

Supplementary Information

**A core-shell type alkyl-Sn-oxo cluster of {Sn₁₄As₁₆} bridged
by 4-aminophenylarsonate ligand and incorporated with
{Na₆} cluster**

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Experimental Section

Materials and Instrumentation.

All the chemical reagents were commercially purchased and used without further purification. IR spectrum was obtained on a Vertex 7.0 spectrometer with pressed KBr pellets in the range of 4000-400 cm^{-1} . Powder XRD patterns was obtained by using a Miniflex II and Miniflex 600 diffractometer diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). Elemental analyses (C, H and N) were performed on a vario MICRO elemental analyzer. Thermogravimetric analysis was performed on a Mettler Toledo TGA/SDTA 851° thermal analyzer in flowing N_2 atmosphere with a heating rate of 10 $^\circ\text{C}/\text{min}$. The ^1H NMR experiments were carried on a JNM-ECZ400S spectrometer at frequency of 400 MHz. Gas chromatography (GC) was performed with an GC-2014C (SHIMADZU) gas chromatography system equipped with flame ionization detectors and a thermal conductivity detector (TCD).

Synthesis of TOC-7: Butyltin hydroxide oxide (208.8 mg, 1.0 mmol), 4-aminophenylarsonic acid (217.2 mg, 1.0 mmol), NaOH (10.1 mg, 0.25 mmol), acetonitrile (5.0 mL) were mixed and sealed in a 20 mL vial, then transferred to a preheated oven at 80 $^\circ\text{C}$ for 5 days. After cooling to room temperature, colorless crystals were obtained (yield: 25 % based on Sn). Anal. calcd for $\text{Na}_6\text{Sn}_{14}\text{O}_{72}\text{C}_{152}\text{H}_{254}\text{N}_{16}\text{As}_{16}$ (%): C, 28.26; H, 3.94; N, 3.47; Found: C, 28.14; H, 3.82; N, 3.39.

Electrochemical measurements: Electrochemical experiments were performed on a CHI 760e electrochemical workstation (Chenhua, Shanghai, China) using a gas-tight two-compartment electrochemical cell with a Nafion-117 proton exchange membrane

as the separator. Each compartment contained 12 mL of 0.5 M KHCO₃ electrolyte, and the electrolyte was pre-saturated with high-purity Ar or CO₂ (Ar: pH = 8.74; CO₂: pH = 7.50). The platinum net (1.0 × 1.0 cm²) electrode and the Ag/AgCl electrode (the saturated KCl filling solution) were used as counter and reference electrode, respectively. The reference electrode potentials were converted to the value versus RHE by the equation: E (vs. RHE) = E (vs. Ag/AgCl) + 0.197 V + 0.0591 V × pH. Typically, 5.5 mg of sample was dispersed into H₂O/ ethanol (370/ 80 uL) solution followed by adding 80 uL Nafion, then the mixture was ultrasonicated for 10 min to achieve a homogeneous ink. The working electrode was prepared by pipetting the 100 uL of sample ink onto a carbon paper electrode (1 × 1 cm²) with a loading of 1.04 mg/cm². Then it was naturally dried in air, subsequently used as the working electrode for the further test.

For CO₂ electroreduction reaction, a flow of 20 sccm of CO₂ was continuously bubbled into the electrolyte to maintain its saturation. The linear sweep voltammetry (LSV) was performed at a scan rate of 5 mV/s. The electrolysis was conducted at selected potentials for 1 h to determine the reduction products and their Faradaic efficiencies.

Product analysis of CO₂ electroreduction:

The liquid products were quantified by nuclear magnetic resonance (NMR) spectroscopy at the end of each electrolysis. 10.0 mL of D₂O was mixed with 3.53 μL of dimethyl sulfoxide (DMSO) as solution A for next step. Then, 500 μL of the electrolyte after electrolysis was mixed with 100 μL of D₂O and 50 μL of solution A (DMSO as internal standard) for ¹H NMR analysis. The water suppression method was used. The peak was quantified by the integral area ratio of the reduction product

formate to DMSO. The concentration of formate was obtained using the calibration curve shown in Figure S12. The calibration curve was made by measuring standard solutions of formate.

