Supporting Information

Constructing metallosalen poly(ionic liquid)s to boost photocatalytic CO_2 reduction

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†X. Chen and W. Zhou contributed equally to this work.

16 **Table of contents**

30

1. Supplemental experimental procedures

1.1. Characterization

The FT-IR spectra were recorded by Bruker's VERTEX 70v in the range of 400-4000 cm^{-1}. Solid-state ^{13}C CP/MAS NMR was performed on a Bruker ADVANCE III HD 400 MHz spectrometer. Thermogravimetric analysis was performed by using Netzsch Model STA449C instrument over the temperature range from room temperature to 800 ℃ under Ar atmosphere. Gaseous products were detected using gas chromatography (Agilent Technologies-8890). UV–vis spectra were recorded using an Agilent Cary 5000 spectrometer from 200 to 1400 nm. Nitrogen sorption isotherms were measured at 77 K with Quantachrome Automated Surface Area & Pore Size Analyzer.

1.2 Synthetic procedures

1.2.1 The synthesis of Co(Salen)

4-Hydroxynicotinaldehyde (491.4 mg, 4 mmol) was placed in 100 mL flask, vacuumed and then passed through nitrogen for three times. Ethylenediamine (0.1336 mL, 2 mmol) was mixed with ethanol (20 mL), and then the mixture was injected into the flask with a syringe. After stirring well at room temperature, the solution appeared yellow. Then $CoSO_4 \cdot 7H_2O$ (562.4 mg, 2mmol) was dissolved in 5mL deionized water, the solution was injected into a flask with a syringe, and the temperature was raised to 75 °C and stirred for 50 min in a nitrogen atmosphere. After the reaction was completed and cooled to room temperature, the mixture was drained and washed with absolute ethanol, and finally the yellow powder was dried under vacuum at 60 °C for 12 h to obtain Co (Salen). The final product mass was 760 mg, and the yield was 64.7%.

1.2.1 The synthesis of Co(Salen)-PIL

Co(Salen) (327 mg, 1mmol), heptazine chloride (HTC) (166 mg, 0.6 mmol) were placed in a 25 mL flask, evacuated and passed with nitrogen, and then toluene (5 mL) was injected into the flask with a syringe, and the mixture was condensed and refluxed for 72 h at 150 °C under a nitrogen atmosphere. After the reaction was completed and cooled to room temperature, the mixture was filtered and washed with tetrahydrofuran, toluene, chloroform and methanol. Finally, the yellow solid was dried under vacuum at 60 °C for 12 h to obtain a final product mass of 117 mg, and then Co(Salen)-PIL and $CoSO_4 \cdot 7H_2O$ (mass ratio 1: 10) placed in a flask, vacuumed with nitrogen, and then injected methanol into the flask with a syringe. The mixture was then condensed and refluxed under nitrogen atmosphere for 72 h at 70 °C. After the reaction was completed and cooled to room temperature, the mixture was drained and washed out with DMF\ MeOH to remove excess $CoSO_4 \cdot 7H_2O$, and finally the yellow powder was dried under vacuum at 60 °C for 12 h to give Co(Salen)-PIL. M(Salen)-PILs (M=Cu, Ni, Zn, Fe) is consistent with the above method, only by replacing the metal salts with $CuSO_4$, $NiSO_4 \cdot 6H_2O$, $ZnSO_4 \cdot 7H_2O$, $FeCl_3$ respectively.

1.2.3 The synthesis of Co(Salen)-CHO

4-Hydroxyisophthaladehyde (750 mg, 5 mmol) was placed in 100 mL flask, vacuumed and then passed through nitrogen for three times. Ethylenediamine (0.167 mL, 2.5 mmol) was mixed with ethanol (20 mL), and then the mixture was injected into the flask with a syringe. After stirring well at room temperature, the solution appeared yellow. Then $CoSO_4 \cdot 7H_2O$ (702.75 mg, 2.5 mmol) was dissolved in 5 mL deionized water, the solution was injected into a flask with a syringe, and the temperature was raised to 50 °C and stirred for 6 h in a nitrogen atmosphere. After the reaction was completed and cooled to room temperature, the mixture was drained and washed with

absolute ethanol, and finally the brownish powder was dried under vacuum at 60 °C for 12 h to obtain Co(Salen)-CHO.

