ml. b: Optimum reaction amount of H_2O_2: 1.1 mmol.

Table S5. Results for oxygenation of various thioethers with 30% H_2O_2 without catalyst in MeCN.

Entry[a]	**Substrate**	**Time (h)**	**Temp (℃)**	**Conv (%)**[a]	**Selectivity (%)**

1		3	80	8	8
2		3	80	38	11
3		3	80	14	6
4		3	80	9	15
5		3	80	1	13
6		3	80	14	7
7		3	80	69	61
8		3	80	20	12
9		3	80	Trace	
10		3	80	50	13

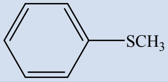
a: Reaction conditions: substrate, 0.5 mmol; H_2O_2, 1.1 mmol; temperature, 80 ℃; time, 3 h; MeCN, 10 ml.

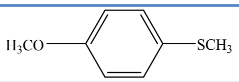
Table S6. Recycle experiments of oxidation reaction in entry 6 with **3** as catalyst.

Run	**1**	**2**	**3**	**4**	**5**
Conversion (%)	99	100	100	99	100
Selectivity (%)	99	99	100	100	100

a: Reaction conditions: substrate, 0.5 mmol; compound **3**, 0.25×10^{-2} mmol; H_2O_2, 1.1 mmol; temperature, 80 ℃; time, 3 h; MeCN, 10 ml.

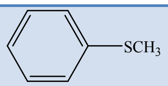
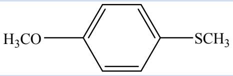
Table S7. Oxygenation of various thioethers with 30% H_2O_2 catalyzed by **1** in MeCN.

Entry[a]	**Substrate**	**Time (h)**	**Temp (℃)**	**Conv (%)**	**Selectivity (%)**
1		3	80	99	100

6		3	80	100	100

a: Reaction conditions: substrate, 0.5 mmol; H_2O_2, 1.1 mmol; temperature, 80 ℃; compound **1**, 0.25×10^{-2} mmol; time, 3 h; MeCN, 10 ml.

Table S8. Oxygenation of various thioethers with 30% H_2O_2 catalyzed by **2** in MeCN.

Entry[a]	**Substrate**	**Time (h)**	**Temp (℃)**	**Conv (%)**	**Selectivity (%)**
1		3	80	100	99
6		3	80	100	99

a: Reaction conditions: substrate, 0.5 mmol; H_2O_2, 1.1 mmol; temperature, 80 ℃; compound **2**, 0.25×10^{-2} mmol; time, 3 h; MeCN, 10 ml.