The gaseous products (H₂ and CO) were periodically sampled and examined by gas chromatography (GC-2014C, SHIMADZU) with N₂ as the carrier gas. They were first analyzed by a thermal conductivity detector (TCD) for the H₂ concentration, and then analyzed by flame ionization detector (FID) with a methanizer for CO. The concentration of gaseous products was quantified by the integral area ratio of the reduction products to standards.

The faradic efficiency of formate was calculated as follow^[1]:

$$FE(\%) = \frac{Q_{formate}}{Q_{total}} = \frac{n_{formate} \times N \times F \times 100 \%}{j \times t} \quad (1)$$

Where $n_{formate}$ is the measured amount of formate in the cathodic compartment; N is the number of electrons required to form a molecule of formate ($N = 2$); F is the Faraday constant; j is the recorded current; t is the reaction time.

The faradic efficiencies of gaseous products were calculated as follow^[1]:

The volume of the sample loop (V_0) in GC is 1 cm³ and the flow rate of the gas is $v = 20$ cm³/min. The time it takes to fill the sample loop is:

$$t_0 = \frac{V_0}{v} = \frac{1 \text{ cm}^3}{20 \text{ cm}^3/\text{min}} = 0.05 \text{ min} = 3 \text{ s} \quad (2)$$

According to the ideal gas law, under ambient temperature of 25 °C, the amount of gas in each vial ($V_0 = 1$ cm³) is:

$$n = \frac{P \times V_0}{R \times T_0} = \frac{1.013 \times 10^5 \text{ Pa} \times 1 \times 10^{-6} \text{ m}^3}{8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 298.15 \text{ K}} = 4.0866 \times 10^{-5} \text{ mol} \quad (3)$$

The number of electrons required to form a molecule of CO or H₂ are 2. Therefore, the number of electrons (n_i) needed to get x_i ppm of CO or H₂ is:

$$n_i = x_i \times n \times N_A \times 2 \quad (4)$$

Total number of electrons (n_{total}) measured during this sampling period:

$$n_{total} = \frac{j \times t_0}{e} \quad (5)$$

The Faraday constant F is:

$$F = N_A \times e = 6.022 \times 10^{23} \text{ mol}^{-1} \times 1.6022 \times 10^{-19} \text{ C} = 96484.484 \text{ C} \cdot \text{mol}^{-1} \quad (6)$$

Hence, the faradic efficiency of CO or H₂ is

$$\text{FE}(\%) = \frac{n_i}{n_{total}} \times 100 \% = \frac{x_i \times n \times F \times 2}{I_0 \times t_0} \times 100 \% \quad (7)$$

Where i represents CO or H₂; I_0 is the recorded current obtained from the chronoamperogram; N_A is the Avogadro constant; e is elementary charge.

X-ray Crystallography:

X-ray diffraction data of compound **TOC-7** was collected on a MM007-Saturn724+ diffractometer with graphite-monochromated MoK_α ($\lambda = 0.71073 \text{ \AA}$) radiation. The program SADABS was used for absorption correction. The structure was solved by direct methods and refined on F² by full-matrix least-squares methods with the SHELX 2016 program package.^[2] Due to the intensity of diffraction at high angles is weak, the disordered solvent molecules of **TOC-7** are not identified in the structure, and are removed by using the SQUEEZE routine of PLATON.^[3] The details of the SQUEEZE corrections, including the volume of void space and electron counts, are provided in the cif file. CCDC 1939505 contains the supplementary crystallographic data for this paper.

Table S1. Crystal data collection and refinement details for **TOC-7**.

Compound	TOC-7
Formula	Na ₆ Sn ₁₄ O ₇₂ C ₁₅₂ H ₂₅₄ N ₁₆ As ₁₆
Fw	6456.02
Crystal system	Monoclinic
space group	C2/c
a/ Å	28.003(3)
b/ Å	38.235(4)
c/ Å	26.324(3)
α/deg.	90
β/deg	99.404(2)
γ/deg	90
V/ Å ³	27807(5)
Z	4
Dc /g cm ⁻³	1.542
F(000)	12592
T /K	293(2)
μ /mm ⁻¹	3.198
θ range / °	2.131-27.488
Reflections collected	111284
Independent reflections	31728
GOF (F ²)	1.027
R ₁ /wR ₂ [I > 2σ (I)]	0.0535/ 0.1377
R ₁ /wR ₂ ^[a] (all data)	0.0615/ 0.1433

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)} \right]^{1/2}.$$

Table S2. Bond valence sum calculations^[a] of μ₂-O and μ₃-O atoms in asymmetric unit of **TOC-7**.