1.2.4 The synthesis of Co(Salen)-CMP

Co(Salen)-CHO (194.4 mg, 0.6 mmol), melem (87 mg, 0.4 mmol) were placed in a 25 mL flask, evacuated and passed with nitrogen, and then DMSO (5 mL) was injected into the flask with a syringe. The flask was further placed in oil bath. In presence of nitrogen protection, the mixture was heated in 120 ℃ for 6 h. Then, the temperature of the oil bath turned to150 ℃ for 36 h. After cooling down to room temperature naturally, the formed precipitate was separated by the operation of centrifugation. The product was then washed with methanol solvent to remove unreacted monomers and formed oligomers. Finally, the yellow-brown powder was dried under vacuum at 60 °C for 12 h, and then Co(Salen)-PIL and $CoSO_4 \cdot 7H_2O$ (mass ratio 1: 10) placed in a flask, vacuumed with nitrogen, and then injected methanol into the flask with a syringe. The mixture was then condensed and refluxed under nitrogen atmosphere for 72 h at 70 °C. After the reaction was completed and cooled to room temperature, the mixture was drained and washed out with DMF \ MeOH to remove excess $CoSO_4 \cdot 7H_2O$, and finally the yellow-brown powder was dried under vacuum at 60 °C for 12 h to give Co(Salen)-CMP.

1.4 Photoelectrochemical measurements

2 mg of the photocatalyst and 10 μL Nafion were dispersed in 0.2 mL ethanol and ultrasonicated for 10 minutes giving a slurry. The slurry was then coated onto ITO glass electrodes with an active area of 1 cm^2 and dried overnight at room temperature. The photocurrent response was tested using a three-electrode system with a working electrode (M(Salen)-PILs on ITO glass), counter electrode (Pt wire), and reference electrode (Hg/Hg_2Cl_2) in 0.2 M Na_2SO_4 (pH = 7) aqueous solution. Photocurrent test is conducted at a constant voltage of 1.4 V vs. reversible hydrogen electrode (RHE).

1.5 Mott–Schottky plots

2 mg M(Salen)-PILs powder was mixed with 1.0 mL ethanol and 10 μL Nafion solutions and sonicated for 20 min. The resulting mixture was deposited evenly on a glassy carbon electrode and left in air to dry. Mott-Schottky measurements were performed on an electrochemical workstation in 0.2 M Na_2SO_4 electrolyte with a Hg/Hg_2Cl_2 electrode as the reference electrode and a Pt plate as the counter electrode.

1.6 Solid-state photoluminescence

PL spectra were recorded by a FSL 1000 Edinburgh Instruments spectrofluorimeter at 25 °C. The spectral acquisition was collected with excitation of 312 nm, and emission range from 340 nm to 800 nm. Decay time was calculated using 3 exponentials. All samples were tests on a quartz chip.

1.7 Photocatalytic CO_2 reduction recycling experiments

The container was filled with a mixed solution of CH_3CN, TEOA, and H_2O (15: 4: 1 ratio, 100 mL), Co(Salen)-PIL (5 mg) and $[Ru(bpy)_3]Cl_2$ (30 mg). After evacuating the container, CO_2 was injected to a pressure of 75 kPa. The photocatalytic reaction was tested for two hours each time and seven cycles were completed.

2. Supplemental figures and data

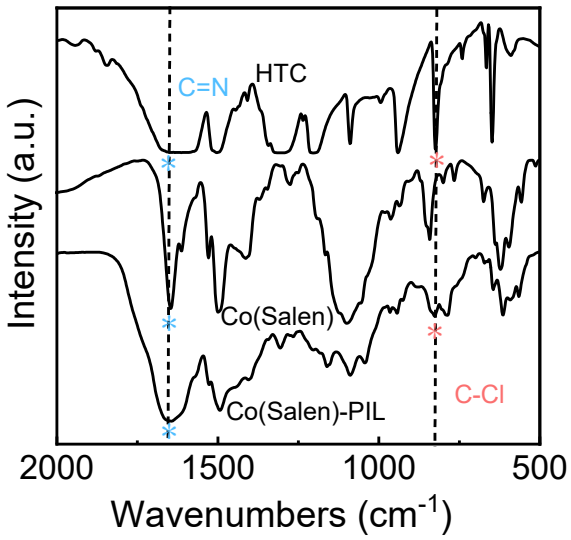


Fig. S1. Fourier-transform infrared (FT-IR) spectra of Co(Salen)-PIL and monomers.