Section S3 Additional Structural Figures

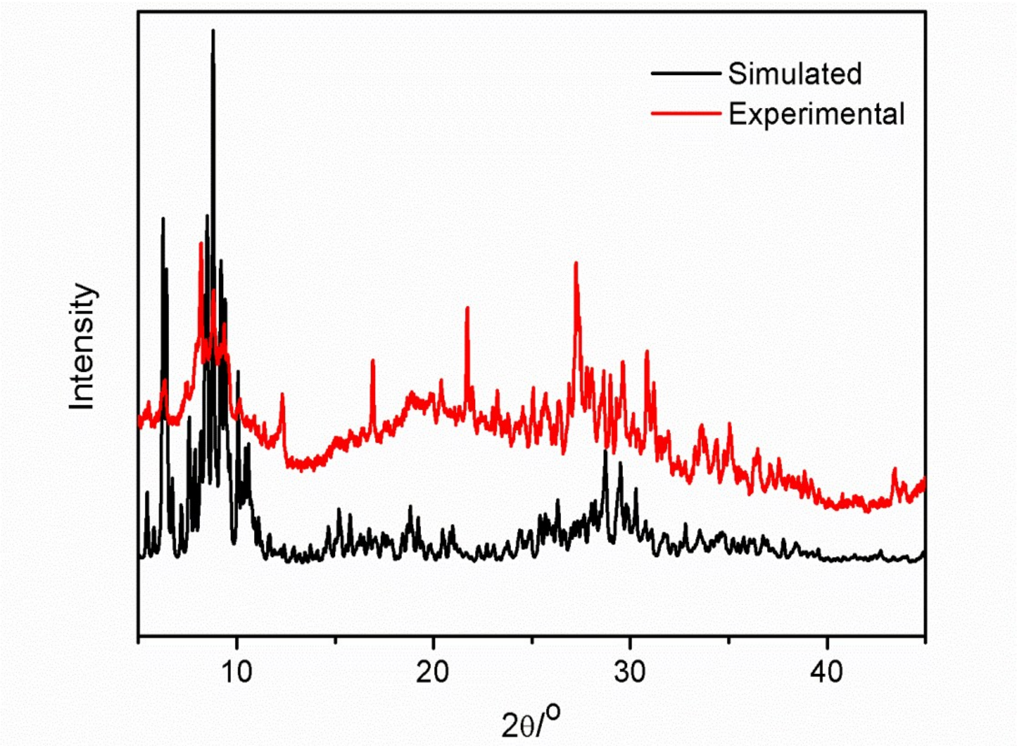


Figure S1. PXRD patterns of simulated **1** (black) and as-synthesized samples of **1** (red), showing the as-synthesized sample **1** is some impure. We tried our best to get pure sample but failed.

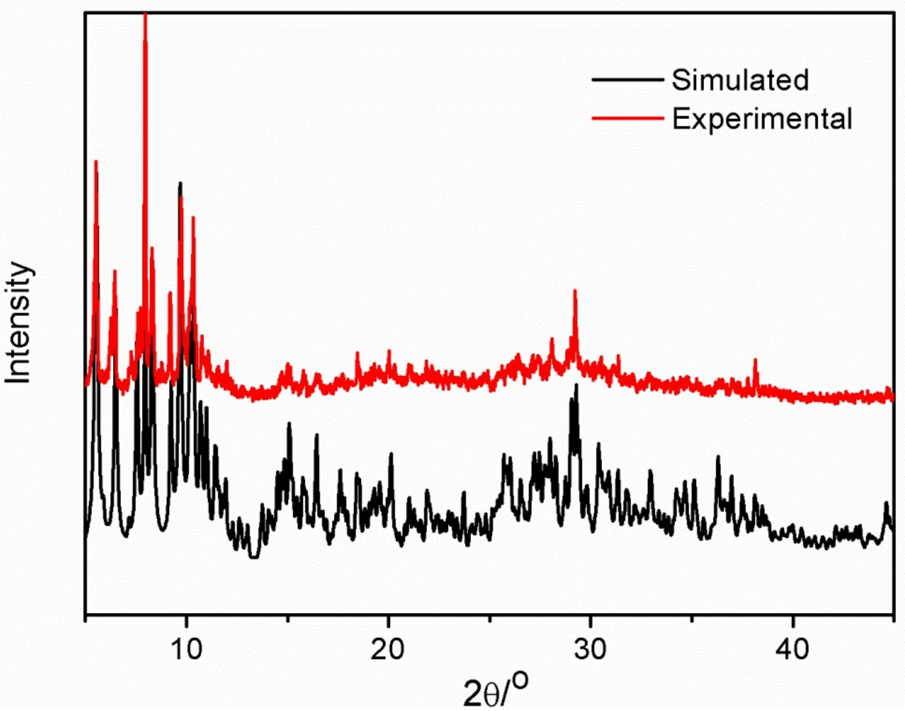


Figure S2. PXRD patterns of simulated **2** (black) and as-synthesized samples of **2** (red), showing the as-synthesized sample **2** is pure phase.