O7 0.998 Sn1-O7 0.465 d=2.188(4) Sn5-O7 0.533 d=2.138(4)	O19 1.058 Sn5-O19 0.568 d=2.114(4) Sn3-O19 0.490 d=2.169(4)	O4 1.061 Sn2-O4 0.540 d=2.133(4) Sn3-O4 0.521 d=2.146(3)
O28 1.024 Sn6-O28 0.541 d=2.132(4) Sn7-O28 0.483 d=2.174(4)	O12 1.956 Sn1-O12 0.672 d=2.052(3) Sn3-O12 0.656 d=2.061(3) Sn5-O12 0.628 d=2.077(3)	O18 1.994 Sn4-O18 0.737 d=2.018(4) Sn6-O18 0.620 d=2.082(4) Sn7-O18 0.637 d=2.072(4)

^[a] $V_i = \sum_j v_{ij} = \sum_j \exp[(r_0 - r_{ij})/B]$, where r_0 is the bond-valence parameter (here $r_0 = 1.905$ for Sn^{IV}-O), r_{ij} is the bond length between atoms i and j ; B is a constant, the “universal parameter” ~ 0.37 Å; v_{ij}

is the valence of a bond between atoms i and j ; V_i is the sum of all bond valences of the bonds formed by a given atom i .^[4]

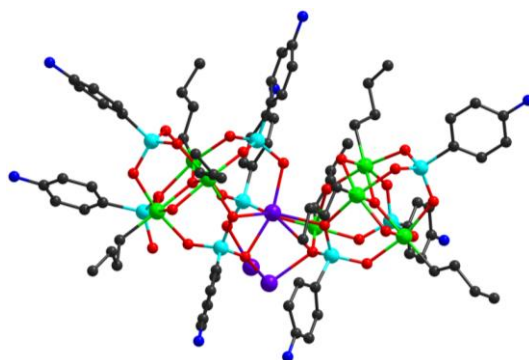


Figure S1. The asymmetric unit of **TOC-7**. Atom color code: green Sn; light blue As; purple Na; red O; black C; dark blue N.

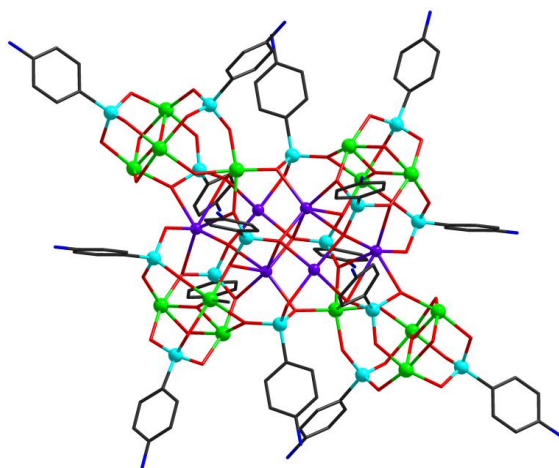


Figure S2. Ball-and-stick view of $\{\text{Na}_6\text{Sn}_{14}\text{As}_{16}\}$. Atom color code: green Sn; light blue As; purple Na.