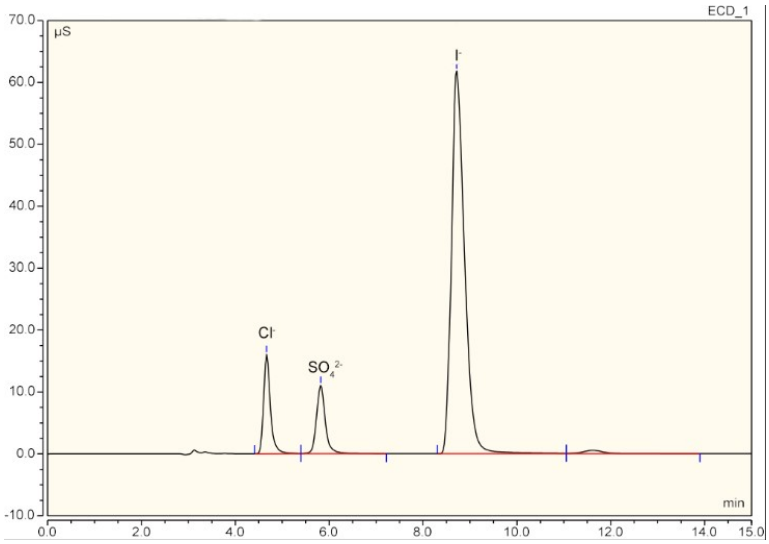
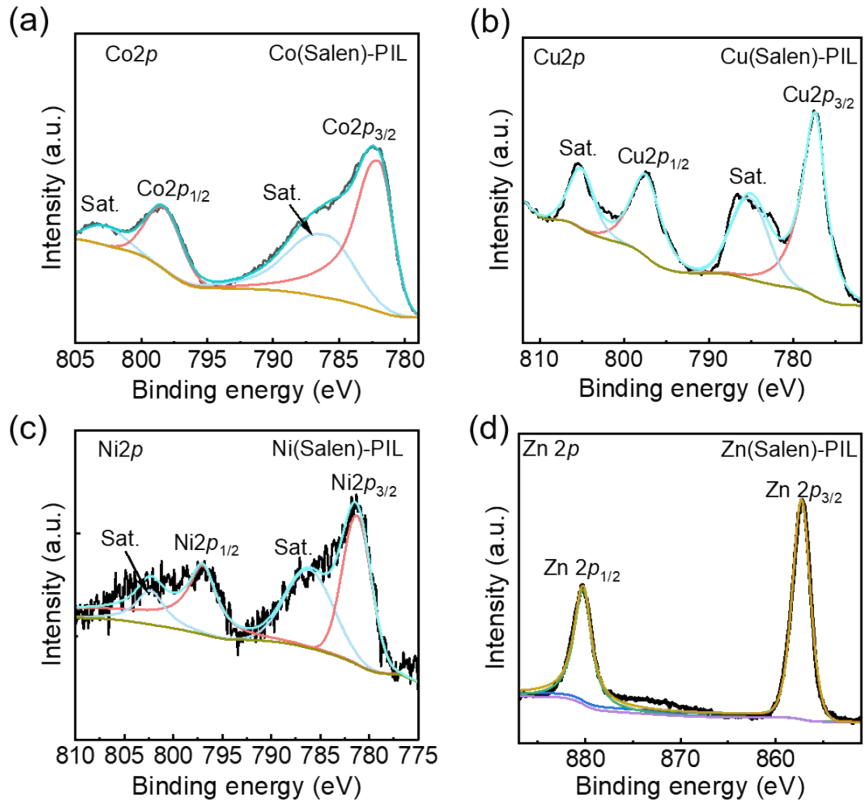


Fig. S2. Ion chromatography of Co(Salen)-PIL.



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129 **Fig. S3.** (a) Co 2*p* XPS spectrum of Co(Salen)-PIL, (b) Cu 2*p* XPS spectrum of Cu(Salen)-PIL, (c)
130 Ni 2*p* XPS spectrum of Ni(Salen)-PIL, (d) Zn 2*p* XPS spectrum of Zn(Salen)-PIL.