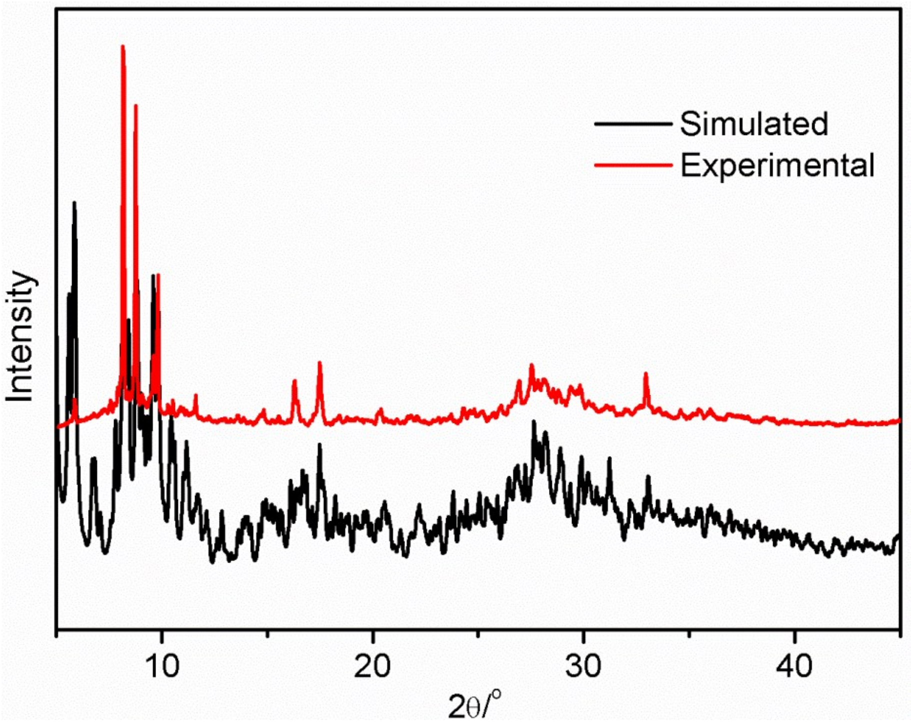


Figure S3. PXRD patterns of simulated **3** (black) and as-synthesized samples of **3** (red), showing the as-synthesized sample **3** is pure phase.

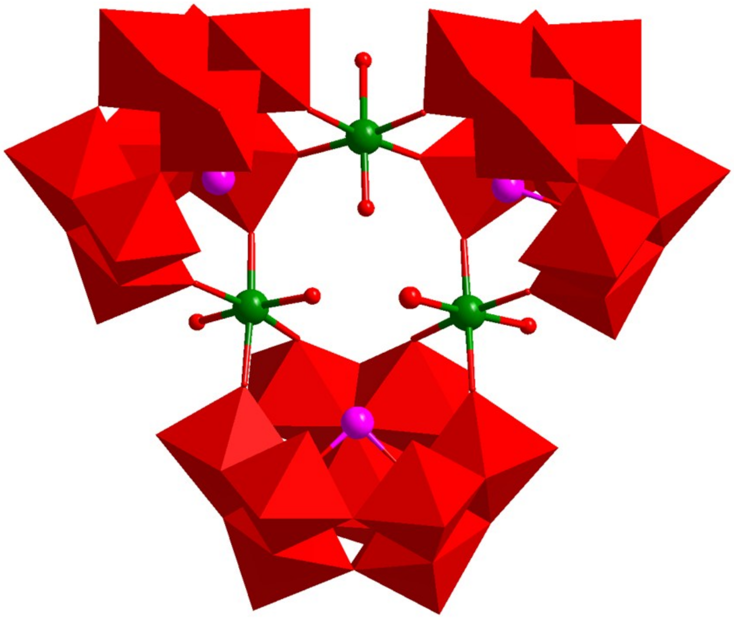


Figure S4. View of the common structural fragment of $\{Sc_3(SbW_9)_3\}$ in **1**-**3**.

