

## **Supplementary Information**

### **Nanobelt assembly from molecular cobalt complexes as a photocatalyst boosts hydrogen evolution**

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## 1. Materials

5-Bromosalicylaldehyde and 2-thiopheneboronic acid were purchased from Aladdin. Tetrakis(triphenylphosphine)palladium, DMF (dry), Tetrabutylammonium perchlorate, ethylenediamine, sodium carbonate, and ascorbic acid were purchased from Adamas. Ethanol, methylene chloride,  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ , were purchased from Sinopharm Chemical reagent Co., Ltd. All chemicals were used directly without further purification.

## 2. Methods

$^1\text{H}$  nuclear magnetic resonance (NMR) was recorded on a JEOL 400 M NMR spectrometer. Ultraviolet-visible absorption spectrum (UV-vis) and UV-vis diffuse reflectance spectrum were performed on a Shimadzu UV-3600PLUS spectrophotometer. Powder X-ray diffraction (PXRD) characterization was carried out using Cu K $\alpha$  radiation on a Bruker D8 diffractometer with a  $2\theta$  range of  $5^\circ$  to  $80^\circ$ . X-ray photoelectron spectroscopy (XPS) was recorded on a Thermo Scientific K-Alpha instrument. Transmission electron microscopy (TEM) analyses were performed on a Talos F200X (200 kv). Photoluminescence (PL) spectrum was measured on an F-4500 spectrophotometer with an excitation wavelength of 350 nm. Single crystal was selected as a suitable crystal and tested on a Bruker APEX-II CCD diffractometer. The crystal was kept at 200.0 K during data collection. Using Olex2<sup>1</sup>, the structure was solved with the olex2.solve<sup>2</sup> structure solution program using Charge Flipping and refined with the olex2.refine<sup>2</sup> refinement package using Gauss-Newton minimization. Figures were created with Diamond.

## 3. Photocatalytic experiments

Generally, 2 mg of catalyst, 5 mL of water and 0.1 mol L<sup>-1</sup> ascorbic acid were added to the Pyrex tube and sonicated for 10 min, then the pH was adjusted to 4~5. Argon was then purged into the solution for 30 min to remove oxygen from the solution. After sealing, the system was irradiated with a 450 nm LED lamp. During photocatalysis, the reaction system was stirred vigorously with a magnetic stirrer. At the end of the reaction, the gas products were measured using the SP-3420A gas

chromatograph. Stability test conditions: 2 mg of thiophene Co-salen as catalyst, 5 mL of water, 0.1 mol/L ascorbic acid as a sacrificial agent, the reaction was carried out under the irradiation of LED lamp at 450 nm, and the amount of hydrogen evolution was measured by gas chromatography every hour, every five hours as a cycle.

#### 4. Electrochemistry measurements

Electrochemistry measurements were carried out with a CHI 660E electrochemical workstation. 2 mg of catalyst was mixed with 300 uL of ethanol, 100 uL of H<sub>2</sub>O, and 40 uL of Nafion to sonicate the sample, and then the sample was uniformly applied to an area of 1 cm<sup>2</sup> of ITO. Electrochemical impedance and Mott Schottky experiments were carried out in 0.5 mol/L sodium sulfate solution using ITO coated with the sample as the working electrode, Ag/AgCl as the reference electrode, and Pt as an assistant electrode. 1 mmol/L of catalyst and 0.1 mol/L of tetrabutylammonium perchlorate (supporting electrolyte) was added to 10 mL of dry DMF and dissolved, and then nitrogen was passed through for 30 min to remove oxygen from the solution. Cyclic voltammetry experiments were carried out using a glassy carbon electrode as the working electrode, Ag/Ag<sup>+</sup> as the reference electrode, and Pt as an assistant electrode.

#### 5. The measurement of apparent quantum yield (AQY)

Briefly, 2 mg of catalyst was mixed with 5 ml of aqueous ascorbic acid solution, placed in a light test tube and irradiated under an LED lamp with a light intensity of 14 mW/cm<sup>2</sup> for 4 h. The photocatalytic hydrogen yield was analyzed by gas chromatography. The light absorbing area was calculated from the sectional area of the Pyrex tube. The light intensity was measured by PLS-MW2000 optical power meter; therefore, the number of absorbed photons can be calculated as:

$$N_{\text{photon}} = \frac{t(s) \times P(W \cdot \text{cm}^{-2}) \times S(\text{cm}^2) \times \lambda(m)}{h(J \cdot s) \times c(m \cdot s^{-1})} \quad (1)$$

$$AQY = \frac{N}{N_{\text{photon}}} \times 100\% \quad (2)$$

The specific calculations are as follows:

$$N_{\text{photon}} = \frac{4 \times 3600(\text{s}) \times 0.014(\text{W}\cdot\text{cm}^{-2}) \times 8(\text{cm}^2) \times 450 \times 10^{-9}(\text{m})}{6.626 \times 10^{-34}(\text{J}\cdot\text{s}) \times 3 \times 10^8(\text{m}\cdot\text{s}^{-1})} \quad (3)$$

$$= 3.65 \times 10^{21}$$

$$AQY = \frac{N}{N_{\text{photon}}} \times 100\% \quad (4)$$

$$= \frac{2n(\text{H}_2) \times 6.02 \times 10^{23}}{N_{\text{photon}}} \times 100\%$$

