Electronic Supplementary Information (ESI) for

A Supersalt-type Copper(I)-Thiolate Cluster with Applications for Mechano/Thermochromism and Oxygen Evolution Reaction

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Part I: Experimental Section

1. Copper(I)–thiolate cluster preparation (1)

Hexamethylenetetramine (0.100g, 0.72mmol), CuCl (0.107g,0.1mmol), dimethylsulfoxide (2.0ml), methanol(2.0ml), $NH_3 \cdot H_2O$(0.5ml) were sealed in a 20ml Teflon-lined reactor at 120℃ for 10 days and then cooled to room temperature. Block crystals **1** were obtained (Yield:20%). Elemental analysis (EA) calc. (%): C, 5.30; H, 2.67; N, 6.18; S, 14.14. Found: C, 5.97; H, 2.66; N, 6.78; S, 13.64.

2. Single-crystal characterization

Suitable single crystals of compounds **1** was selected and glued to thin glass fibers. Crystallographic data of **1** was collected on a on a SuperNova (Cu) single crystal diffractometer equipped with graphite-monochromatic Cu Kα radiation (λ = 1.54184 Å) at room temperature. The structures were solved by direct methods. Crystal data as well as details of data collection and refinement for **1** was summarized in Table 1.

3. Basic physical measurements.

Powder X-ray diffraction (PXRD) analyses were recorded on a Rigaku Dmax2500 diffractometer with Cu Kα radiation (λ = 1.54056 Å) with a step size of 0.05°. Thermogravimetric analyses (TGA) were carried out at a heating rate of 10 °C/min under a nitrogen atmosphere. EA for C, H, N and S were performed on an EA1110 CHNS0 CE elemental analyzer. Fourier transform infrared (FT-IR) spectra were taken on a Nicolet Magna 750 FT−IR spectrometer in the 4000−500 cm^{-1} region by using KBr pellets. photoluminescence spectra were performed by using an Edinburgh FLS920 spectrometer equipped with a continuous Xe 900 Xenon lamp.

4. Electrochemical characterization

Oxygen evolution reaction measurements were performed in a standard three-electrode glass cell at ambient environment. The data were studied by a CHI760 D. The synthesized 1 was coated a substrate (e.g., Ni foam~ 0.6 cm x 0.6 cm), acting as the working electrode for electrochemical test. Also, Ag/AgCl and Carbon rod were used as counter electrode and the reference electrode, respectively. According to the Nernst equation ($E_{RHE} = E_{Ag/Ag/Cl} + 0.059 \times pH + 0.217$), the potentials tested in the work were converted to reversible hydrogen electrode (RHE). Prior to the measurements, a flow of N_2 was maintained over half hour into the electrolyte (1.0 MKOH). The polarization curves

were obtained with a sweep rate of 5 mVs^{-1}. All electrochemical studies were measured without iR-correction. Electrochemical impedance spectroscopy (EIS) was carried out in a frequency range from 1 Hz to 1000 KHz.

4.1 1 coated on NF electrode (1@NF)

The as-prepared 1 was ultrasonically dispersed in the Milli-Q water(1ml) and then transferred onto the NF electrode (0.6cm x 0.6cm) with a thin layer of 0.5 wt.% Nafion solution (with a loading amount: ~ 0.33 mg cm^{-2}), and drying in air for another 5h. Meanwhile, the same size of NF was used to control sample.

4.2 RuO_2 coated on NF (RuO_2@NF)

The procedure for preparation of RuO_2@NF was the same as that for **1@NF** except for using **RuO_2** instead of **1**.

4.3 1 coated on glassy carbon electrode (1@GC)

The method for fabrication of 1@GC was the same as that for 1@NF except for using glassy carbon electrode instead of NF.

Part II: Supplementary Results

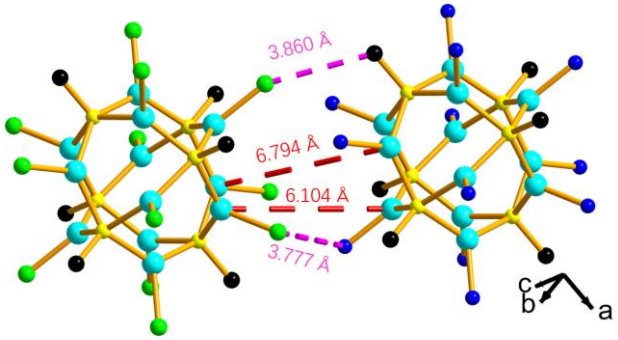

Figure S1. The Cu···Cu distances, C-H···Cl bond, and C-H···N bond of 1. Blue, black, yellow, green, and cyan balls represent N, C, S, Cl and Cu atoms, respectively.