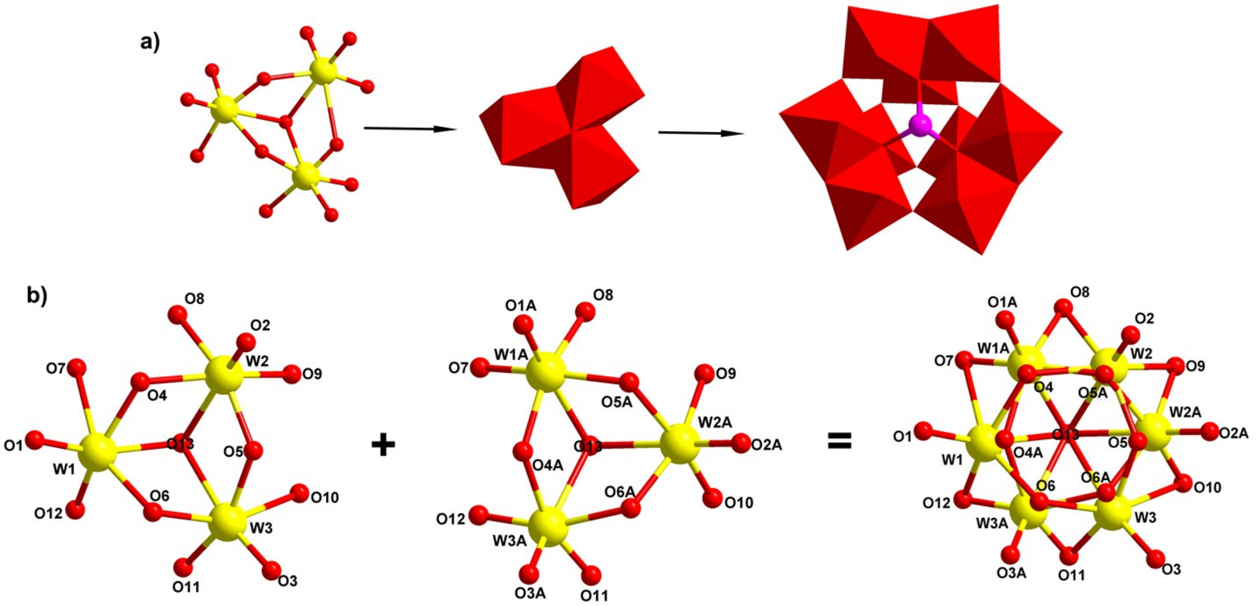


Figure S5. a) View of structure of $\{B\text{-}\alpha\text{-}Sb^{III}W_9O_{33}\}$ cluster constructed from three corner-sharing W_3O_{13} groups and one central Sb atom. b) View of disordered W_3O_{13} group found in **1-3**, showing each W_3O_{13} group is disordered into two groups.

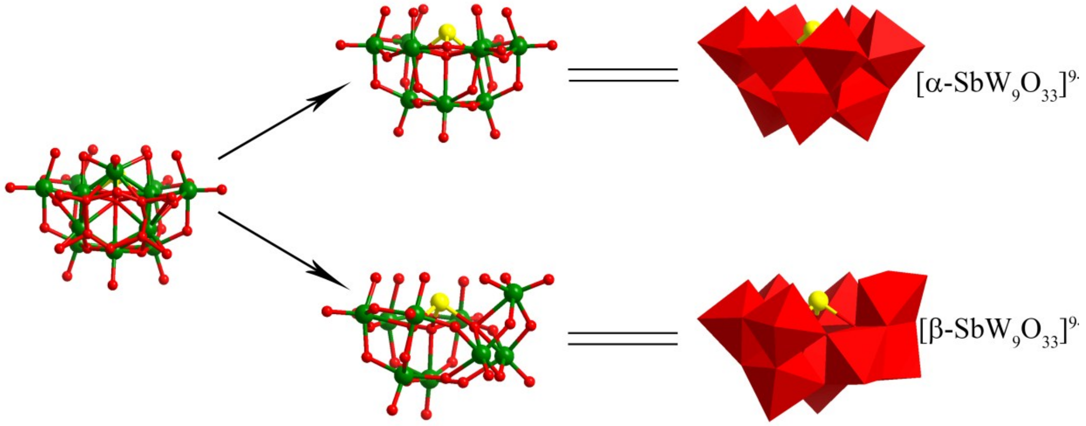


Figure S6. View of disordered $\{SbW_9O_{33}\}$ structure in **1-3**, showing it can be viewed as a combination of $\{\alpha\text{-}SbW_9O_{33}\}$ and $\{\beta\text{-}SbW_9O_{33}\}$ isomers.

As shown in Figure S6, the disordered $\{SbW_9O_{33}\}$ cluster in **1-3** can be viewed as a coexistence of $\{\alpha\text{-}SbW_9O_{33}\}$ and $\{\beta\text{-}SbW_9O_{33}\}$ isomers. For **1**, each hexameric polyoxoanion contains four crystallographically unique disordered $\{SbW_9O_{33}\}$ clusters, in which the ratios of $\{\alpha\text{-}SbW_9O_{33}\}/\{\beta\text{-}SbW_9O_{33}\}$ were refined freely to 0.471/0.529, 0.504/0.496, 0.887/0.113, and 0.900/0.100. For **2**, each hexameric polyoxoanion contains three crystallographically unique disordered $\{SbW_9O_{33}\}$ clusters, in which the ratios of $\{\alpha\text{-}SbW_9O_{33}\}/\{\beta\text{-}SbW_9O_{33}\}$ were refined freely to 0.561/0.439, 0.357/0.643, and 0.721/0.279. For **3**, each hexameric polyoxoanion contains five crystallographically unique disordered $\{SbW_9O_{33}\}$ clusters, in which the ratios of $\{\alpha\text{-}SbW_9O_{33}\}/\{\beta\text{-}SbW_9O_{33}\}$ were refined freely to 0.615/0.385, 0.732/0.268, 0.772/0.228, 0.795/0.205, and 0.839/0.161.