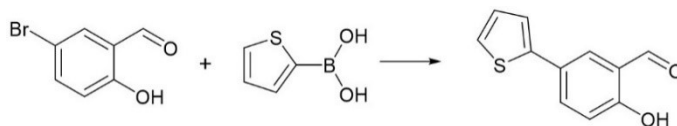
$$= \frac{2 \times 6 \times 10^{-7}(\text{mol}) \times 6.02 \times 10^{23}}{3.65 \times 10^{21}} \times 100\%$$

$$= 0.02\%$$

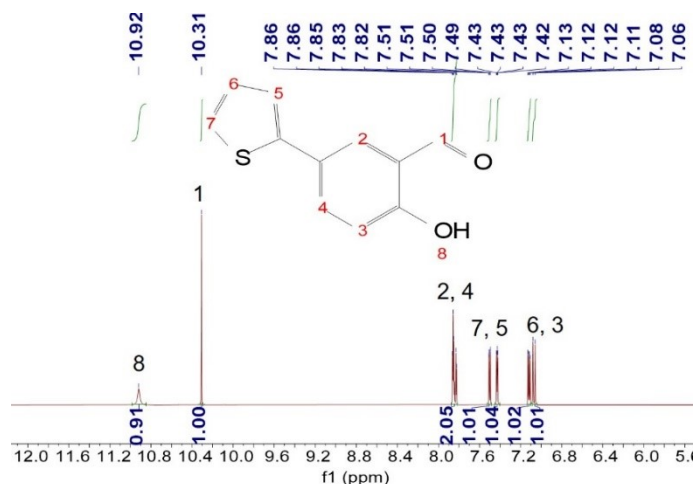
As a result, the apparent quantum yield of the catalyst under 450 nm LED light is about 0.02%. The lower AQY is partly due to the light scattering and refingency of the glass tube.

## 6. Synthesis of 2-hydroxy-5-(thiophen-2-yl)benzaldehyde

According to a method reported in the literature<sup>3</sup>. Under N<sub>2</sub> atmosphere, 5-bromosalicylaldehyde (5.5 mmol), 2-thiopheneboronic acid (4.5 mmol), tetrakis(triphenylphosphine)palladium (0.25 mmol) and sodium carbonate (5 mmol) were added in a solvent of 1,2-Dimethoxyethane: H<sub>2</sub>O=3:1, and heated to react for 12 h at 100 °C, then the mixture was extracted with dichloromethane and water. The resultant mixture was purified by silica gel column chromatography, and the solvent was evaporated to obtain bright yellow solid 2-hydroxy-5-(thiophen-2-yl)benzaldehyde, yield 59%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 10.92 (s, 1H), 10.31 (s, 1H), 7.87 – 7.82 (m, 2H), 7.50 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.43 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.12 (dd, *J* = 5.1, 3.6 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H).



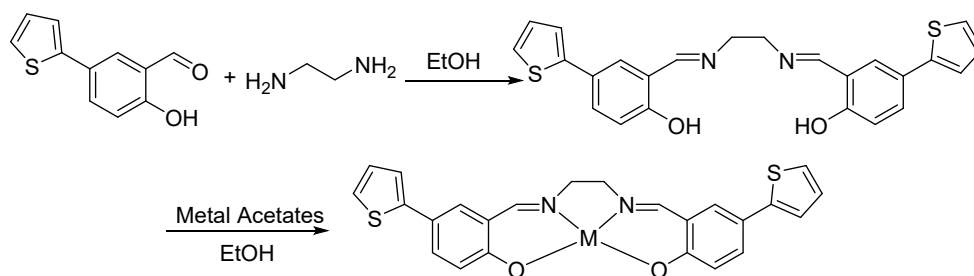
**Scheme S1.** Synthesis of 2-hydroxy-5-(thiophen-2-yl)benzaldehyde.



