

Supplementary Information

**Construction and two-dimensional assembly of double-shell
Na@Sn₆L₆@Sn₃L₃ clusters through tetrahedral citrate
ligands**

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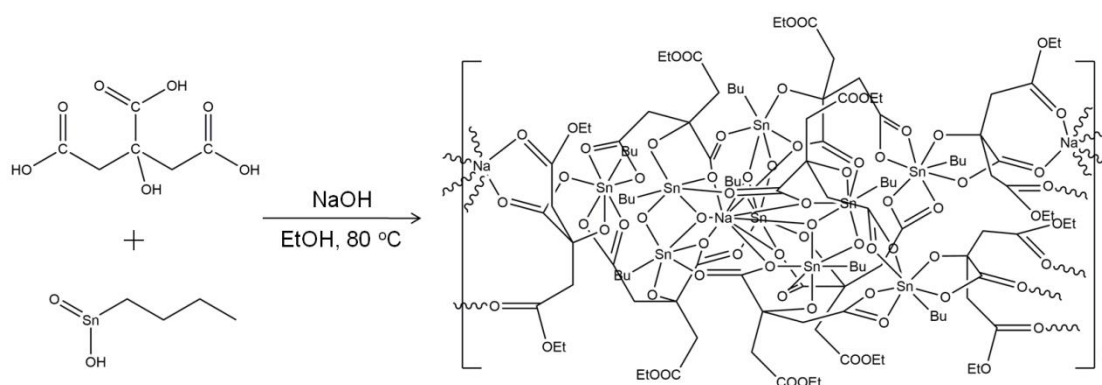
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Experimental Section

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 600 diffractometer diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). The optical diffuse reflectance spectra were measured at room temperature using a Perkin-Elmer Lambda 950 UV-vis spectrophotometer equipped with an integrating sphere attachment and BaSO_4 as reference. Elemental analyses (C, H and N) were performed on a vario MICRO elemental analyzer. 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).



Scheme S1. Illustration of the synthesis for **TOC-10**.

Synthesis of TOC-10: Butyltin hydroxide oxide (208.8 mg, 1.0 mmol), citric acid monohydrate (210 mg, 1.0 mmol), NaOH (10.0 mg, 0.25 mmol), ethanol (5.0 mL) were mixed and sealed in a 20 mL vial, then transferred to a preheated oven at 80 °C for 16 days, and cooling crystallized at room temperature to obtain the colorless

crystals (yield: 14 % based on Sn). IR (KBr, cm^{-1}): 3556 w, 2958 w, 1720 m, 1595 s, 1566 s, 1425 m, 1367 m, 1334 s, 1211 s, 1112 m, 1024 s, 923 m, 864 m, 846 m, 785 m, 732 w, 683 m, 644 m ($\nu(\text{O-Sn-O})$), 586 m ($\nu(\text{Sn-C})$), 484 s ($\nu(\text{Sn-O})$), 449 w. Anal. calcd for $\text{Na}_3\text{Sn}_9\text{O}_{74}\text{C}_{124}\text{H}_{213}$ (%): C, 36.97; H, 5.29; Found: C, 35.88; H, 4.93.

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 KHCO_3 electrolyte, and the electrolyte was pre-saturated with high-purity Ar or CO_2 (Ar: pH = 8.74; CO_2 : pH = 7.50). The platinum net ($1.0 \times 1.0 \text{ cm}^2$) 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: $E (\text{vs. RHE}) = E (\text{vs. Ag/AgCl}) + 0.197 \text{ V} + 0.0591 \text{ V} \times \text{pH}$. The working electrode was prepared by pipetting the 60 μL of sample ink onto a carbon paper electrode ($1 \times 1 \text{ cm}^2$) with a loading of 0.636 mg/cm^2 . Typically, 5.3 mg of sample was dispersed into H_2O / ethanol (370/ 80 μL) solution followed by adding 50 μL Nafion, then the mixture was ultrasonicated for 10 min to achieve a homogeneous ink. 60 μL of the sample ink was pipetted and homogeneously coated onto the carbon paper with an area of $1 \times 1 \text{ cm}^2$. Then it was naturally dried in air, subsequently used as the working electrode for the further test.