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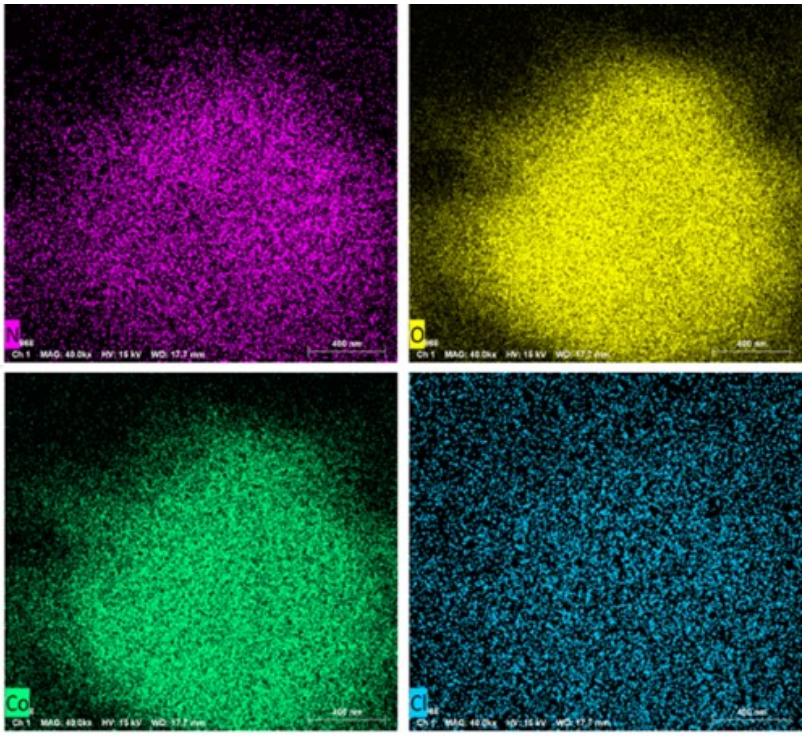


Fig. S4. SEM mapping image of Co(Salen)-PIL.

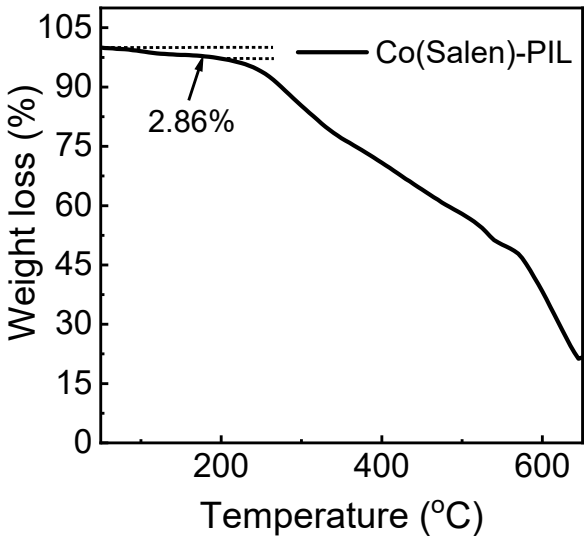
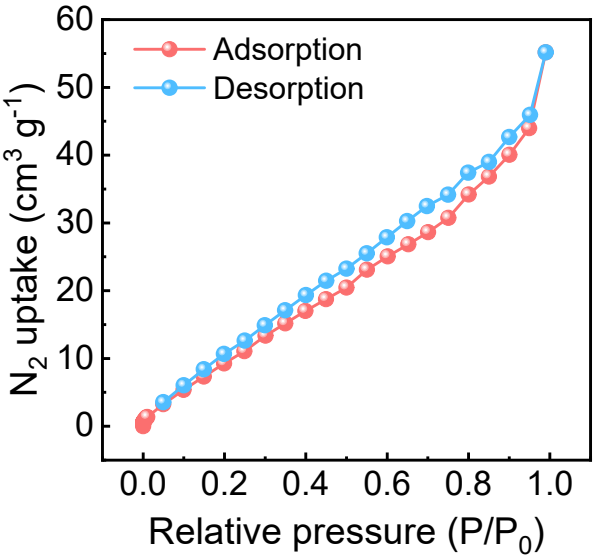


Fig. S5. Thermal gravimetric analysis (TGA) of Co(Salen)-PIL in Ar.