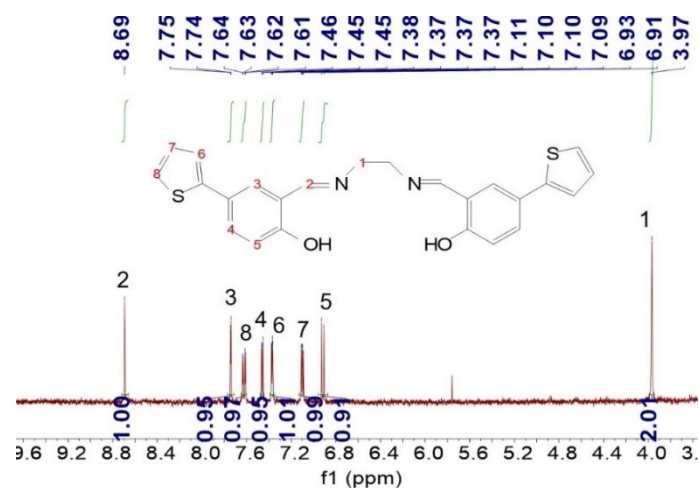
**Figure S1.**  $^1\text{H}$  NMR of 2-hydroxy-5-(thiophen-2-yl)benzaldehyde.

## 7. Synthesis and assembly of thiophene-M-salen (M=Co; Ni; Zn)

According to a method reported in the literature<sup>4, 5</sup>. The thiophene-salen ligand was obtained by the condensation reaction of 2-hydroxy-5-(thiophen-2-yl)benzaldehyde and ethylenediamine in ethanol solution for 4 h. The reaction was continued for 4 h with the addition of  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  under nitrogen atmosphere to obtain the thiophene-Co-salen complexes, yield 96%. The synthesis steps of thiophene-Ni-salen and thiophene-Zn-salen are the same as those of thiophene-Co-salen with yields of 89% and 60%, respectively. The self-assembly of thiophene-M-salen is carried out during the reaction process, as the ligand is coordinated with the metal in ethanol solution, which makes the solubility of thiophene-M-salen decrease, and then the self-assembled molecules lead to the precipitation of a large number of precipitates by non-covalent interactions, i.e., the assemblies.  $^1\text{H}$  NMR of thiophene-salen ligand (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  8.69 (s, 2H), 7.74 (d,  $J = 2.4$  Hz, 2H), 7.62 (dd,  $J = 8.7, 2.4$  Hz, 2H), 7.48 – 7.44 (m, 2H), 7.37 (dd,  $J = 3.6, 1.2$  Hz, 2H), 7.10 (dd,  $J = 5.1, 3.6$  Hz, 2H), 6.92 (d,  $J = 8.6$  Hz, 2H), 3.97 (s, 4H).

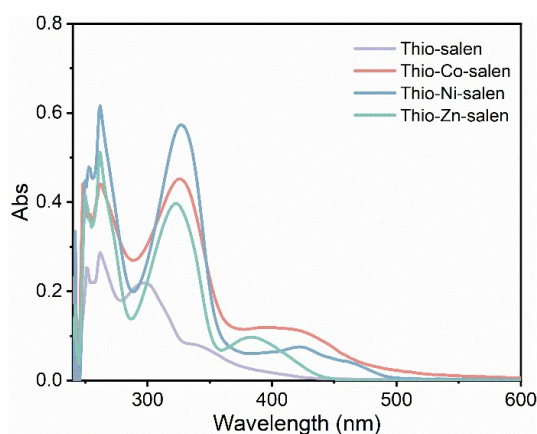


**Scheme S2.** Synthesis of thiophene-M-salen.



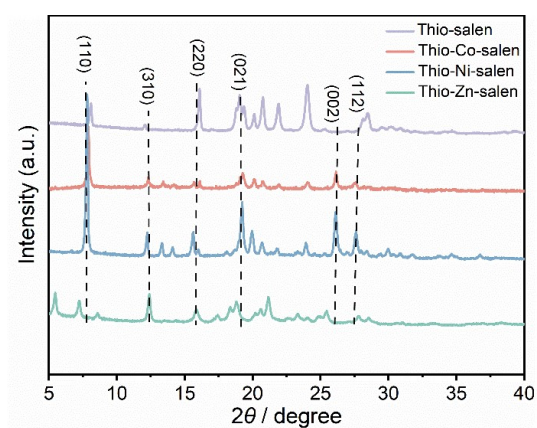
**Figure S2.**  $^1\text{H}$  NMR of thiophene-salen ligand.

The UV-Vis absorption spectra (Figure S3) show the absorption peaks of thiophene-ligand and thiophene-M-salen. The ligand has three absorption peaks at 250 nm, 260 nm and 300 nm, which correspond to  $\pi-\pi^*$  leaps on the benzene ring,  $\pi-\pi^*$  leaps on the  $-\text{C}=\text{N}$  double bond and  $n-\pi^*$  leaps on the  $-\text{C}=\text{N}$  double bond, respectively. However, when the ligand is coordinated to the metal, the absorption peaks of the complexes are red-shifted and change in intensity, and new absorption peaks also appear.