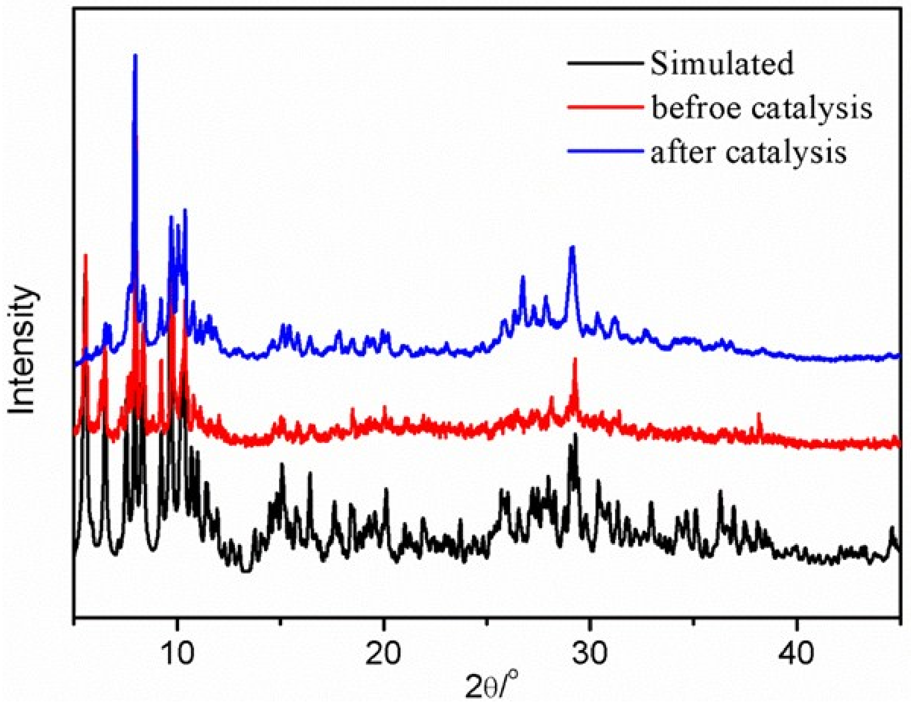


Figure S7. PXRD patterns of catalyst **3** before and after five-run H_2O_2-based oxidation reactions of MSB.