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143 **Fig. S6.** Nitrogen adsorption and desorption isotherms for Co(Salen)-PIL.

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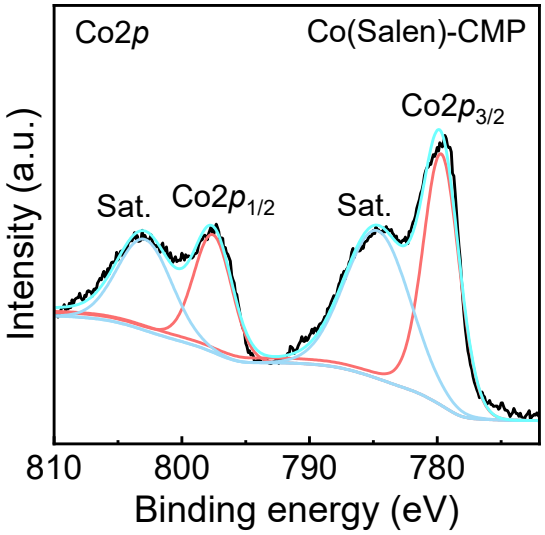

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146 **Fig. S7.** Co 2*p* XPS spectrum of Co(Salen)-CMP.

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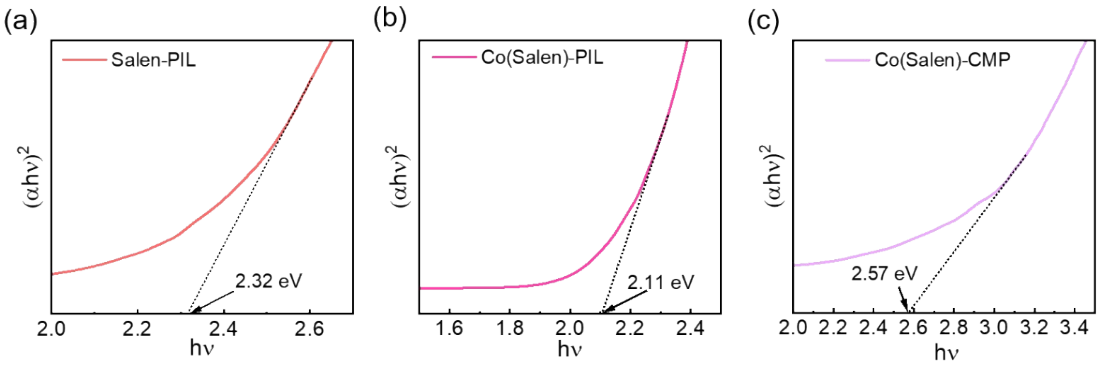


Fig. S8. band gaps of Salen-PIL, Co(Salen)-PIL and Co(Salen)-CMP determined using the Kubelka–Munk function.

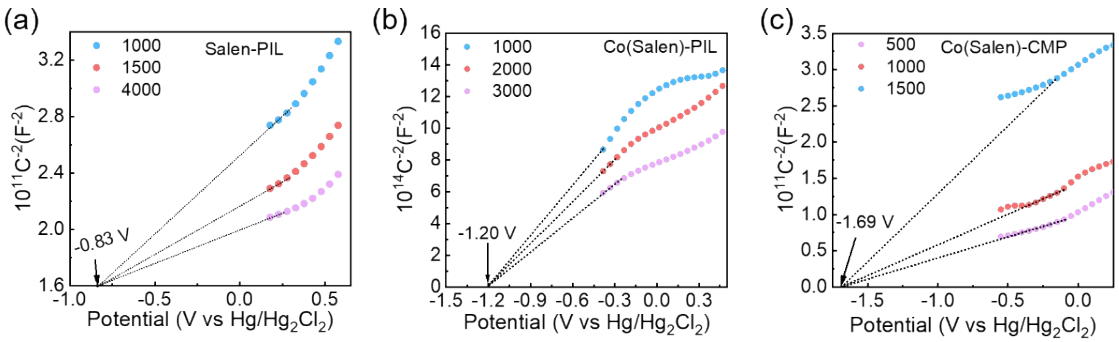
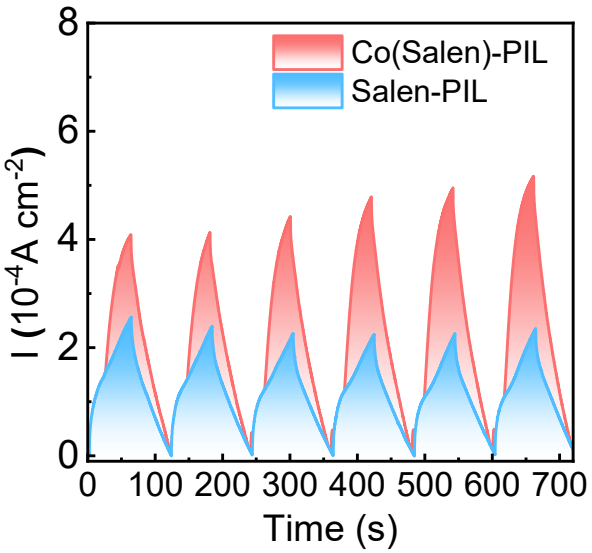