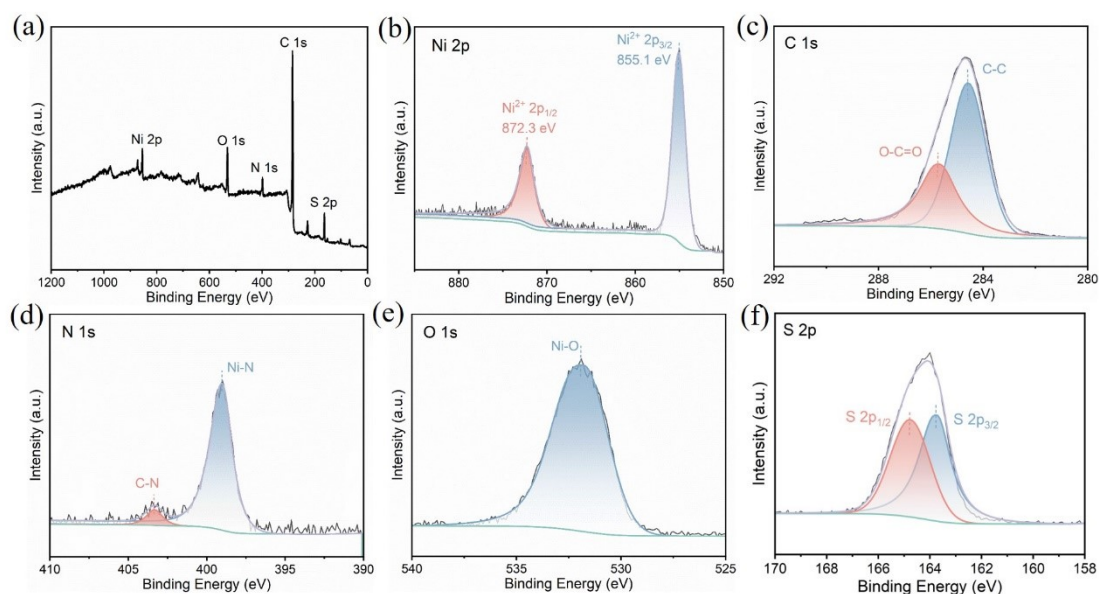
**Figure S3.** UV-vis spectra of thiophene-ligand and thiophene-M-salen.

As shown in the Figure S4, all showed distinct diffraction peaks, indicating a high degree of crystallinity. Among them, thiophene-Co-salen and thiophene-Ni-salen showed the same PXRD pattern, indicating that both have the same crystalline form and stacking mode. However, the diffraction peaks of thiophene-salen ligand and thiophene-Zn-salen are not identical to them, but all of them have high crystallinity, which suggests that there may be different crystalline forms and stacking modes among them.



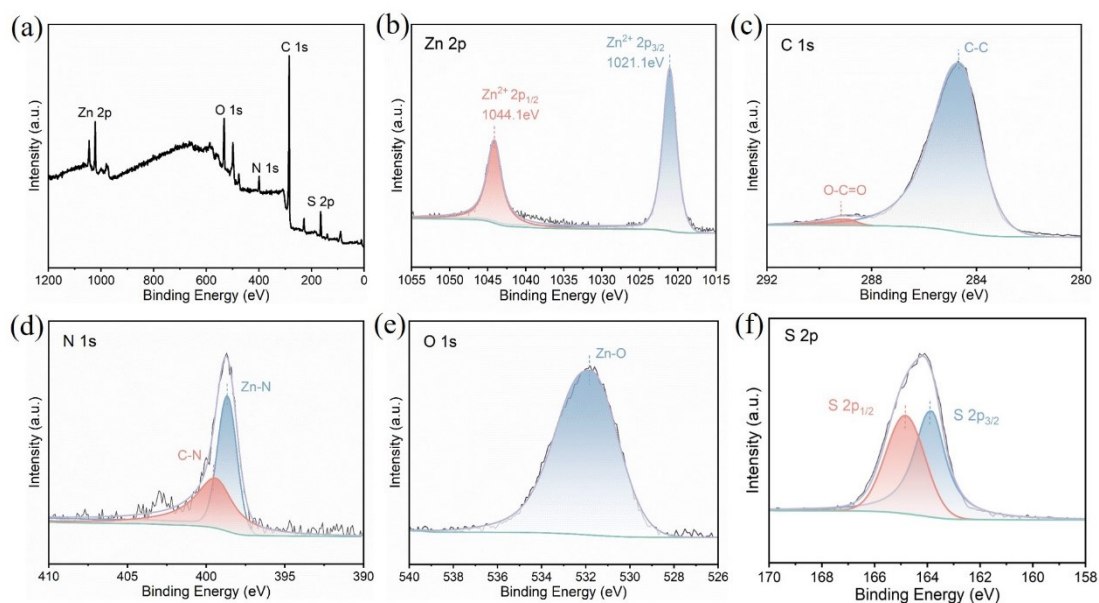
**Figure S4.** PXRD of thiophene-ligand and thiophene-M-salen.