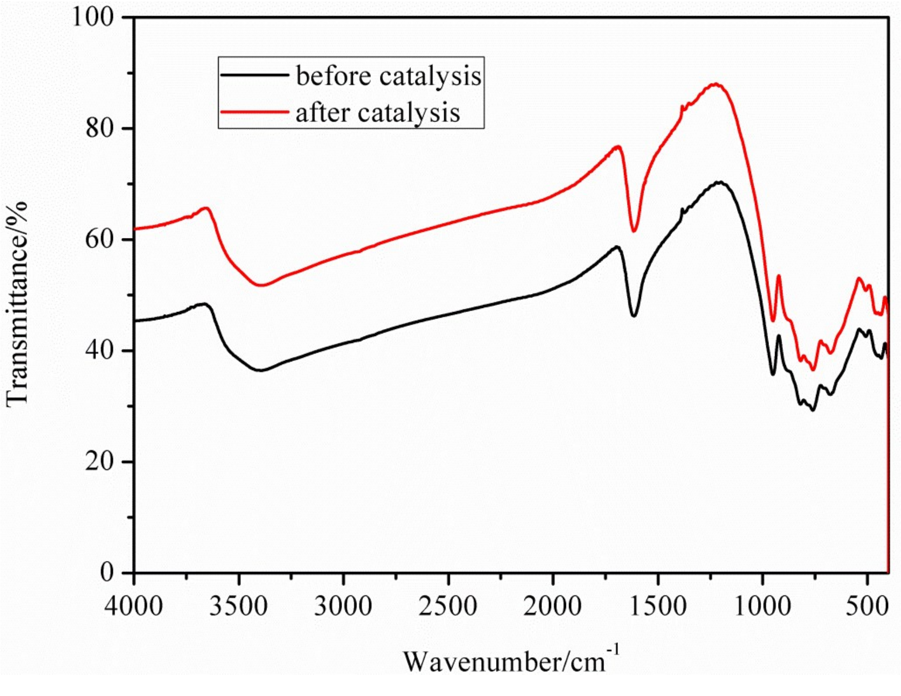


Figure S8. IR spectra of catalyst **3** before and after five-run H_2O_2-based oxidation reactions of MSB.

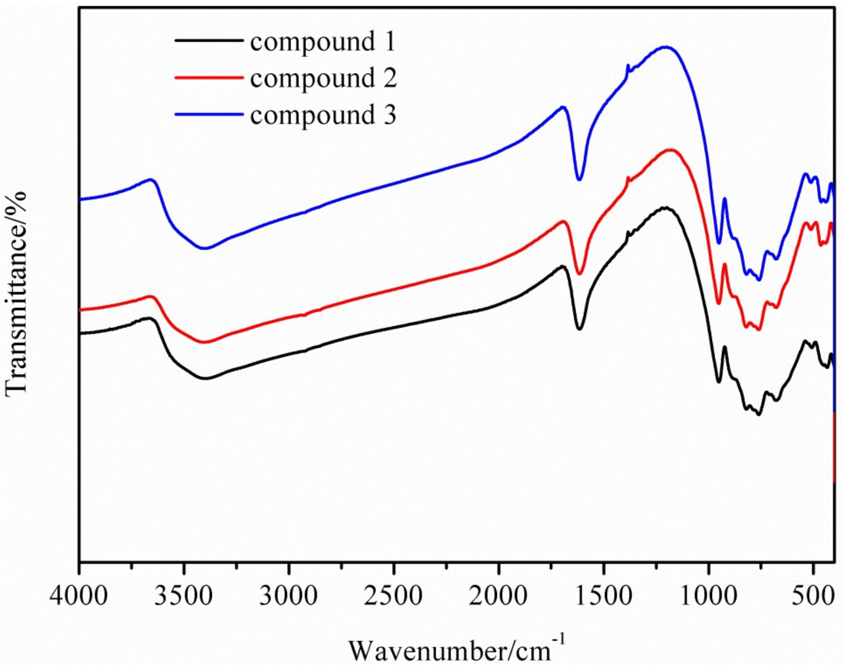


Figure S9. IR spectra of compounds **1-3**.

In the IR spectra of **1-3**, the broad peak at 3400 cm^{-1} and the strong peak at 1629 cm^{-1} are assigned to OH stretching and scissoring. The characteristic peaks at ca. 950 cm^{-1} correspond to $\nu_{as}(W = O_d)$ and the series of peaks in the range of 800-600 cm^{-1} are assigned to vibrations of $\nu_{as}(M–O–M)$ (M = W, Sb, and Sc).