For CO_2 electroreduction reaction, a flow of 20 sccm of CO_2 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 S11. 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]:

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

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 cm^3 and the flow rate of the gas is $v = 20 \text{ cm}^3/\text{min}$. 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 $25 \text{ }^\circ\text{C}$, the amount of gas in each vial ($V_0 = 1 \text{ cm}^3$) 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-10** 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 F^2 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-10** are not identified in the structure, and are removed by using the SQUEEZE routine of PLATON.^[3] CCDC 2103689 contains the supplementary crystallographic data for this paper.

Table S1. Crystal data collection and refinement details for **TOC-10**.

Compound	TOC-10
Cryst. Formula	Na ₃ Sn ₉ O ₇₄ C ₁₂₄ H ₂₀₇
Fw	4019.06
Crystal system	Monoclinic
space group	<i>P</i> 2(1)/ <i>n</i>
<i>a</i> / \AA	19.425(3)
<i>b</i> / \AA	28.029(4)
<i>c</i> / \AA	31.983(5)
α /deg.	90
β /deg	91.322(2)
γ /deg	90
<i>V</i> / \AA^3	17409(4)
<i>Z</i>	4
<i>D</i> _c /g•cm ⁻³	1.533
<i>F</i> (000)	8104
<i>T</i> /K	293(2)
μ /mm ⁻¹	1.362
θ range / $^\circ$	2.044-25.500
Reflections collected	117173
Independent reflections	32298
GOF (F^2)	1.041

$R_1/wR_2 [I > 2\sigma (I)]$	0.0462/ 0.1211
$R_1/wR_2^{[a]} (\text{all data})$	0.0567/ 0.1299

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

Table S2. Bond valence sum calculations^[a] of μ_2 -O, μ_3 -O atoms in asymmetric unit of **TOC-10**.

O8 1.229 Sn2-O8 0.593 d=2.098(3) Sn3-O8 0.636 d=2.072(3)	O10 1.200 Sn6-O10 0.600 d=2.094(3) Sn1-O10 0.600 d=2.094(3)	O27 1.235 Sn4-O27 0.621 d=2.081(3) Sn5-O27 0.614 d=2.085(3)
O33 1.225 Sn4-O33 0.538 d=2.134(3) Sn5-O33 0.570 d=2.113(3) Na1-O33 0.117 d=2.595(3)	O22 1.217 Sn2-O22 0.551 d=2.125(3) Sn3-O22 0.554 d=2.123(3) Na1-O22 0.112 d=2.614(3)	O26 1.201 Sn6-O26 0.542 d=2.131(3) Sn1-O26 0.550 d=2.126(3) Na1-O26 0.109 d=2.624(3)

^[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 $\text{Sn}^{\text{IV}}\text{-O}$, and 1.803 for $\text{Na}^{\text{I}}\text{-O}$), 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]

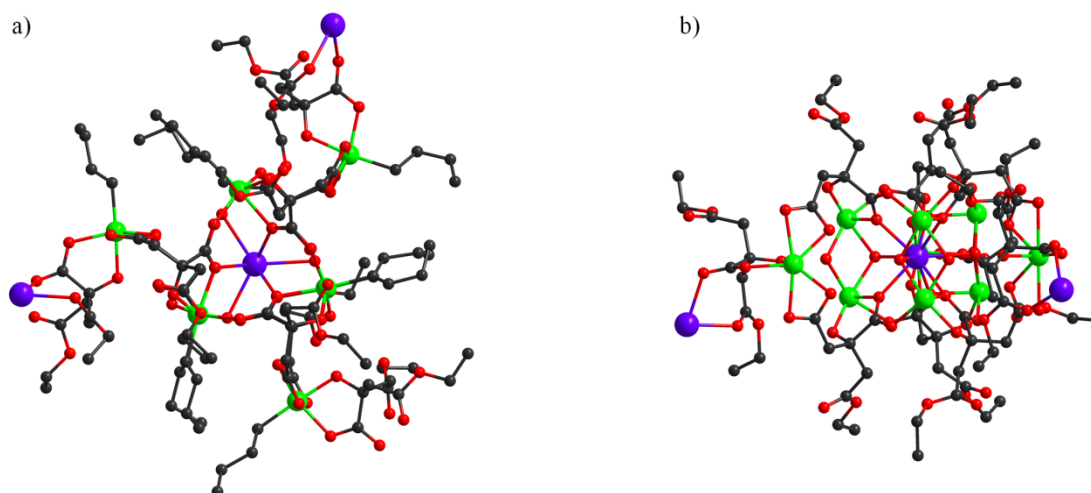


Figure S1. Side (a) and top (a) view of the asymmetric unit for compound **TOC-10**. Atom color code: green Sn; purple Na; red O; black C. Hydrogen atoms are omitted for clarity.