Fig. S9. Mott-Schottky plots of Salen-PIL, Co(Salen)-PIL and Co(Salen)-CMP.



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156 **Fig. S10.** Photocurrent measurement of Salen-PIL and Co(Salen)-PIL.

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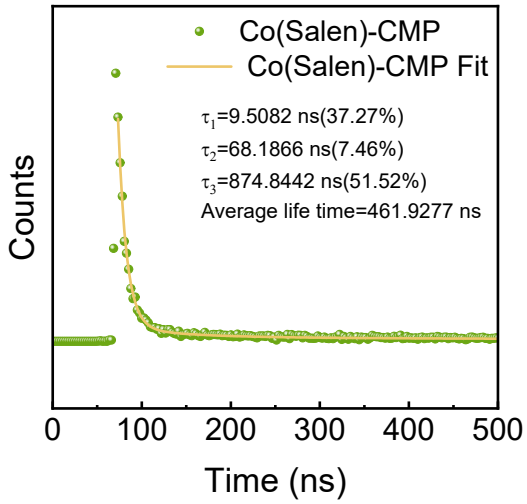
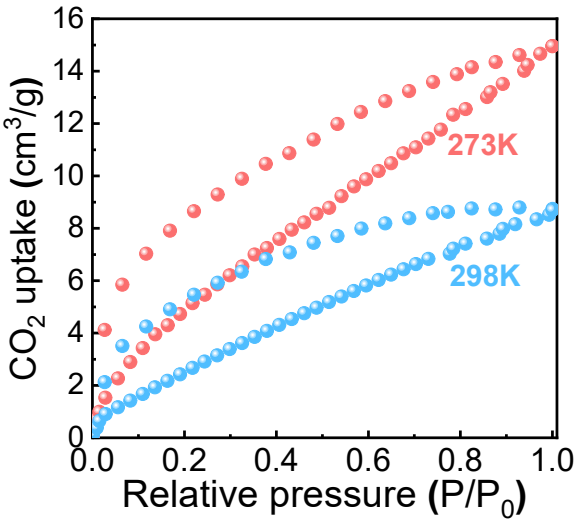


Fig. S11. Time-resolved PL decay spectra for Co(Salen)-CMP.



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163 **Fig. S12.** CO_2 adsorption isotherms for Co(Salen)-PIL at 273 K and 298 K.

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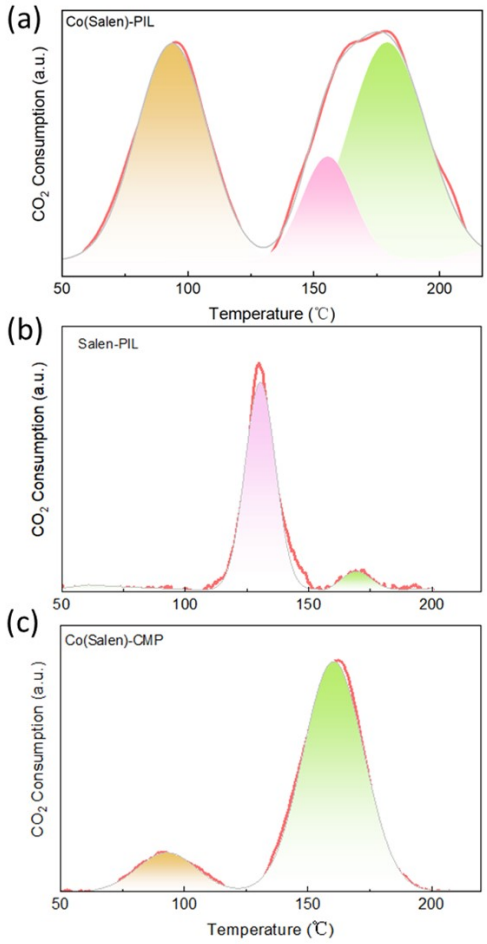

