

Supporting information

Designing Photothermal Catalytic Systems in Multi-Component MOFs for Enhanced Conversion of Carbon Dioxide

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Experimental Methods

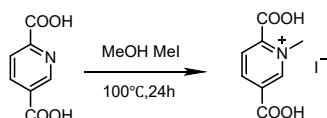
General Methods

All the reagents and solvents were commercially available and used as received. Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). Single-crystal X ray diffraction intensity data for Zr-TTF, Zr-TTF-L₁ and Zr-TTF-L₁-L₂ were collected on a Bruker D8 Venture diffractometer. ¹H-NMR were recorded on a Bruker Avance III 400 NMR spectrometer. FT-IR spectra were recorded on a Vector 27 Bruker Spectrophotometer by transmission through KBr pellets containing the ground crystals in the range 4000 - 400 cm⁻¹. Gas adsorption/desorption isotherms were measured using a Micromeritics ASAP 2020 system, and a BSD-PS4 gas adsorption analyzer. TGA data were obtained on a TGA 4000 thermal analysis system at a heating rate of 10 °C min⁻¹ under air atmosphere. The powder X-ray diffraction (PXRD) patterns were collected at room temperature using a scan speed of 0.1 s/step on a Bruker Advance D8 (40 kV, 40 mA) diffractometer equipped with Cu radiation. Simulated PXRD patterns were generated from single crystal data using Mercury 3.0. UV-Vis absorbance spectra were recorded on Shimadzu UV-3600. ESI-MS data were performed on a LCQ Fleet MS system. Electron paramagnetic resonance (EPR) spectra were obtained by using a Bruker EMX-10/12 variable temperature apparatus at 298 K. An 808 nm laser source were purchased from Shanghai Connet Fiber Optics.

Synthesis

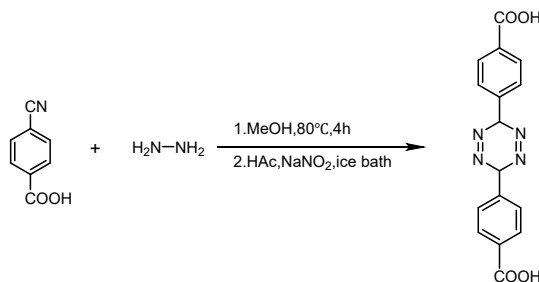
Synthesis of compound Me-H₄TTFTB

Me-H₄TTFTB were prepared adopting the previously reported procedure [1]. Me-H₄TTFTB in red solid was obtained with a yield of 36%. ¹H-NMR (400 MHz, d₆-DMSO) δ 13.06 (br, 4H), δ 7.73 (s, 4H), δ 7.66-7.64 (d, 4H), δ 7.40-7.39 (d, 4H), δ 2.32 (s, 12H); ESI-MS m/z calculated for C₃₈H₂₈O₈S₄ [M-H] 739.08, found 739.07. FT-IR (KBr pellet, cm⁻¹): 2971 w, 2532 w, 1692 vs., 1660 s, 1563 m, 1417 m, 1288 vs., 1257 s, 1190 s, 1125 s, 1048 m, 903 m, 839 m, 758 s, 559 m, 445 m.



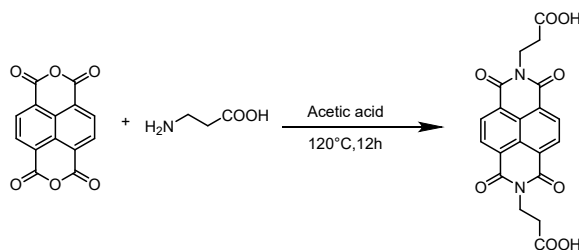
Scheme S1. Synthesis of 2,5-Dicarboxy-1-methylpyridinium (L₁)

Synthesis of 2,5-Dicarboxy-1-methylpyridinium: 2,5-Pyridinedicarboxylic acid (1.0 g, 6 mmol) and iodomethane (1.7 g, 12 mmol) were added into 7 ml Methanol. The mixture was added to a 35 ml Pyrex tube and heated at 100 °C for 24 hours to obtain a brownish-yellow solution, after cooling to room temperature, 25 ml of ethyl acetate was added, and a yellow precipitate was precipitated. Washed with ethyl acetate and ether for three times, dried under vacuum at 45 °C to obtain bright yellow powder (1.48 g, 84%). ¹H-NMR (400 MHz, d₆-DMSO) δ 13.78 (s, 1H), δ 9.16-9.14 (d, 1H), δ 8.47-8.42 (m, 1H), δ 8.19-8.14 (d, 1H), δ 3.91 (s, 3H) ppm.



Scheme S2. Synthesis of 4,4'-(1,2,4,5-tetrazine-3,6-diyl) dibenzoic acid (L₂).

Synthesis of 4,4'-(1,2,4,5-tetrazine-3,6-diyl) dibenzoic acid: A hydrazine solution 35 wt.% in H₂O (40 ml) was added dropwise to 4-cyanobenzoic acid (5.89 g, 40 mmol). Subsequently, the mixture was heated at 80 °C for 4 h. After cooling to room temperature, the formed yellowish precipitate was filtered off and washed with small volumes of MeOH (100 mL). To remove the starting material, the solid was stirred in MeOH for a few minutes, and filtered off the yellowish solid was suspended in acetic acid (120 mL) and oxidized by slow addition an aqueous solution of sodium nitrite (16.56 g in 60 mL H₂O) while in an ice bath and subsequently stirred for 4 h. The purple solid in the suspension was collected by filtration, washed with water and finally dried in an oven at 90 °C to afford 3.49 g (yield ~54%) of 4,4'-(1,2,4,5-tetrazine-3,6-diyl) dibenzoic acid. ¹H-NMR (400 MHz DMSO-d₆) δ 8.24 (d, 4H); δ 8.67 (d, 4H). C₁₆H₁₀N₄O₄, M.W. 322.28.



Scheme S3. Synthesis of 3,3'-(1,3,6,8-tetraoxo-1,3,6,8-tetrahydrobenzo[lmn][3,8] phenanthroline-2,7-diyl)

dipropionic acid (**NDI-P**).

Synthesis of 3,3'-(1,3,6,8-tetraoxo-1,3,6,8-tetrahydrobenzo[lmn][3,8] phenanthroline-2,7-diyl) dipropionic acid: 1,4,5,8-naphthalenetetracarboxylic acid anhydride (1.55 g, 5.81 mmol), β -alanine (1.29 g, 14.41 mmol) were added into acetic acid (40 ml). The reaction mixture was then stirred and heated at 110 °C for 12 h under nitrogen. After the reaction being allowed to cool to room temperature ice water (50 ml) was added into the mixture. The mixture was filtered and the yellow precipitates were obtained to be recrystallized by ethanol. This yield NDI-P as a faint yellow solid (2.1 g, 90%). ¹H-NMR (DMSO-d₆, 400 MHz, ppm): δ 12.43 (br. s, 2H), 8.63 (s, 4H), 4.28-4.24 (t, J = 7.6 Hz, 2H), 2.65-2.61 (t, J = 7.6 Hz, 2H). C₂₀H₁₃N₂O₈ M.W. 409.067; found: 409.067.