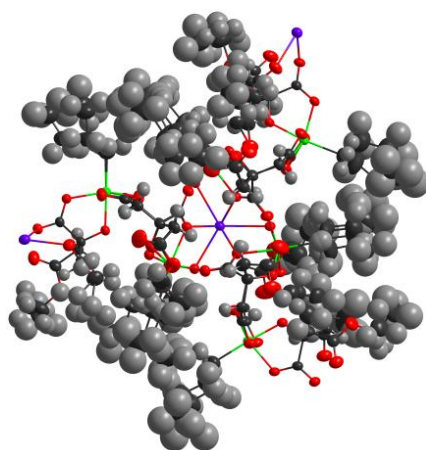


Figure S2. The thermal ellipsoid view of **TOC-10**. Thermal ellipsoids displayed at 30% probability. All the splitting C atoms and H atoms are showed. Atom color code: green Sn; purple Na; red O; black C; gray H.

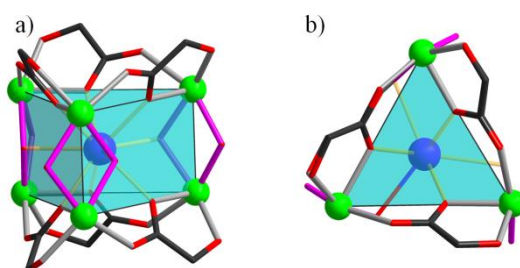


Figure S3. Side (a) and top (a) view of $\text{Na}@\text{Sn}_6\text{L}_6$ cage. Atom color code: green Sn; purple Na.

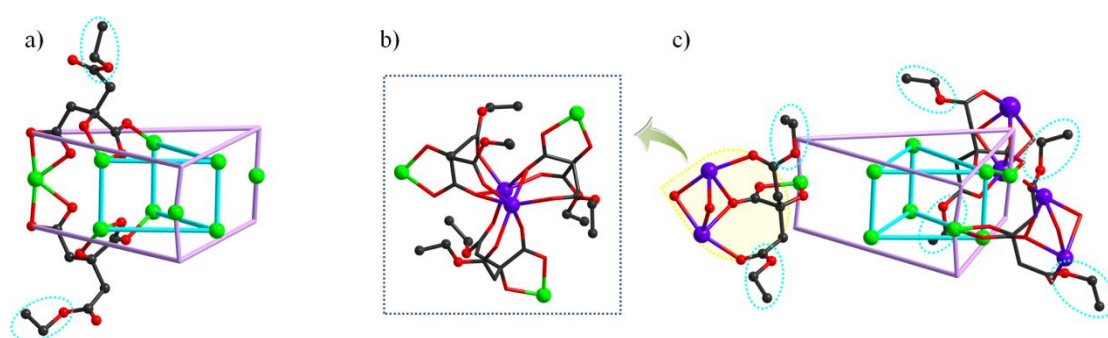


Figure S4. Sites of esterification reactions between the carboxyl groups of citrate ligands and ethanol solvent.

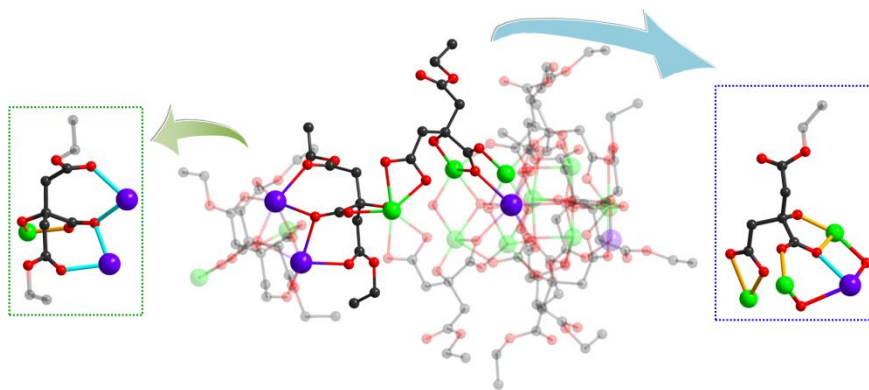


Figure S5. The illustration of different coordination models of citrate ligands. Atom color code: green Sn; purple Na; red O; black C.