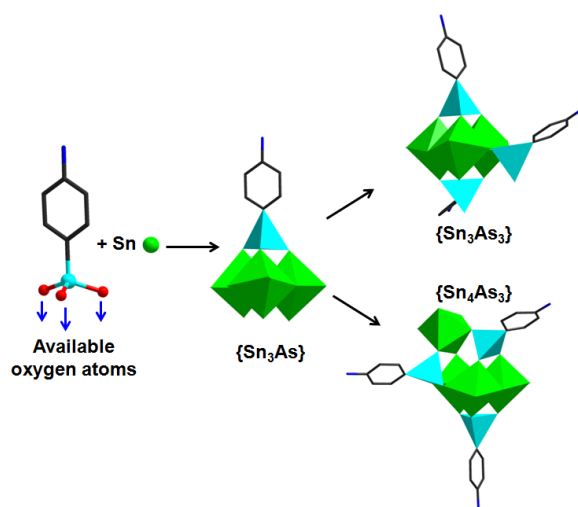


Figure S3. The relationship among APA ligand and $\{\text{Sn}_3\text{As}\}$, $\{\text{Sn}_3\text{As}_3\}$, $\{\text{Sn}_4\text{As}_3\}$ moieties. Atom color code: green Sn; light blue As; red O. Polyhedral color code: green SnO_5C ; light blue AsO_3C .

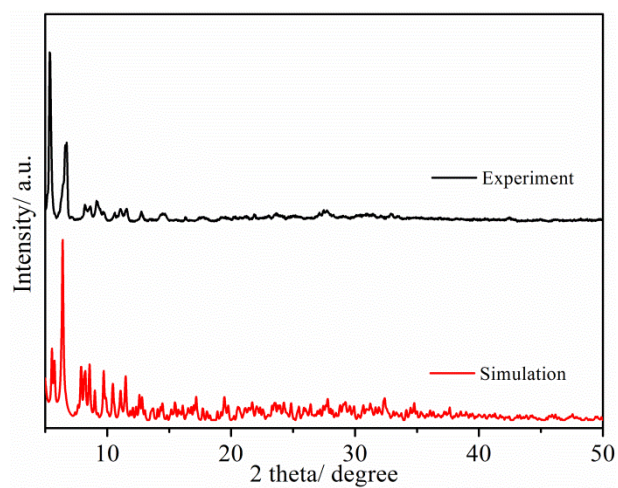


Figure S7. Simulated and experimental PXRD patterns (from 5° to 50°) of compound **TOC-7**.

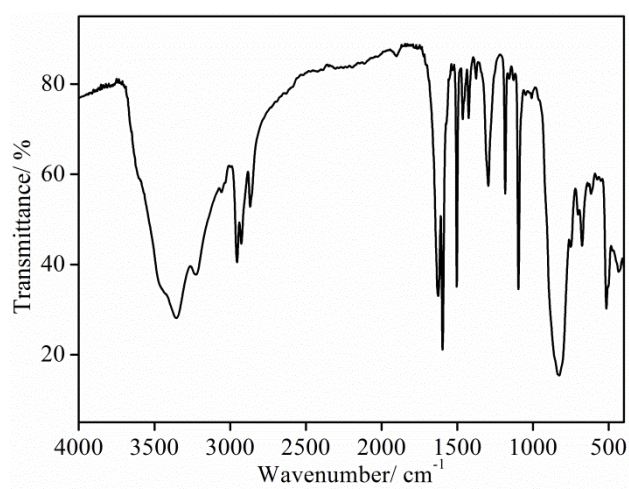


Figure S8. IR spectrum of compound **TOC-7**.

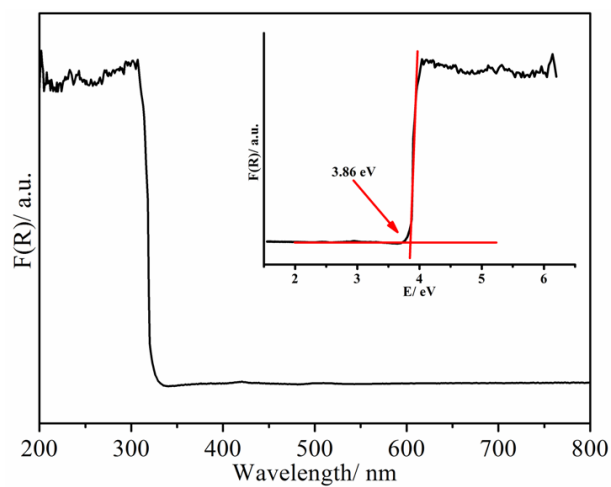


Figure S9. UV-vis diffuse reflectance spectrum of compound **TOC-7**.