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166 **Fig. S13.** CO_2-TPD curves of the Co(Salen)-PIL, Salen-PIL and Co(Salen)-CMP.

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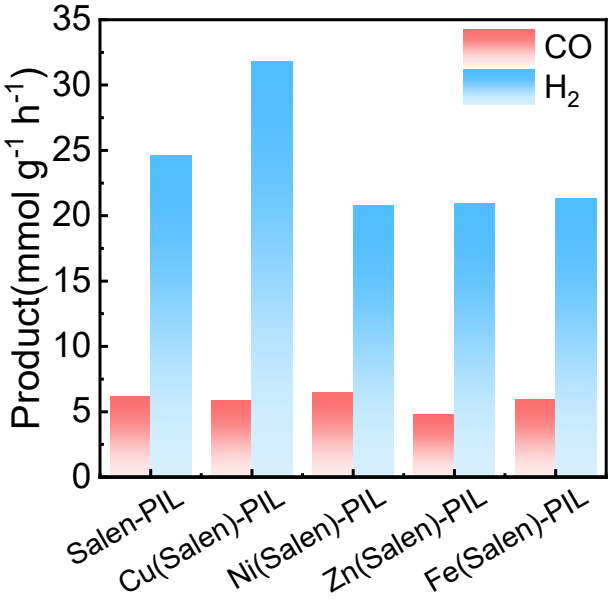

Fig. S14. Photocatalytic CO_2 reduction performance of Salen-PIL and M(Salen)-PILs (M=Cu, Ni, Zn, Fe) under visible light irradiation (λ > 420 nm, 300 W Xe light source), in 100 mL solvent (MeCN / TEOA/ H_2O = 15/ 4/ 1) for 2 h.

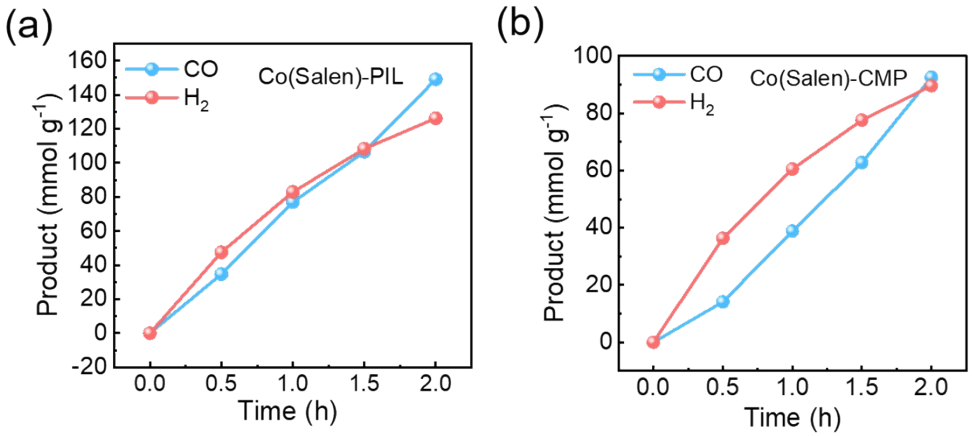

Fig. S15. CO production and H_2 production, under visible light irradiation ($\lambda > 420$ nm, 300 W Xe light source), from 1 mg Co(Salen)-PIL (a) and Co(Salen)-CMP (b) in 100 mL solvent (MeCN/ TEOA/ H_2O = 15/ 4/ 1) for 2 h.