Synthesis of Zr₆(Me-TTFTB)_{1.5}O₄(OH)₁₀(H₂O)₆(Zr-TTF): To a solution of Me-H₄TTFTB (0.010 g, 0.013 mmol), ZrCl₄ (0.030 g, 0.129 mmol) and benzoic acid (0.6 g, 4.91 mmol) in 3 mL DMF was added 0.1 mL water. The mixture was capped and heated to 120 °C for 72 h, then cooled to room temperature at a rate of 5 °C / h⁻¹. Orange-yellow cubic crystals (0.007 g) of Zr-TTF were obtained by filtration and washed with DMF and acetone three times. Yield 25.5% (based on Me-H₄TTFTB).

Synthesis of Zr-TTF-L₁: Zr-TTF (100mg), L₁ (200 mg) and DMF (40 mL) were charged in a Pyrex vial. The mixture was heated in a 75 °C oven for 24 h. The crystals of Zr-TTF-L₁ were collected by filtration and washed with fresh DMF 3 times. (101 mg, yield: 96%).

Synthesis of Zr-TTF-L₁-L₂: Zr-TTF-L₁ (100 mg), L₂ (50 mg) and DMF (100 mL) were charged in a Pyrex vial. The mixture was heated in a 75 °C oven for 24 h. The crystals of Zr-TTF-L₁-L₂ were collected by filtration and washed with fresh DMF 3 times. (110 mg, yield: 98%).

Synthesis of Zr-TTF-L₁-L₃: Zr-TTF-L₁ (100 mg), L₃ (200 mg) and DMF (40 mL) were charged in a Pyrex vial. The mixture was heated in a 75 °C oven for 24 h. The crystals of Zr-TTF-L₁-L₃ were collected by filtration and washed with fresh DMF 3 times. (102 mg, yield: 92%).

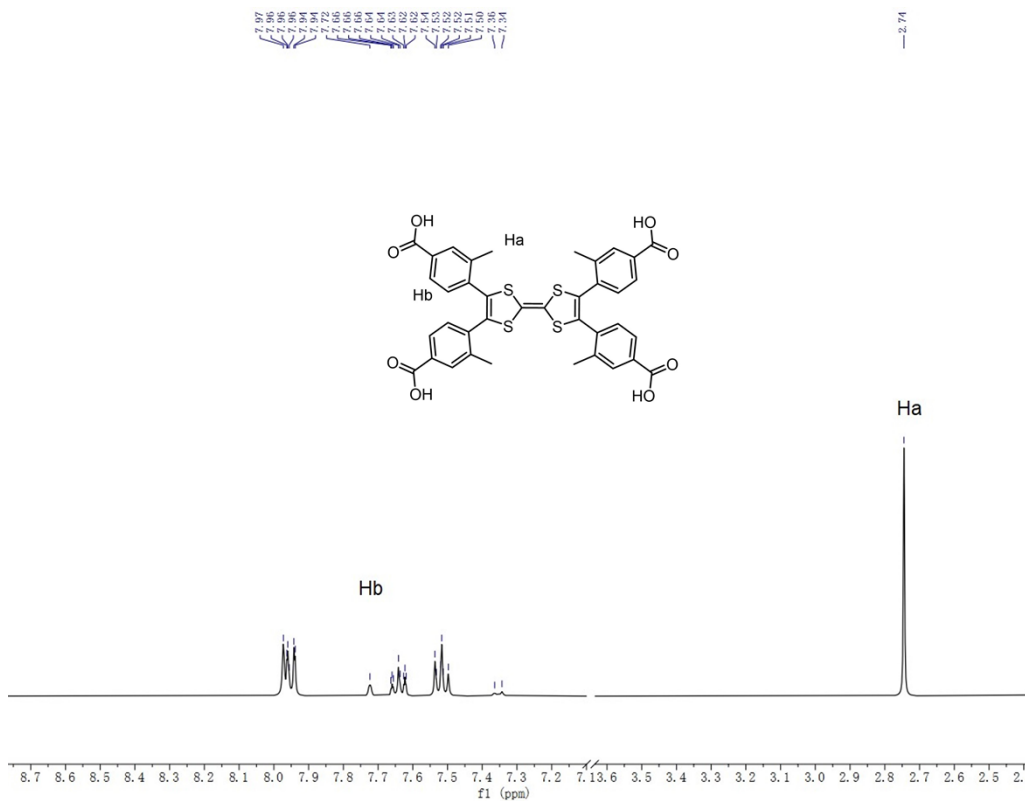


Fig. S1. ¹H-NMR of Zr-TTF.

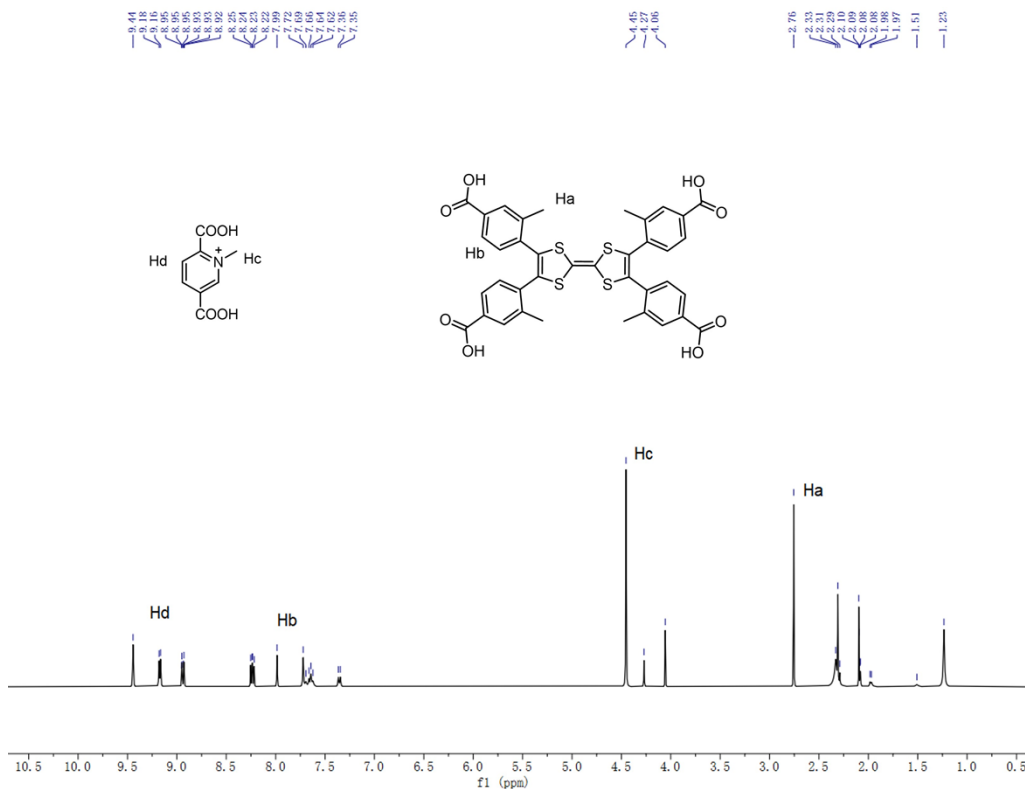


Fig. S2. ¹H-NMR of Zr-TTF-L₁.