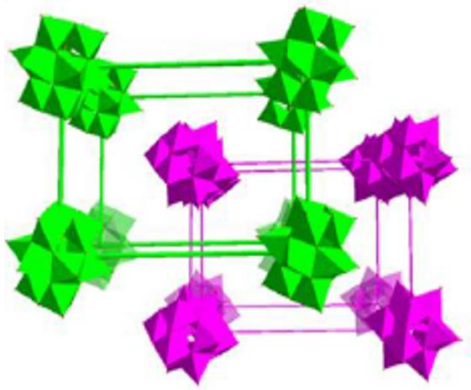

Figure S2. Three-dimensional penetrated diagram of 1 (cationic/ anionic clusters).

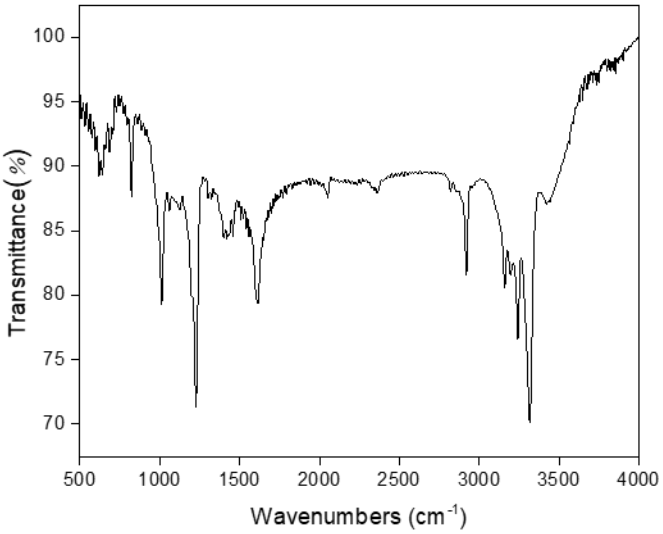

Figure S3. FT-IR spectroscopy of 1.

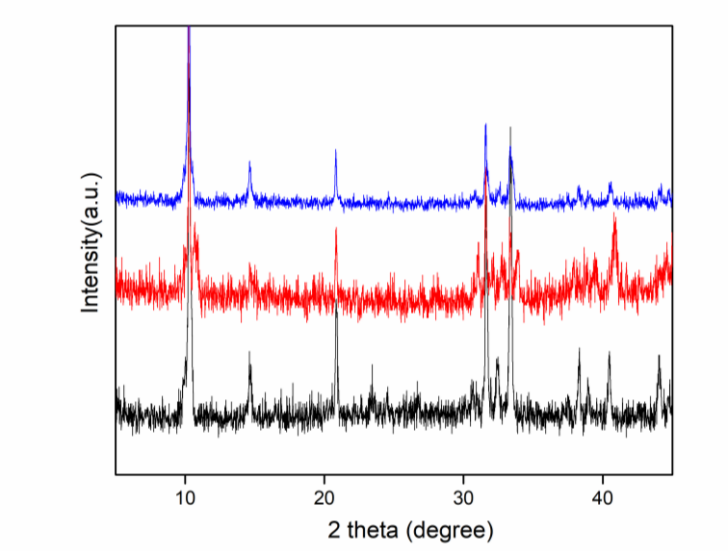

Figure S4. The PXRD of Cu-S Cluster under different conditions (black line: exposed in the air 3 days, red line: placed in water 12 hours, blue line: immersed 1M KOH 6 hours). These main peaks still maintained, indicating its stability.

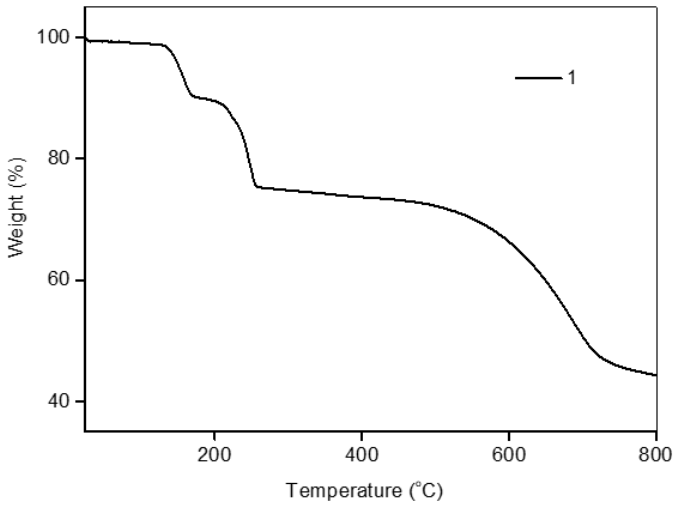

Figure S5. Thermogravimetry curves of 1 measured in N_2.