XPS verified the chemical composition and valence states of thiophene-Ni-salen and thiophene-Zn-salen. In the survey spectra of thiophene-Co-salen (Figure S5a), apparent peaks appear at 284, 398, 532, 163 and 780 eV, which could be assigned to C 1s, N 1s, O 1s, S 2p and Co 2p regions. In the Ni 2p spectra (Figure S5b) of thiophene-Ni-salen has two peaks at 855.1 eV and 872.3 eV, which have been assigned to Ni 2p<sub>3/2</sub> and Ni 2p<sub>1/2</sub>, respectively <sup>6</sup>. In the survey spectra of thiophene-Zn-salen (Figure S6a), apparent peaks appear at 284, 398, 532, 163 and 780 eV, which could be assigned to C 1s, N 1s, O 1s, S 2p and Co 2p regions. In the Zn 2p spectra (Figure S6b) of thiophene-Zn-salen has two peaks at 1021.1 eV and 1044.1 eV, which have been assigned to Zn 2p<sub>3/2</sub> and Zn 2p<sub>1/2</sub>, respectively <sup>7</sup>.

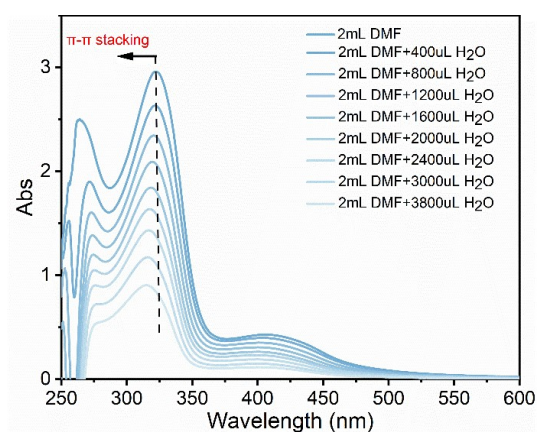


**Figure S5.** XPS spectra of thiophene-Co-salen assembly (a) Survey spectra; high-resolution XPS spectra of (b) Co2p; (c) C1s; (d) N1s; (e) O1s; (f) S2p.

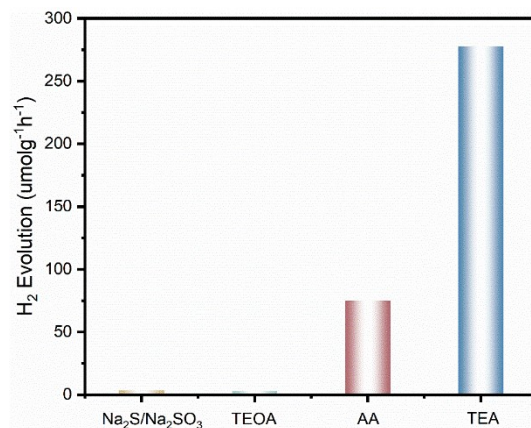




**Figure S6.** XPS spectra of thiophene-Co-salen assembly (a) Survey spectra; high-resolution XPS spectra of (b) Co2p; (c) C1s; (d) N1s; (e) O1s; (f) S2p.

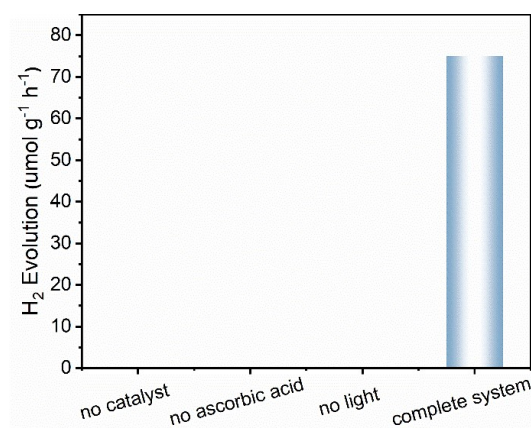


**Figure S7.** UV titration of thiophene-Co-salen. Gradually add different equivalents of H<sub>2</sub>O to 2 ml of DMF dissolved in thiophene-Co-salen.