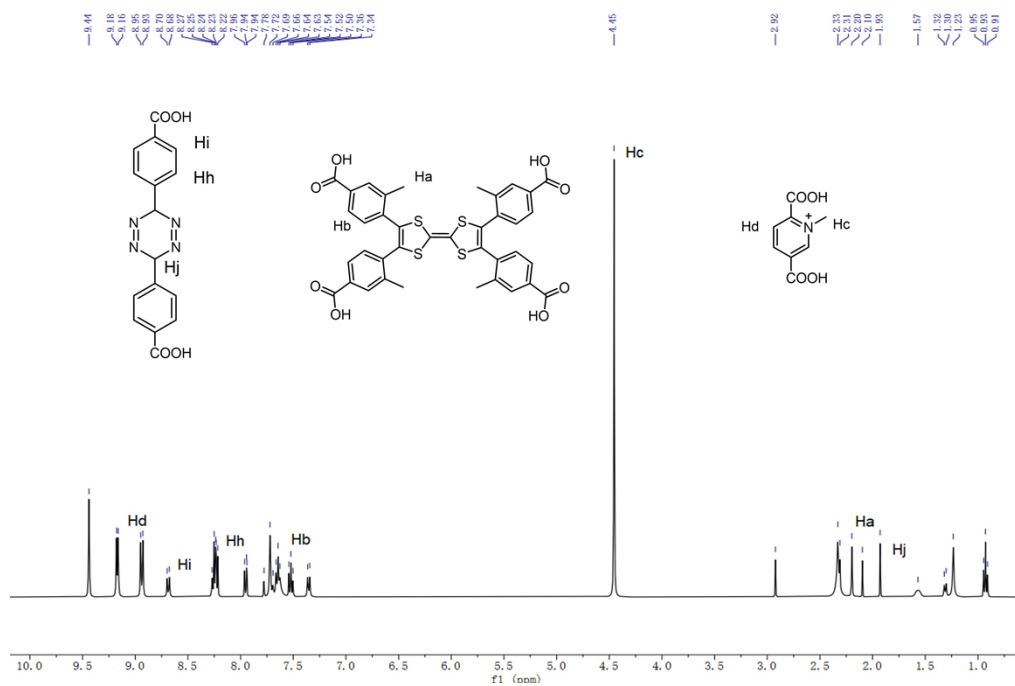


Fig. S3. ¹H-NMR of Zr-TTF-L₁-L₂.

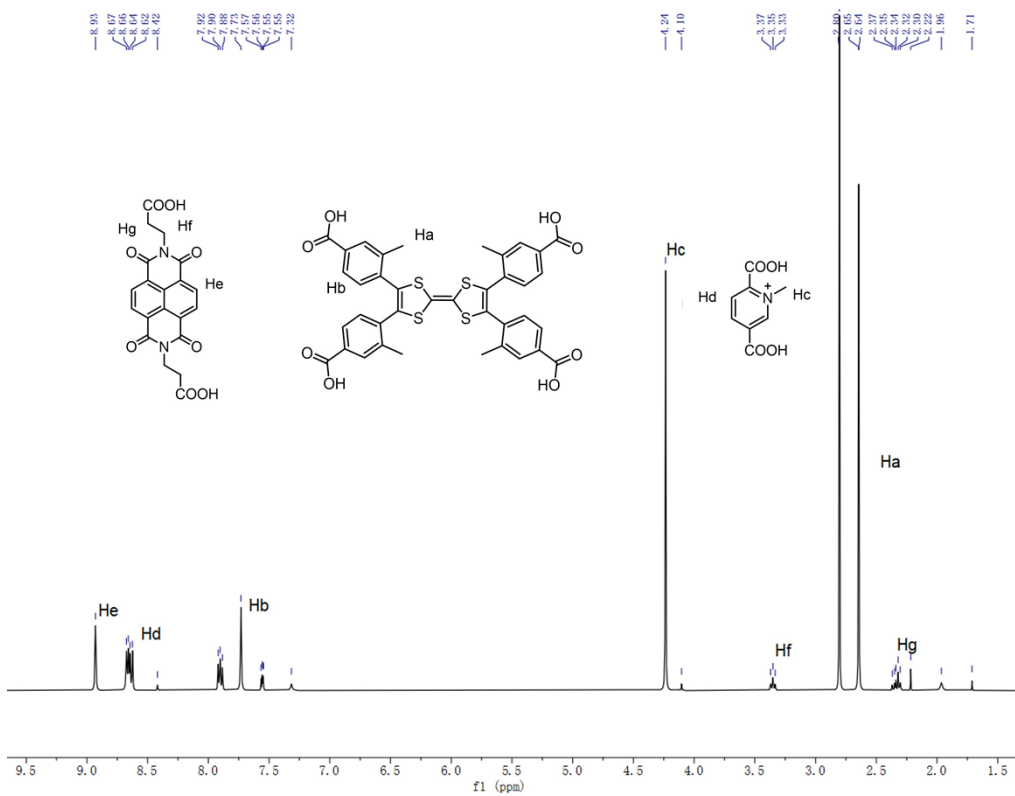


Fig. S4. ¹H-NMR of Zr-TTF-L₁-L₃.

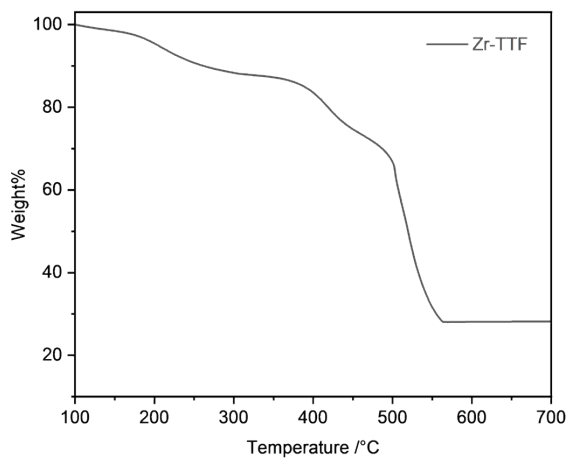


Fig. S5. TGA for the Zr-TTF under air.

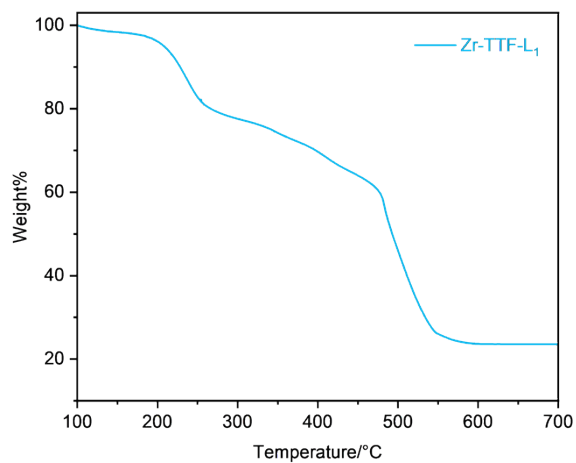


Fig. S6. TGA for the Zr-TTF-L₁ under air.