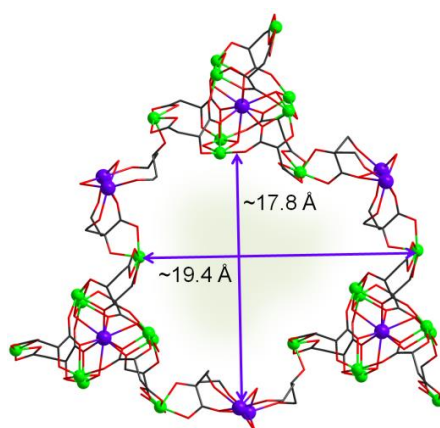


Figure S6. The ring size of 2D framework for TOC-10. Atom color code: green Sn; red O.

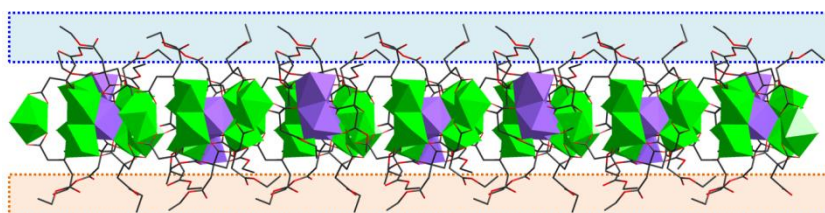


Figure S7. View of the 2D framework for TOC-10 along the c axis. Polyhedral color code: green $\text{SnO}_5\text{C}/\text{SnO}_6\text{C}$; purple NaO_6 .

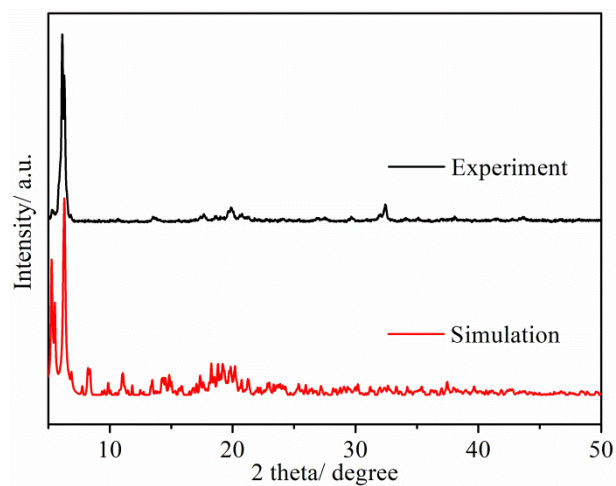


Figure S8. Simulated and experimental PXRD patterns of compound **TOC-10**.

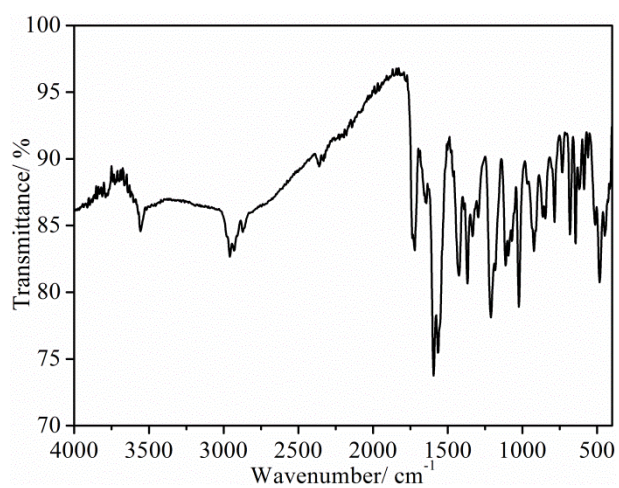


Figure S9. IR spectrum of compound **TOC-10**.