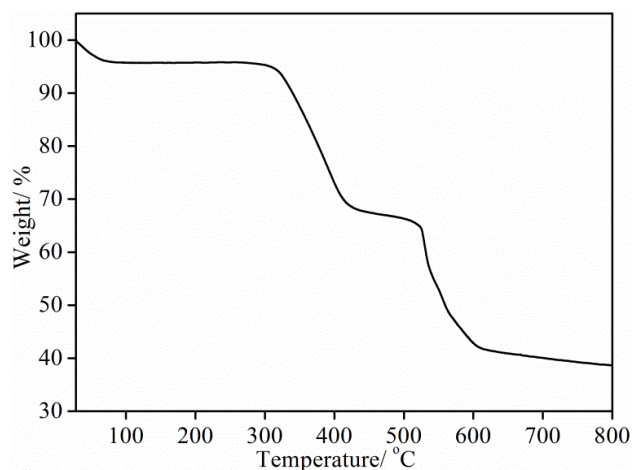


Figure S10. TG curve of compound **TOC-7** in N_2 atmosphere.

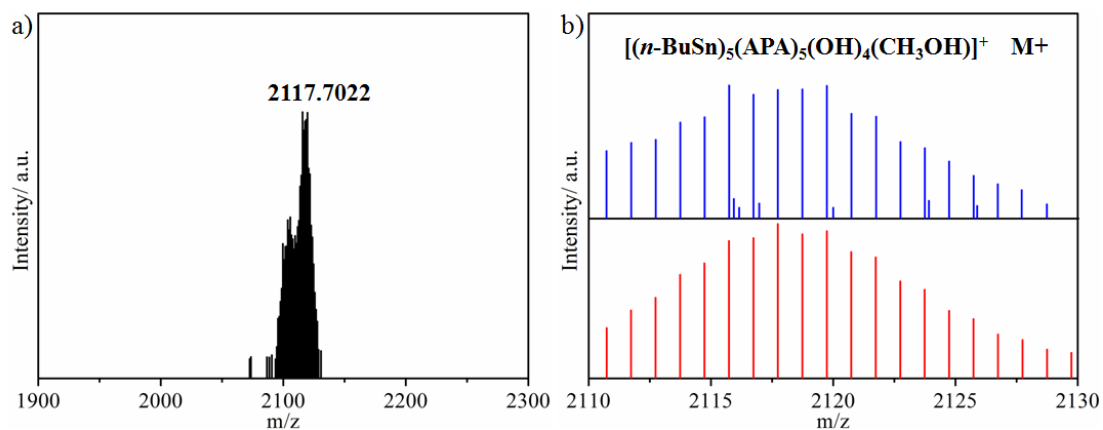


Figure S11. (a) Positive-mode ESI-MS spectrum of **TOC-7**. (b) Experimental ESI-MS (+, blue spectrum) and calculated peak positions (red). The crystals of **TOC-7** were firstly dissolved in N,N-dimethylacetamide, then diluted with methanol for ESI-MS measurement. The obtained spectrometry showed some peaks of fragmentations of the cluster of **TOC-7**, such as $[(n\text{-BuSn})_5(\text{APA})_5(\text{OH})_4(\text{CH}_3\text{OH})]^+$. Such cluster fragmentations during the ionization process is common and has been observed with other reported butyl-tin-oxo and niobate clusters.

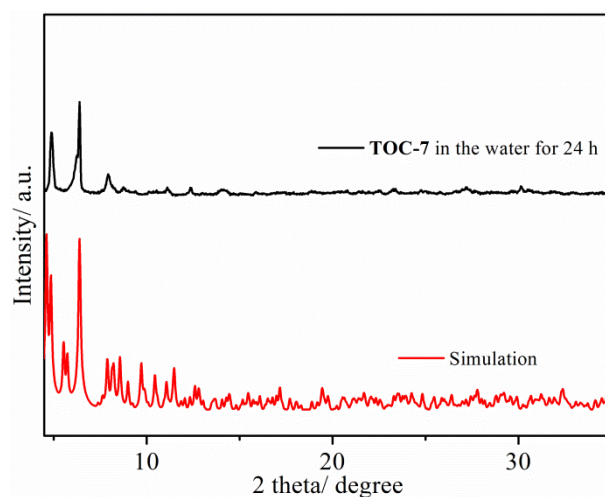


Figure S12. PXRD pattern (from 4.5° to 35°) of **TOC-7** after immersing in water for 24 h.