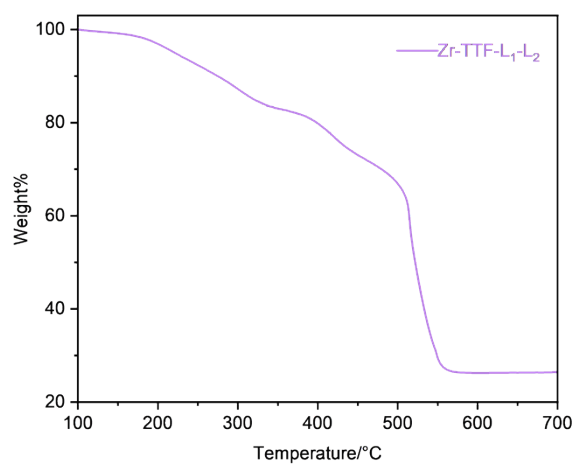


Fig. S7. TGA for the Zr-TTF-L₁-L₂ under air.

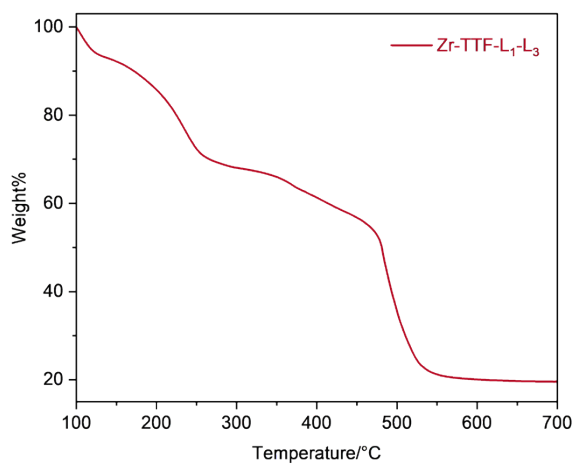


Fig. S8. TGA for the Zr-TTF-L₁-L₃ under air.

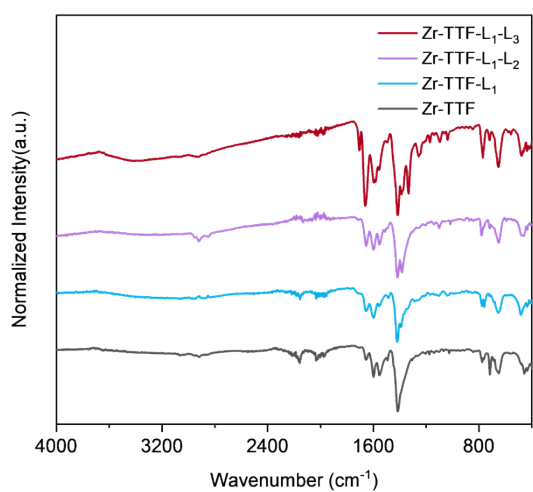


Fig. S9. FT-IR of Zr-TTF (gray), Zr-TTF-L₁ (blue), Zr-TTF-L₁-L₂ (purple), Zr-TTF-L₁-L₃ (red)

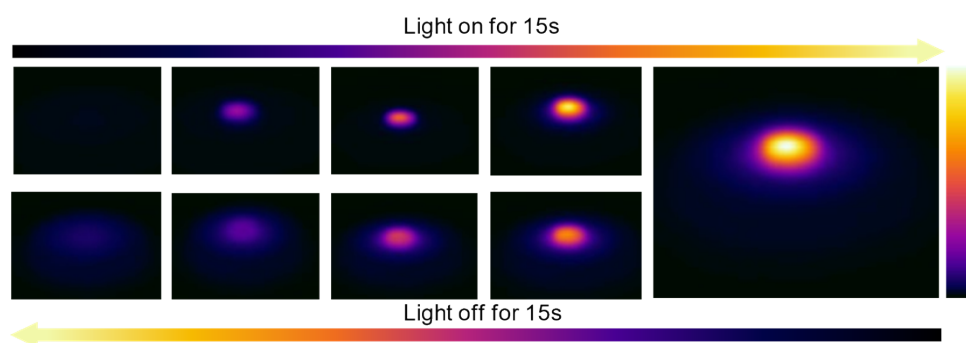


Fig. S10. The IR thermal images of a Zr-TTF-L₁-L₃ pallet under a 0.7 W cm⁻² 808 nm laser.

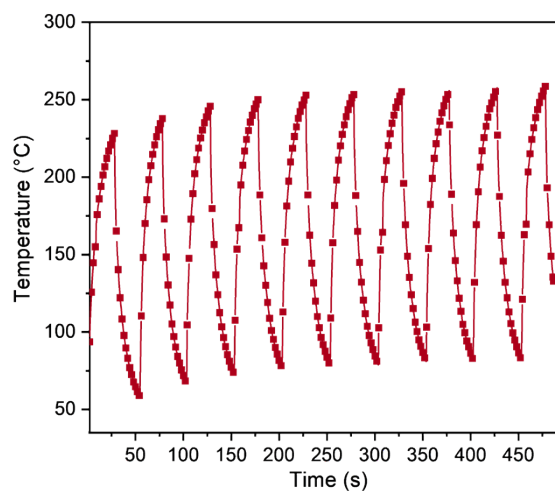


Fig. S11. Photostability test of Zr-TTF-L₁-L₃ during 10 heating/cooling cycles.

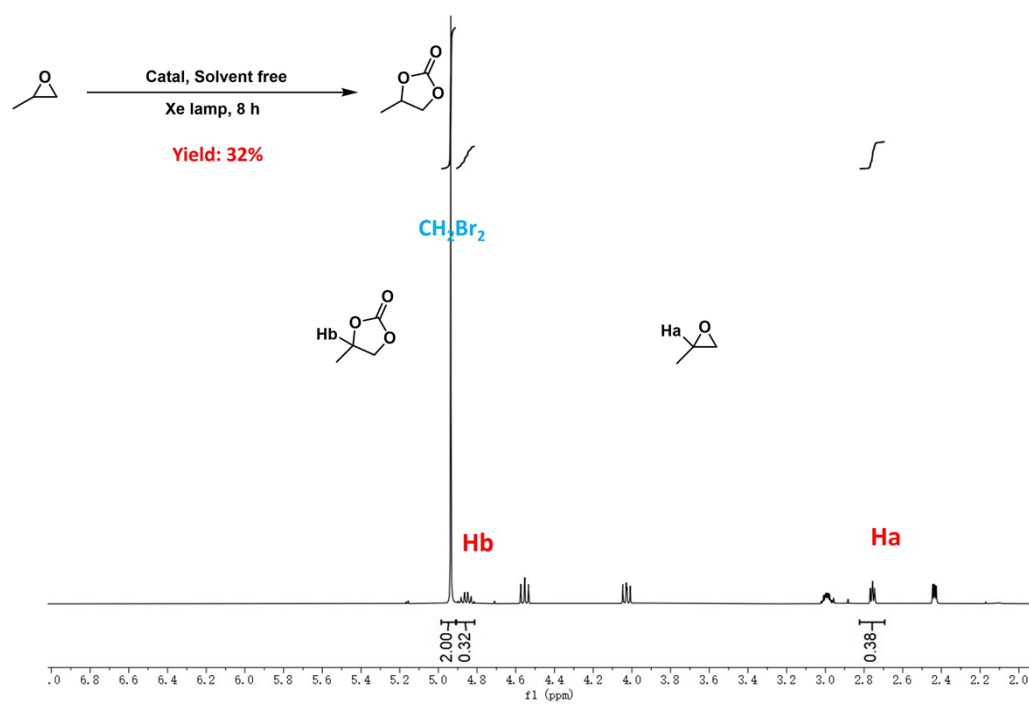


Fig. S12 ¹H-NMR of the product synthesized by cycloaddition of CO₂ to epoxides (R = Me) catalyzed by Zr-TTF-L₃.