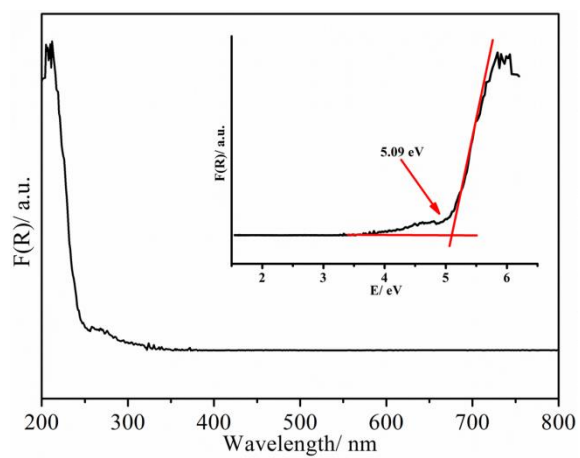


Figure S10. UV-vis diffuse reflectance spectrum of compound **TOC-10**.

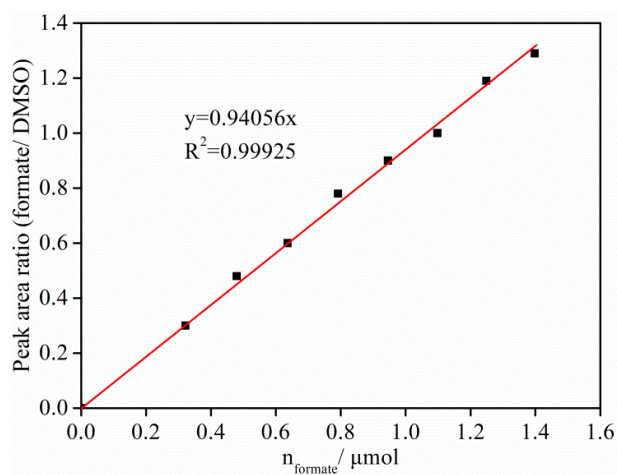


Figure S11. The calibration curve for formate (DMSO as internal standard).

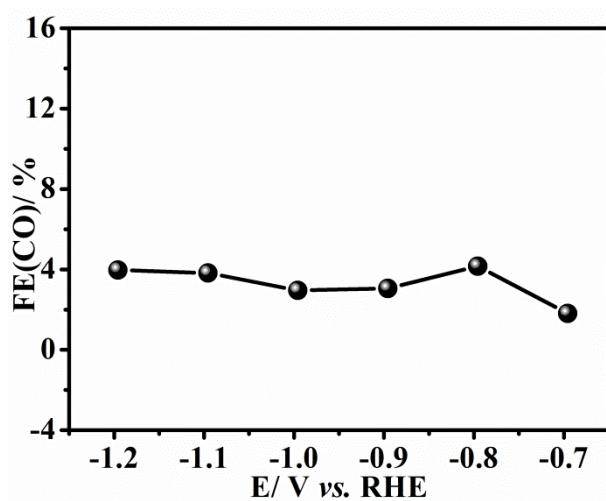


Figure S12. The faradaic efficiencies of CO for TOC-10 derived electrode at various potentials.

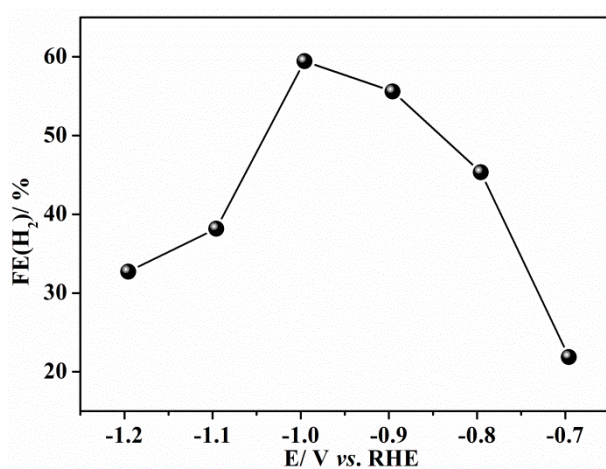


Figure S13. The faradaic efficiencies of H₂ for TOC-10 derived electrode at various potentials.

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.