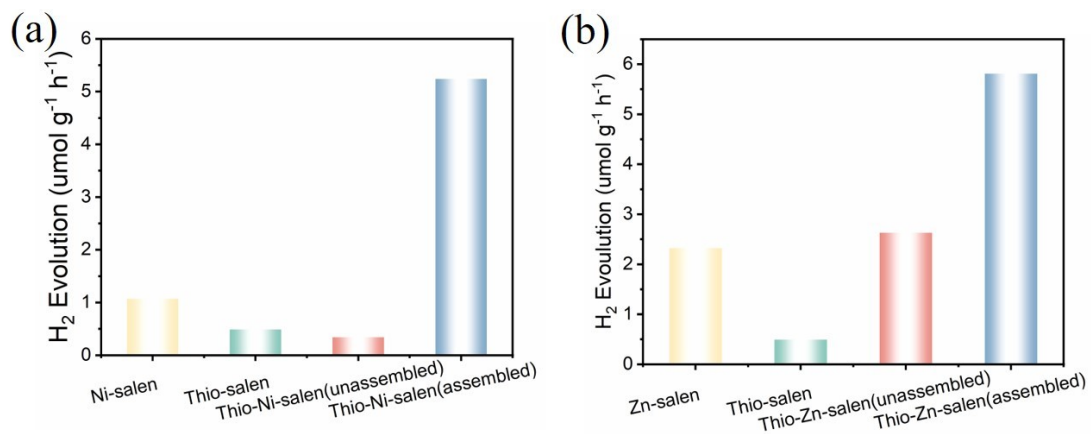


**Figure S8.** The photocatalytic hydrogen evolution tests in 4 hours with different sacrificial agents.

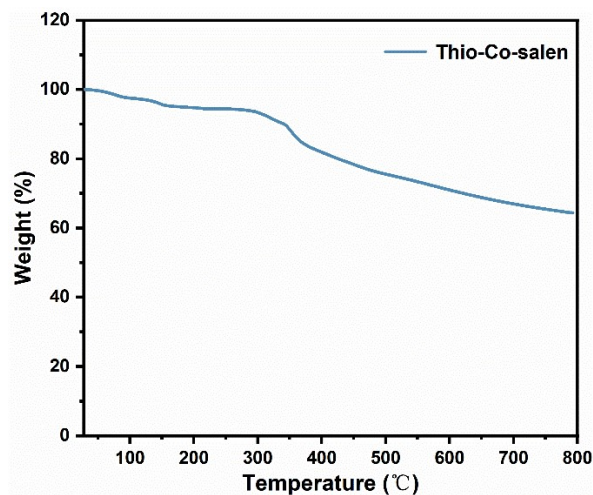
Although system using TEA as sacrificial reagent has better initial activity, the activity decrease dramatically after 4 hours. This is probably due to the assembly collapse resulted from the coordination ability of N atom in TEA.



**Figure S9.** Hydrogen evolution reaction condition-controlled tests.

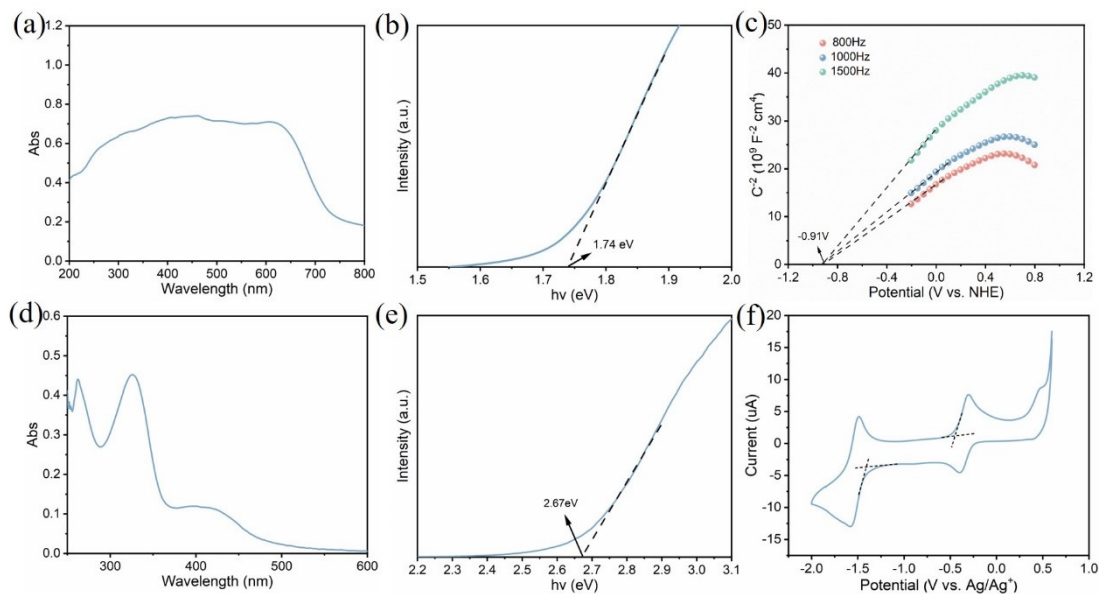


**Figure S10.** Photocatalytic hydrogen evolution based on (a) Different Ni salen catalysts; (b) Different Zn salen catalysts.