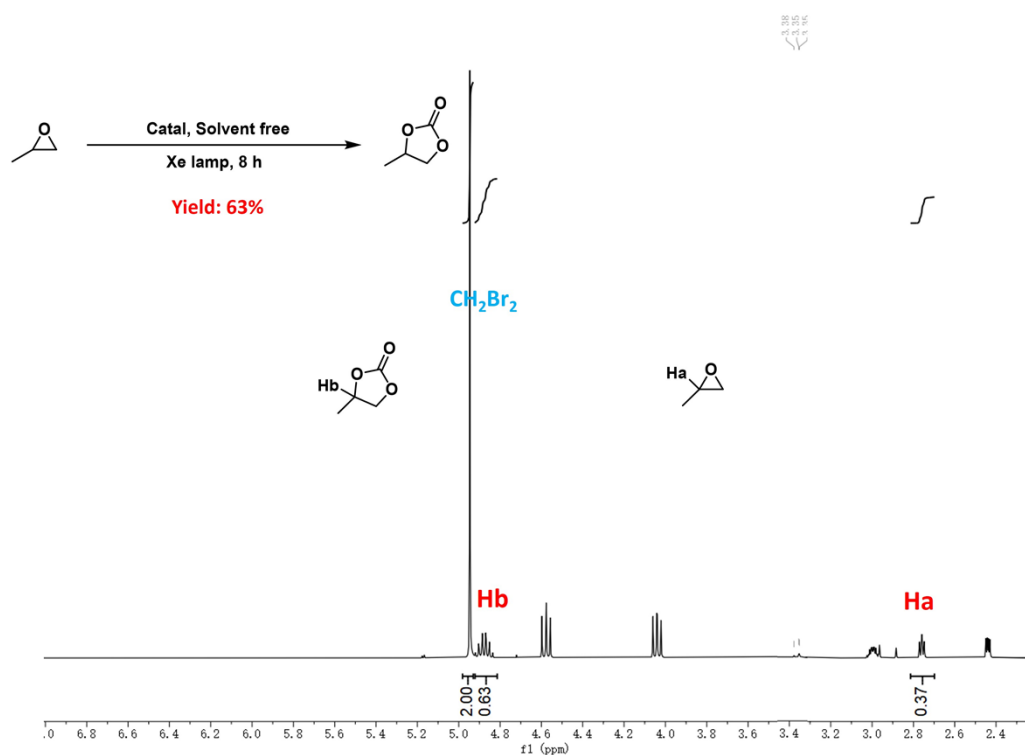


Fig. S13 $^1\text{H-NMR}$ of the product synthesized by cycloaddition of CO_2 to epoxides ($\text{R} = \text{Me}$) catalyzed by $\text{Zr-TTF-L}_1 + \text{Zr-TTF-L}_3$.

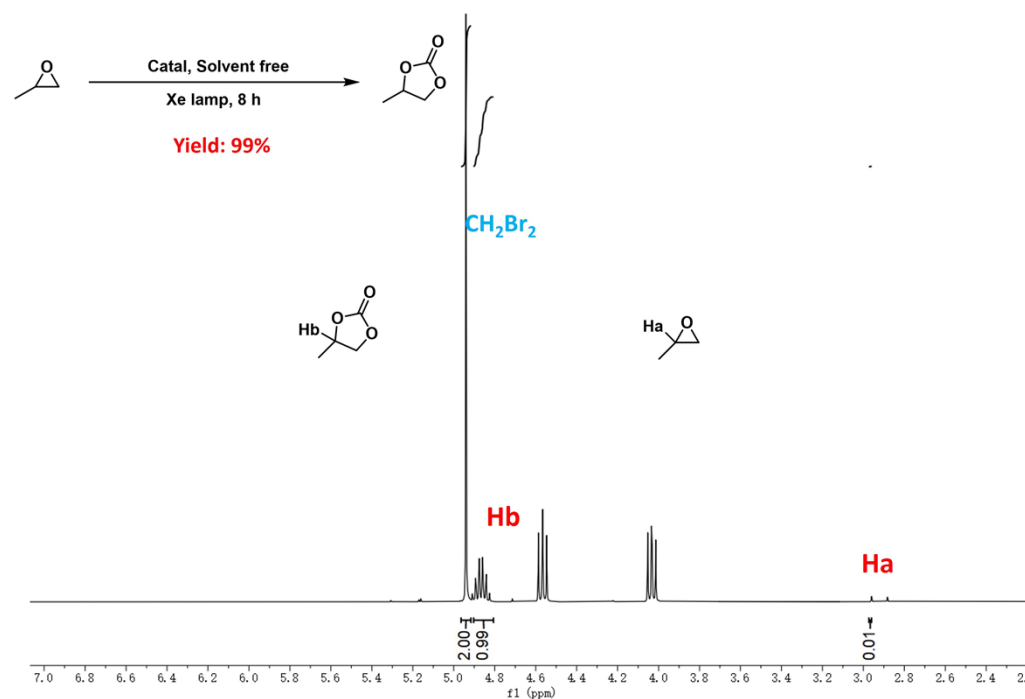


Fig. S14 $^1\text{H-NMR}$ of the product synthesized by cycloaddition of CO_2 to epoxides ($\text{R} = \text{Me}$) catalyzed by $\text{Zr-TTF-L}_1\text{-L}_3$.

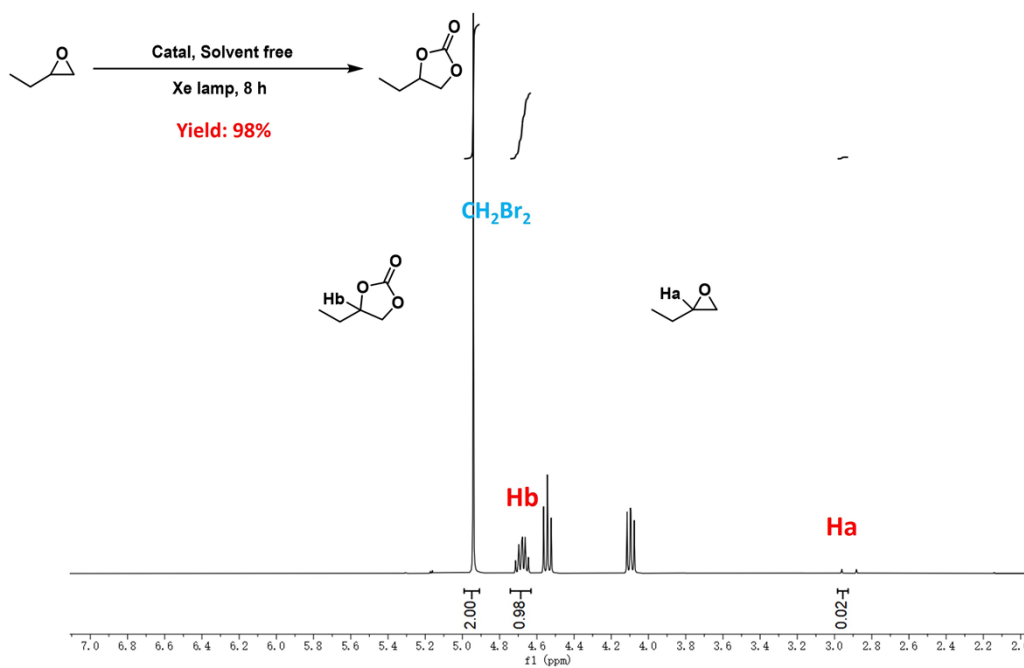


Fig. S15 $^1\text{H-NMR}$ of the product synthesized by cycloaddition of CO_2 to epoxides ($\text{R} = \text{Et}$) catalyzed by $\text{Zr-TTF-L}_1\text{-L}_3$.