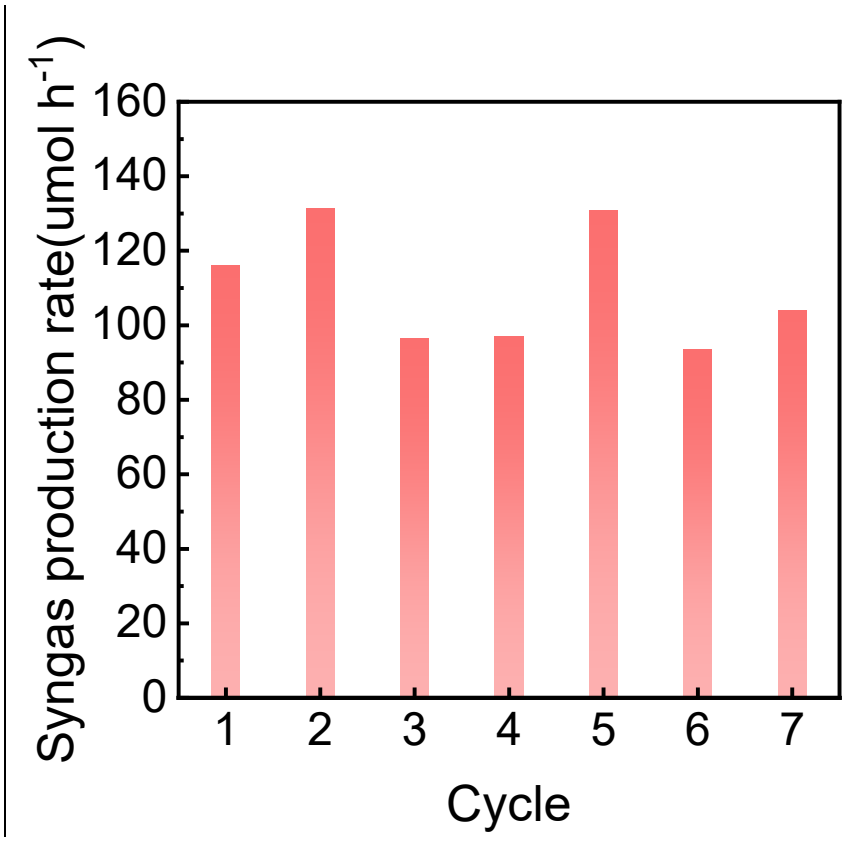

Fig. S16. Stability test of Co(Salen)-PIL in seven recycles for photocatalytic CO_2 reduction.

182 **Table S1.** Previously reported photocatalytic CO_2 reduction.

Catalysts	Co-catalyst	Solvent	CO rate (mmol g^{-1} h^{-1})	H_2 rate (mmol g^{-1} h^{-1})	Ref.
Co(Salen)-PIL	$[Ru(bpy)_3]^{2+}$	CH_3CN/H_2O/TEOA (15/1/4)	74.6	63.1	This work
Co(Salen)-PIL	$[Ru(bpy)_3]^{2+}$	CH_3CN/H_2O/TEOA (31/1/8)	69.3	98.8	This work
Ni-Co_3O_4 NSDHN	$[Ru(bpy)_3]^{2+}$	CH_3CN/H_2O/TEOA (9/4/2)	89.1	80.9	1
Co-TAPT-COF-1	$[Ru(bpy)_3]^{2+}$	CH_3CN/H_2O/TEOA (3/1/1)	8.4	11.3	2
O_1S_3−Ni COPs	$[Ru(bpy)_3]^{2+}$	CH_3CN/H_2O/TEOA (3/1/1)	4.4	4.1	3
$Co(OH)_2$ -GR	$[Ru(bpy)_3]^{2+}$	CH_3CN/H_2O/TIPA (3/2/1)	3.0	10.0	4
CoO-Mo8 UNWs	$[Ru(bpy)_3]^{2+}$	CH_3CN/H_2O/TIPA (4/1/1)	4.2	11.6	5
$Cu_2S@R_{OH}$-$NiCo_2O_3$	$[Ru(bpy)_3]^{2+}$	CH_3CN/H_2O/TIPA (4/1/1)	7.1	2.8	6
POP2-Fe	$[Ru(bpy)_3]^{2+}$	DMF/TEOA (33/1)	3.0	3.8	7
Co@COF-TVBT-Bpy	$[Ru(bpy)_3]^{2+}$	CH_3CN/H_2O/TIPA (4/1/1)	1.1	1.2	8

183

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3. References

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