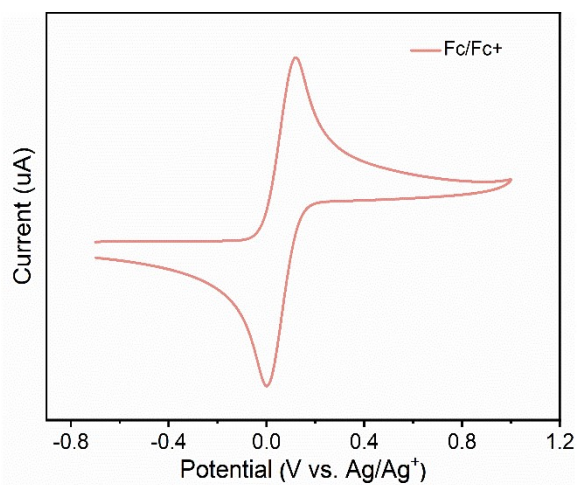


**Figure S11.** Thermogravimetric (TGA) curve of Thio-Co-salen assembly.

The HOMO and the LUMO energy levels of the molecular thiophene-Co-salen were calculated based on CV and UV-vis absorption spectra. The band gap of the molecular thiophene-Co-salen is calculated to be 2.67 eV (vs. NHE) from the UV-vis absorption spectra (Figure S11d) according to the Tauc Plot method (Figure S11e). The HOMO/LUMO energy levels for molecular thiophene-Co-salen were calculated from CV (Figure S11f) by  $E_{\text{LUMO}} = -E [E_{\text{red}} - E_{(\text{Fc}/\text{Fc}^+)} + 4.8]$  eV and  $E_{\text{HOMO}} = E_{\text{LUMO}} - E_g$ <sup>8</sup> to obtain -5.93/-3.26 eV for the molecular thiophene-Co-salen, respectively, and 1.49/-1.18 eV for the HOMO/LUMO relative to the NHE. Where  $E_{(\text{Fc}/\text{Fc}^+)} = 0.14$  eV (Figure S11).



**Figure S12.** Assembled thiophene-Co-salen of (a) UV-vis DRS plot; (b) Tauc Plot; (c) Mott Schottky plot; Molecular thiophene-Co-salen of (d) UV-vis plot; (e) Tauc Plot; (f) Cyclic voltammetry curve.



**Figure S13.** Cyclic voltammetry curves of Fereocene/ferrocenium (Fc/Fc<sup>+</sup>) couple.

**Table S1.** Crystal data and structure refinement for thiophene-Ni-salen

Empirical formula	C <sub>24</sub> H <sub>18</sub> N <sub>2</sub> NiO <sub>2</sub> S <sub>2</sub>
Formula weight	489.23
Temperature/K	200.0
Crystal system	monoclinic
Space group	<i>C2/c</i>
<i>a</i> /Å	26.891(3)
<i>b</i> /Å	12.5045(11)
<i>c</i> /Å	6.7930(6)
$\alpha$ /°	90
$\beta$ /°	96.076(4)
$\gamma$ /°	90
Volume/Å <sup>3</sup>	2271.4(4)
<i>Z</i>	4
$\rho_{\text{calc}}$ /g cm <sup>-3</sup>	1.431
$\mu$ /mm <sup>-1</sup>	6.008
<i>F</i> (000)	1008.0
Crystal size/mm <sup>3</sup>	0.25 × 0.25 × 0.25
Radiation	Ga K $\alpha$ ( $\lambda$ = 1.34139)
2 $\Theta$ range for data collection/°	5.75 to 113.944
Index ranges	-33 ≤ <i>h</i> ≤ 33, -15 ≤ <i>k</i> ≤ 15, -8 ≤ <i>l</i> ≤ 8
Reflections collected	10555
Independent reflections	2321 [ <i>R</i> <sub>int</sub> = 0.0434, <i>R</i> <sub>sigma</sub> = 0.0284]
Data/restraints/parameters	2321/3/141
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.076
Final <i>R</i> indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0638, <i>wR</i> <sub>2</sub> = 0.2257
Final <i>R</i> indexes [all data]	<i>R</i> <sub>1</sub> = 0.0682, <i>wR</i> <sub>2</sub> = 0.2343
Largest diff. peak/hole / e Å <sup>-3</sup>	1.44/-0.73