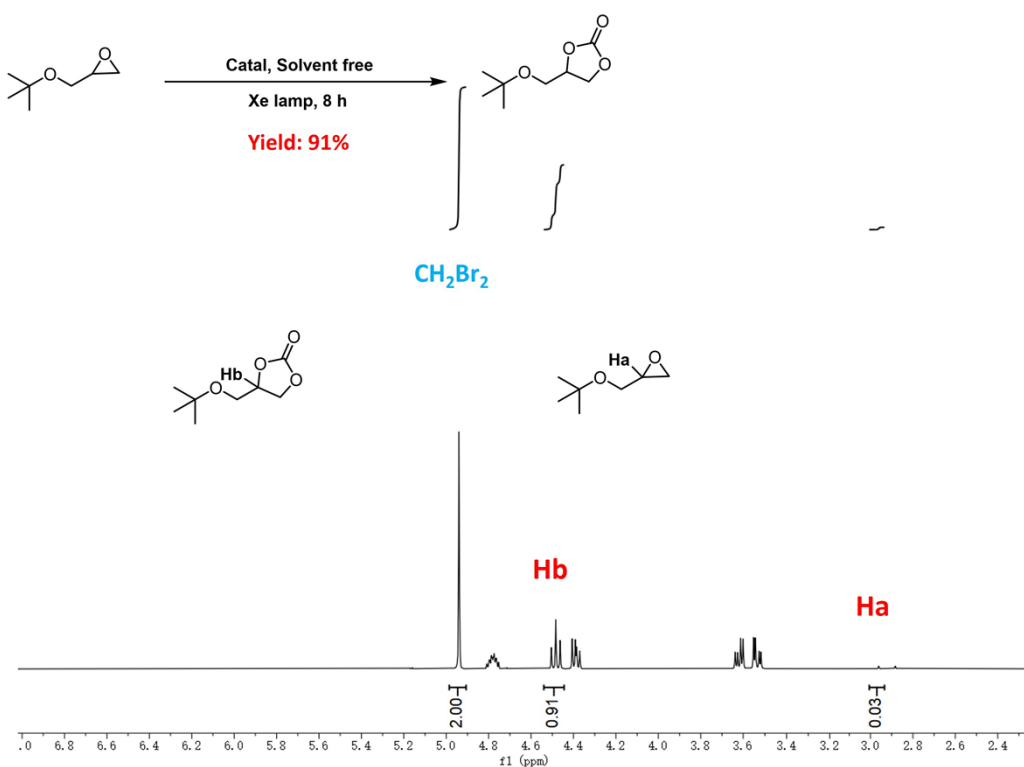


Fig. S16 $^1\text{H-NMR}$ of the product synthesized by cycloaddition of CO_2 to epoxides ($\text{R} = \text{t-BuO}$) catalyzed by $\text{Zr-TTF-L}_1\text{-L}_3$.

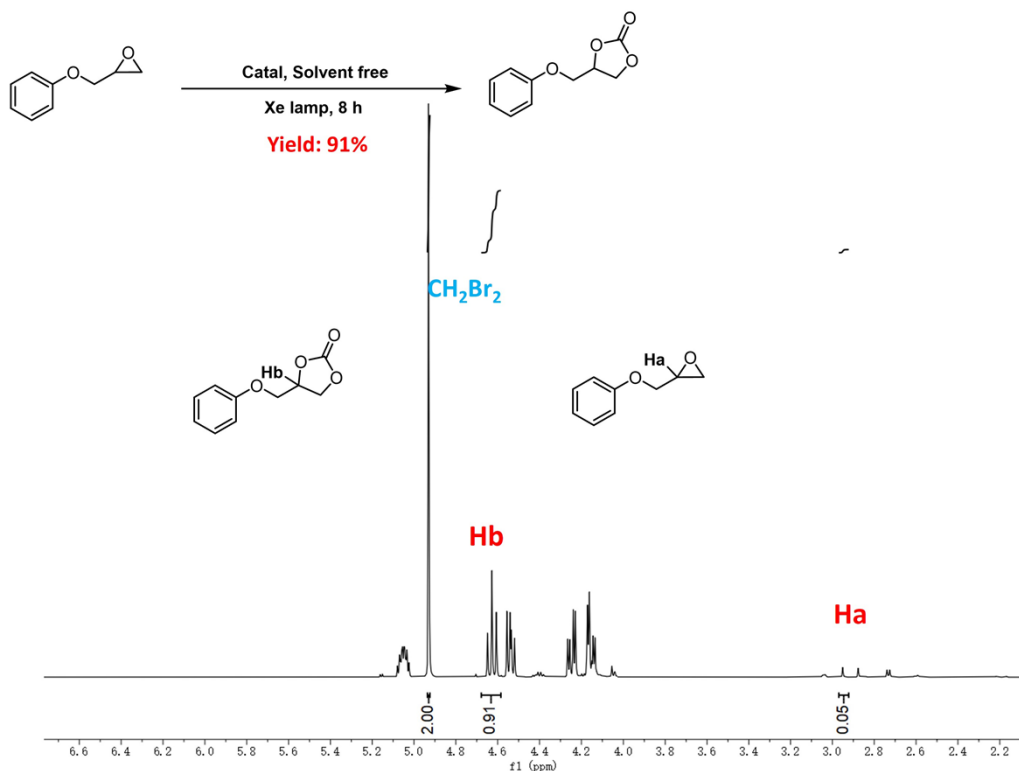


Fig. S17 ¹H-NMR of the product synthesized by cycloaddition of CO₂ to epoxides (R = PhO) catalyzed by Zr-TTF-L₁-L₃.