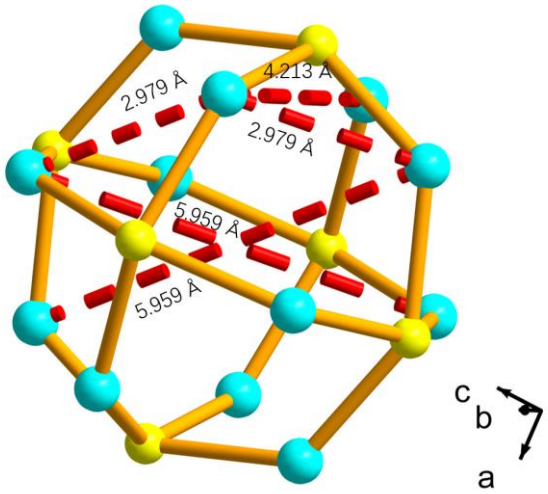

Figure S6. The Cu···Cu distances of isolated Cu-S cluster. Blue: Cu, yellow: S.

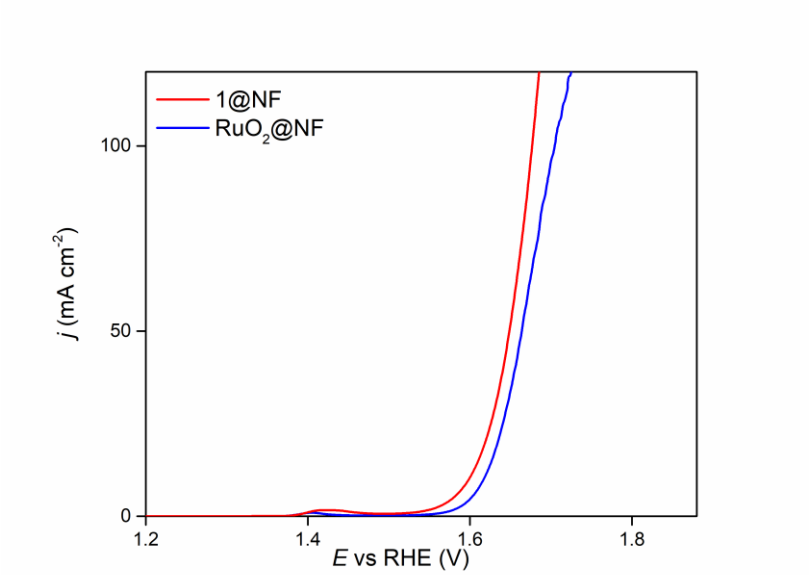

Figure S7. LSV curves of 1@/NF and RuO_2@NF.

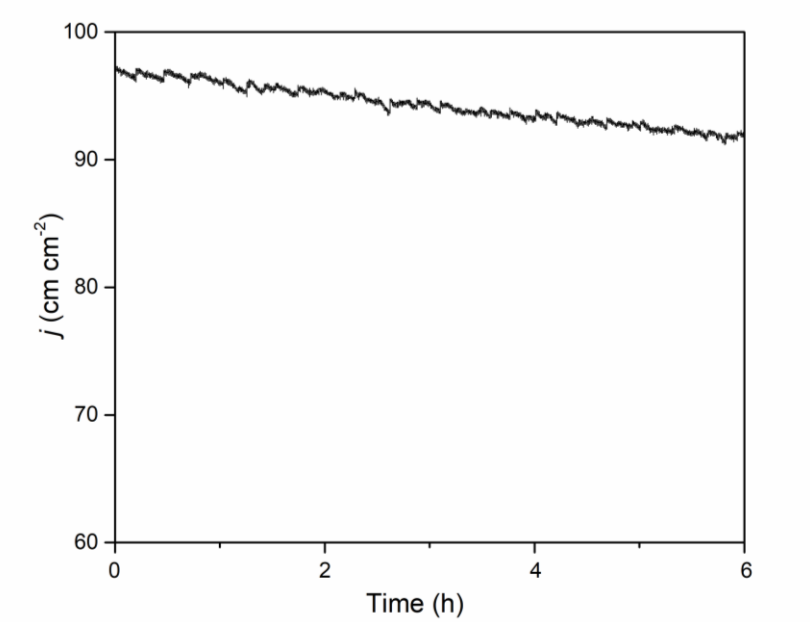

Figure S8. Time-dependent current density curve for 1 under a constant potential of 1.5 V in 1 M KOH aqueous solution.