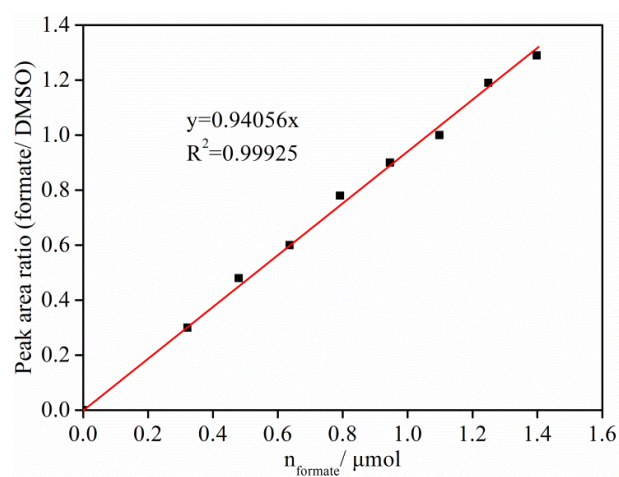


Figure S13. The calibration curve for formate (DMSO as internal standard).

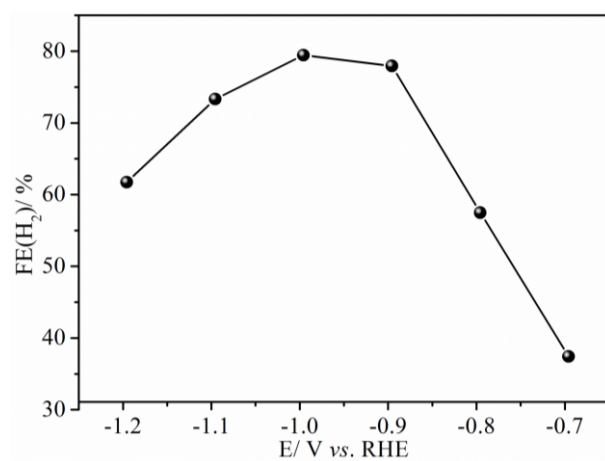


Figure S14. The faradaic efficiencies of H_2 for **TOC-7** at various potentials.

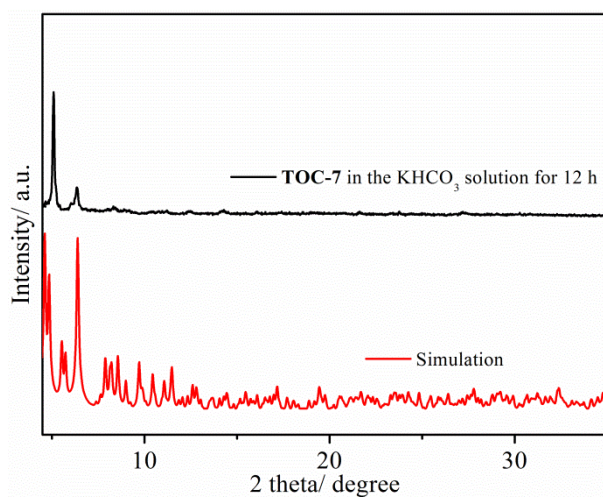


Figure S15. PXRD pattern (from 4.5° to 35°) of **TOC-7** after immersing in the 0.5 M KHCO_3 solution for 12 h.

References

- [1] D. Ren, Y. L. Deng, A. D. Handoko, C. S. Chen and S. Malkhandi, *ACS Catal.*, 2015, **5**, 2814.
- [2] G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3.
- [3] A. L. Spek, *Acta Cryst.*, 2015, **C71**, 9.
- [4] N. E. Brese, M. O' Keffe, *Acta Cryst.*, 1991, **B47**, 192.