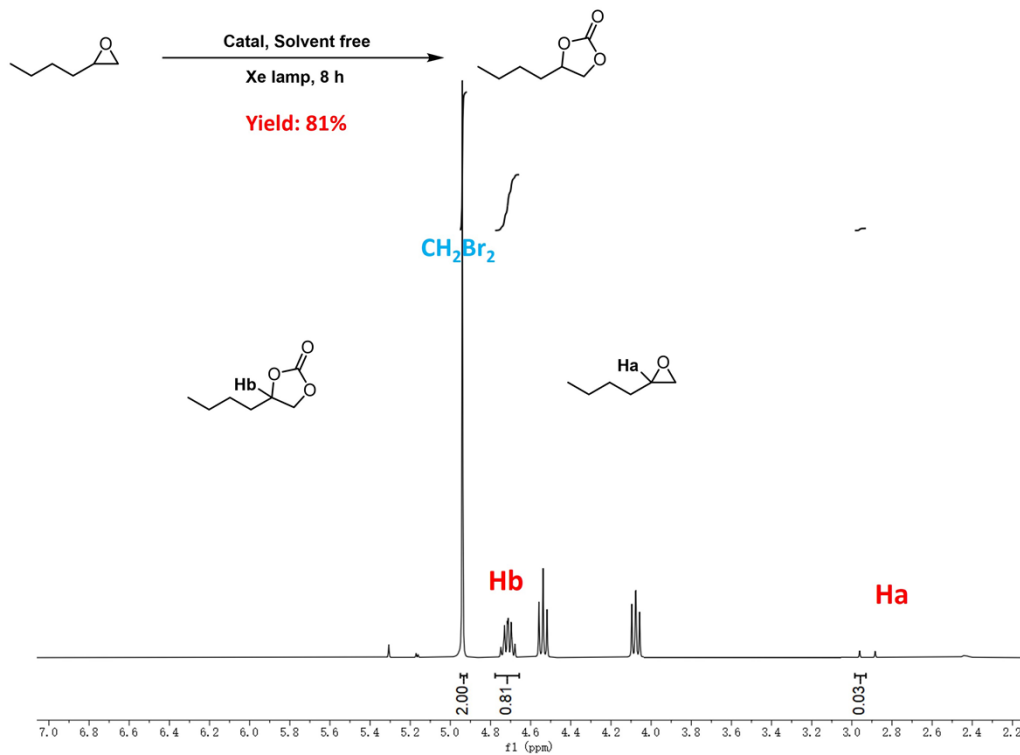


Fig. S18 ¹H-NMR of the product synthesized by cycloaddition of CO₂ to epoxides (R = Bu) catalyzed by Zr-TTF-L₁-L₃.

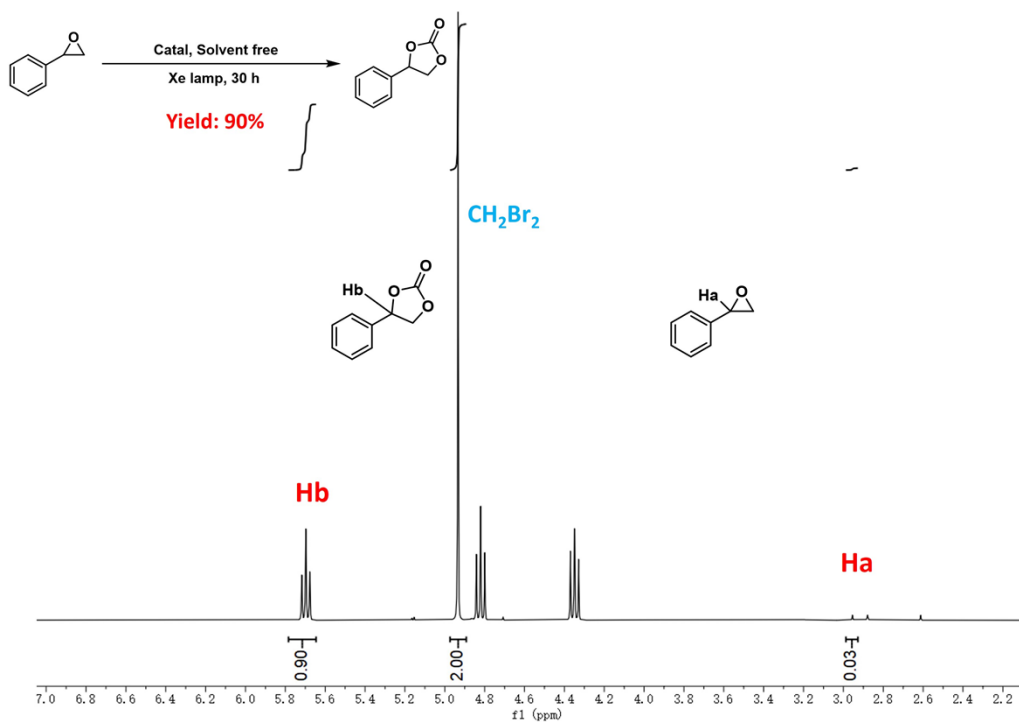


Fig. S19 $^1\text{H-NMR}$ of the product synthesized by cycloaddition of CO_2 to epoxides ($\text{R} = \text{Ph}$) catalyzed by Zr-TTF- $\text{L}_1\text{-L}_3$.

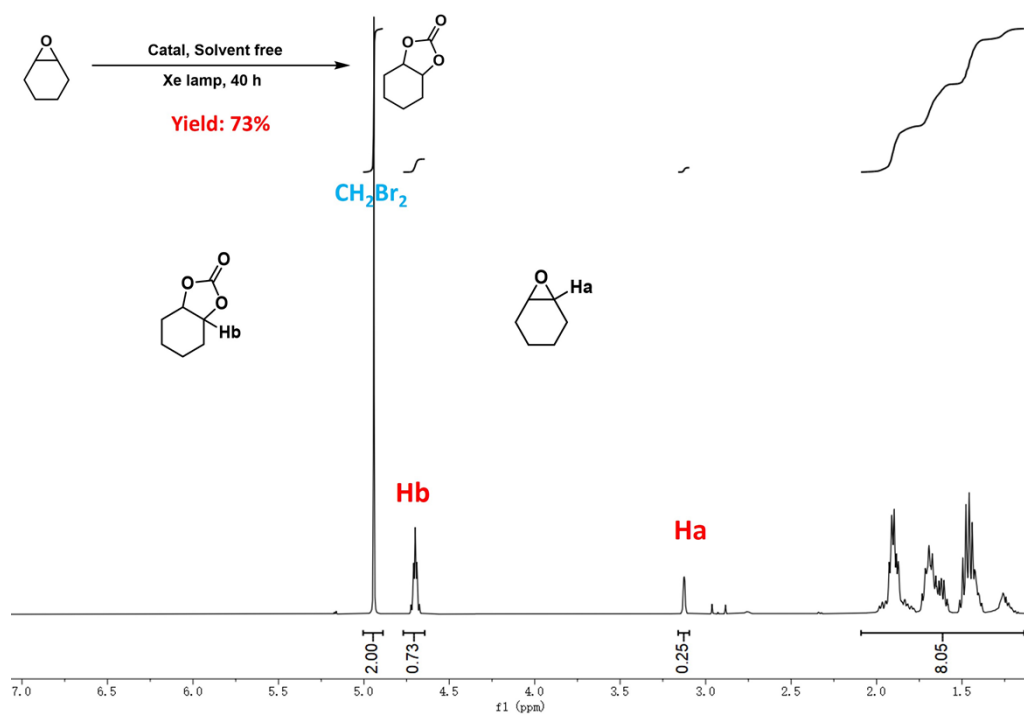


Fig. S20 $^1\text{H-NMR}$ of the product synthesized by cycloaddition of CO_2 to epoxides ($\text{R} = \text{Cy}$) catalyzed by Zr-TTF- $\text{L}_1\text{-L}_3$.