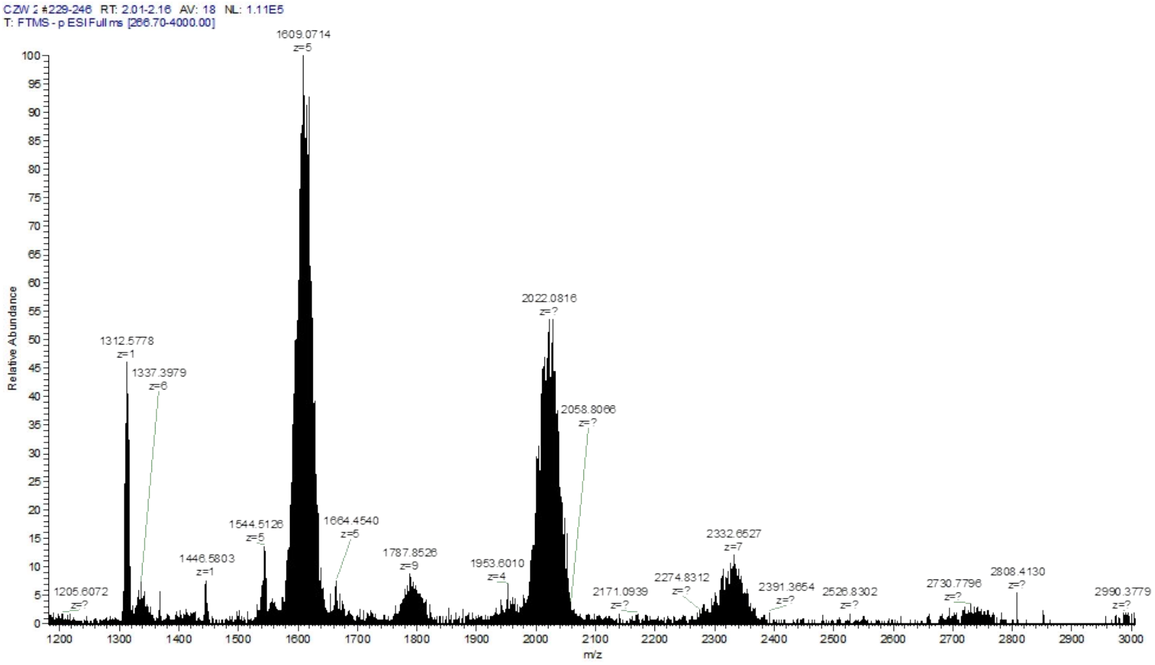


Figure S10. Negative-mode ESI-MS spectrum of polyoxoanion **2** in water solution.

m/z	Charge	Formula
1787.8526	-9	$\{[Sc_7Sb_2W_6O_{20}(H_2O)_8(SbW_9O_{33})_6]K_2Na_2H_{18}\}^{9-}$
2332.6527	-7	$\{[Sc_7Sb_2W_6O_{20}(H_2O)_8(SbW_9O_{33})_6]K_4Na_9H_{11}\}^{7-}$
1337.3979	-6	$\{[Sc_3SbW_3O_{10}(H_2O)_3(SbW_9O_{33})_3]KNa_2H_8\}^{6-}$
1609.0714	-5	$\{[Sc_3SbW_3O_{10}(H_2O)_3(SbW_9O_{33})_3]KNa_3H_8\}^{5-}$

As shown in Figure S10, ESI-MS spectrum shows the centrosymmetric hexameric polyoxoanion $\{Sc_7Sb_2W_6O_{20}(H_2O)_8(SbW_9O_{33})_6\}$ (**2**) is unstable in aqueous medium and might decompose into two halves of trimeric fragments $\{Sc_3SbW_3O_{10}(H_2O)_3(SbW_9O_{33})_3\}$ via the loss of the central $[Sc(H_2O)_2]^{3+}$ ion.

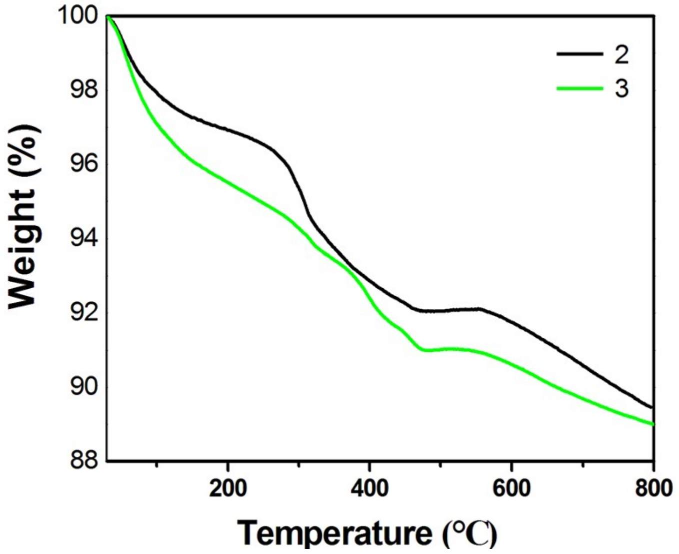


Figure S11. TG curves of compounds **2** and **3**, indicating they can maintain their structures up to ca. 200 °C.