**Table S2.** Bond Lengths for thiophene-Ni-salen

<b>Atom</b>	<b>Length/Å</b>	<b>Atom</b>	<b>Length/Å</b>
Ni <sub>1</sub> -O <sub>1</sub> <sup>1</sup>	1.855(3)	Ni <sub>1</sub> -O <sub>1</sub>	1.855(3)
Ni <sub>1</sub> -N <sub>1</sub> <sup>1</sup>	1.846(3)	Ni <sub>1</sub> -N <sub>1</sub>	1.846(3)
S <sub>1</sub> -C <sub>9</sub>	1.696(4)	S <sub>1</sub> -C <sub>12</sub>	1.656(5)
O <sub>1</sub> -C <sub>4</sub>	1.314(5)	C <sub>10</sub> -C <sub>9</sub>	1.498(5)
C <sub>10</sub> -C <sub>11</sub>	1.472(6)	N <sub>1</sub> -C <sub>2</sub>	1.296(5)
N <sub>1</sub> -C <sub>1</sub>	1.476(5)	C <sub>7</sub> -C <sub>8</sub>	1.377(6)
C <sub>7</sub> -C <sub>9</sub>	1.483(5)	C <sub>7</sub> -C <sub>6</sub>	1.408(6)
C <sub>8</sub> -C <sub>3</sub>	1.419(6)	C <sub>4</sub> -C <sub>3</sub>	1.415(5)
C <sub>4</sub> -C <sub>5</sub>	1.417(5)	C <sub>3</sub> -C <sub>2</sub>	1.426(6)
C <sub>5</sub> -C <sub>6</sub>	1.391(6)	C <sub>1</sub> -C <sub>11</sub>	1.518(7)
C <sub>12</sub> -C <sub>11</sub>	1.352(8)		

**Table S3.** Bond Angles for thiophene-Ni-salen

<b>Atom</b>	<b>Angle/°</b>	<b>Atom</b>	<b>Angle/°</b>
O <sub>1</sub> -Ni <sub>1</sub> -O <sub>1</sub> <sup>1</sup>	84.30(17)	N <sub>1</sub> -Ni <sub>1</sub> -O <sub>1</sub>	94.76(15)
N <sub>1</sub> -Ni <sub>1</sub> -O <sub>1</sub> <sup>1</sup>	178.20(12)	N <sub>1</sub> <sup>1</sup> -Ni <sub>1</sub> -O <sub>1</sub> <sup>1</sup>	94.76(15)
N <sub>1</sub> <sup>1</sup> -Ni <sub>1</sub> -O <sub>1</sub>	178.21(12)	N <sub>1</sub> -Ni <sub>1</sub> -N <sub>1</sub> <sup>1</sup>	86.2(2)
C <sub>12</sub> -S <sub>1</sub> -C <sub>9</sub>	93.5(2)	C <sub>4</sub> -O <sub>1</sub> -Ni <sub>1</sub>	127.4(3)
C <sub>11</sub> -C <sub>10</sub> -C <sub>9</sub>	104.4(3)	C <sub>2</sub> -N <sub>1</sub> -Ni <sub>1</sub>	126.6(3)
C <sub>2</sub> -N <sub>1</sub> -C <sub>1</sub>	117.9(3)	C <sub>1</sub> -N <sub>1</sub> -Ni <sub>1</sub>	115.4(2)
C <sub>8</sub> -C <sub>7</sub> -C <sub>9</sub>	119.3(4)	C <sub>8</sub> -C <sub>7</sub> -C <sub>6</sub>	118.0(3)
C <sub>6</sub> -C <sub>7</sub> -C <sub>9</sub>	122.7(4)	C <sub>7</sub> -C <sub>8</sub> -C <sub>3</sub>	121.8(3)
C <sub>10</sub> -C <sub>9</sub> -S <sub>1</sub>	112.7(3)	C <sub>7</sub> -C <sub>9</sub> -S <sub>1</sub>	121.4(3)
C <sub>7</sub> -C <sub>9</sub> -C <sub>10</sub>	125.6(3)	O <sub>1</sub> -C <sub>4</sub> -C <sub>3</sub>	123.8(3)
O <sub>1</sub> -C <sub>4</sub> -C <sub>5</sub>	118.8(4)	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	117.4(4)
C <sub>8</sub> -C <sub>3</sub> -C <sub>2</sub>	118.2(3)	C <sub>4</sub> -C <sub>3</sub> -C <sub>8</sub>	120.2(3)
C <sub>4</sub> -C <sub>3</sub> -C <sub>2</sub>	121.5(4)	C <sub>6</sub> -C <sub>5</sub> -C <sub>4</sub>	121.0(4)
N <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	125.3(4)	C <sub>5</sub> -C <sub>6</sub> -C <sub>7</sub>	121.5(4)
N <sub>1</sub> -C <sub>1</sub> -C <sub>1</sub> <sup>1</sup>	108.1(2)	C <sub>11</sub> -C <sub>12</sub> -S <sub>1</sub>	113.6(3)
C <sub>12</sub> -C <sub>11</sub> -C <sub>10</sub>	115.8(4)		

## References

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