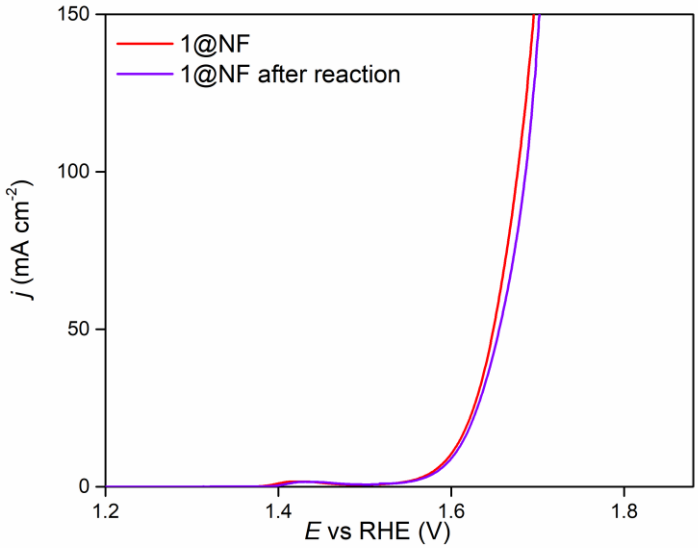

Figure S9. LSV curves of 1@/NF after reaction.

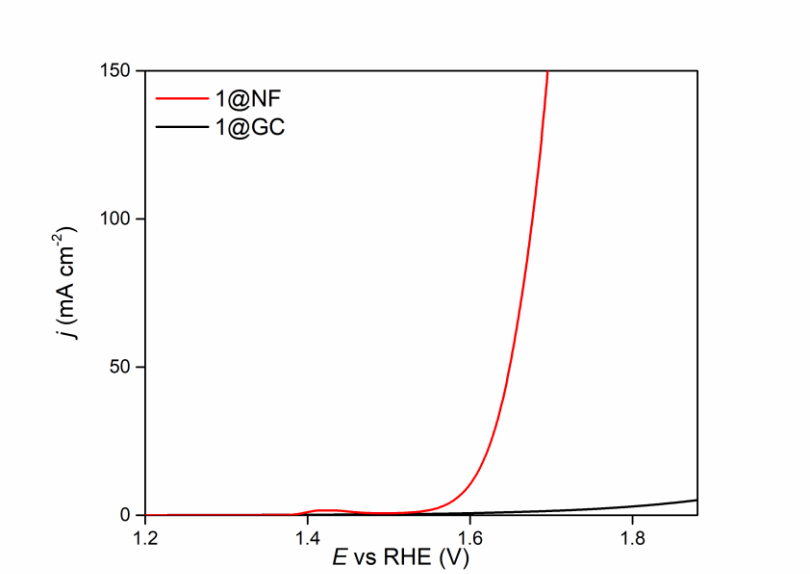

Figure S10. LSV curves of 1 coated on glass carbon substrates and Ni foam.

Table S1. Summary of Crystalographic Data of 1

Name	**1**
chemical formula	$C_6H_{36}Cl_6Cu_{12}N_6S_6S_6$
formula mass	1359.95
Space group	*Pm-3m*
a/Å	12.3881(2)
b/Å	14.0236(8)
c/Å	12.3881(2)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	1901.14(9)
Z, calculated density(g/cm^3)	2, 2.376
absorption coefficient (mm^{-1})	7.325
F(000)	1320.0
R_{int}	0.0266
GOF on F_2	1.088
R_1,[a] wR_2 [I > 2δ(I)]	0.0738, 0.2678
R_1, wR_2 (all data)	0.0759, 0.2711
CCDC Number	1977641

[a]$R_1 = \Sigma(|Fo| - |Fc|)/\Sigma|Fo|$, $wR_2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{0.5}$