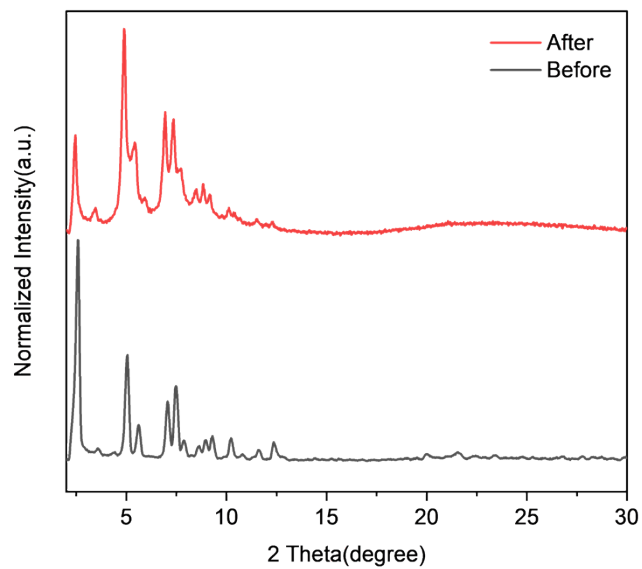


Fig. S21 PXRD of Zr-TTF-L₁-L₃ before and after three catalytic cycles.

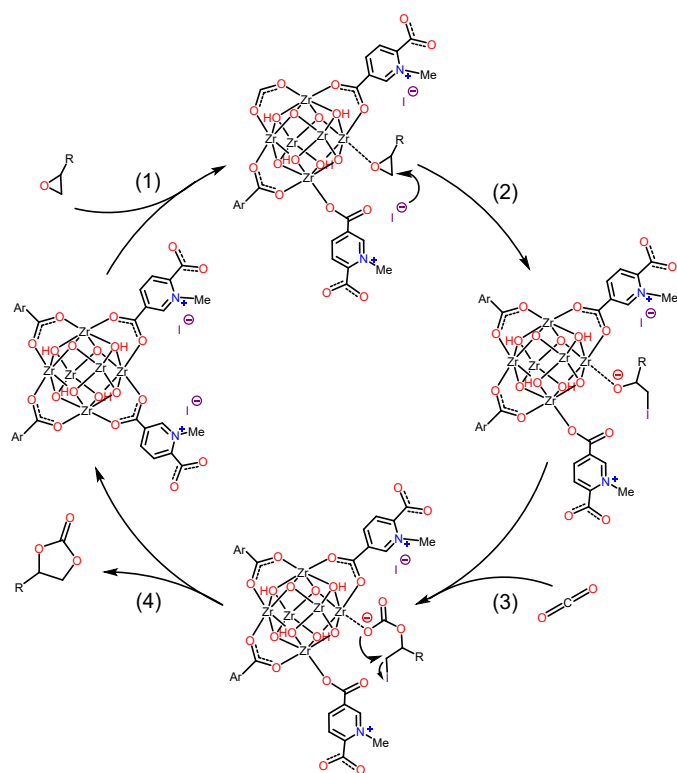
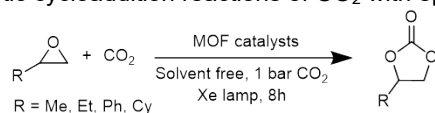


Fig. S22. Proposed mechanism of photothermal catalytic cycloaddition reactions of CO₂ with epoxides by MOF catalysts.

Table S1. Crystal data and structure refinement.

Identification code	Zr-TTF	Zr-TTF-L ₁	Zr-TTF-L ₁ -L ₂
CCDC	1850014	2365200	2365201
Empirical formula	C ₈₄ H ₄₈ O ₄₂ S ₈ Zr ₈	C ₅₃₁ H ₄₂₄ N ₆ O ₂₅₆ S ₄₈ Zr ₄₈	C ₇₂₆ H ₄₅₉ N ₇₀ O ₂₅₆ S ₄₈ Zr ₄₈
Formula weight	2726	16916	20183
Temperature / K	100	100	100
Wavelength / Å	0.71073	1.54184	1.54184
Crystal system	Cubic	Cubic	Cubic
Space group	<i>Pm-3m</i>	<i>Pm-3m</i>	<i>Pm-3m</i>
a / Å	36.1380(13)	35.8923(3)	36.1776(8)
b / Å	36.1380(13)	35.8923(3)	36.1776(8)
c / Å	36.1380(13)	35.8923(3)	36.1776(8)
α / °	90	90	90
β / °	90	90	90
γ / °	90	90	90
Volume / Å ³	47195(5)	46238.5(7)	47350(3)
Z	6	1	1
Density (calculated) / Mg/m ³	0.576	0.607	0.708
Absorption coefficient / mm ⁻¹	0.336	2.898	2.890
F(000)	8048	8395	10045
Theta range for data collection / °	0.976 to 24.702	2.753 to 64.949°	2.115 to 64.599°
Index ranges	-42 ≤ h ≤ 42, -37 ≤ k ≤ 42, -42 ≤ l ≤ 42	-41 ≤ h ≤ 15, -41 ≤ k ≤ 41, -25 ≤ l ≤ 24	-34 ≤ h ≤ 38, -38 ≤ k ≤ 36, -39 ≤ l ≤ 42
Reflections collected	89363	90003	210642
Independent reflections	7534 [R(int) = 0.0718]	7311 [R(int) = 0.1612]	7481 [R(int) = 0.0982]
Completeness to theta	99.2% (24.702°)	98.6% (64.949°)	99.3% (64.599°)
Max. and min. transmission	0.904 and 0.889	0.7525 and 0.5774	0.7525 and 0.6176
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	7534 / 619 / 203	7311 / 354 / 257	7481 / 463 / 326
Goodness-of-fit on F ²	1.156	0.986	1.079
Final R indices [I > 2σ(I)]	R ₁ = 0.0706, wR ₂ = 0.2204	R ₁ = 0.0868, wR ₂ = 0.2449	R ₁ = 0.0613, wR ₂ = 0.1954
R indices (all data)	R ₁ = 0.0769, wR ₂ = 0.2276	R ₁ = 0.1448, wR ₂ = 0.2853	R ₁ = 0.0755, wR ₂ = 0.2037
Largest diff. peak and hole / e.Å ⁻³	0.841 and -1.071	0.812 and -0.722	0.645 and -0.870

Table S2. Photothermal catalytic cycloaddition reactions of CO₂ with epoxides by MOF catalysts.^a

Entry	R	Catalyst	Conditions	Yield (%) ^[a]	TON ^[b]	TOF (h ⁻¹) ^[c]
1	Me	-	Light, 20°C	2	-	-
2	Me	Zr-TTF	Light, 20°C	28	24.4	3.05
3	Me	Zr-TTF-L ₁	Light, 20°C	45	39.2	4.90
4	Me	Zr-TTF-L ₃	Light, 20°C	32	27.8	3.48
5	Me	Zr-TTF-L ₁ + Zr-TTF-L ₃	Light, 20°C	63	54.8	6.85
6	Me	Zr-TTF-L ₁ -L ₃	Dark, 20°C	18	15.7	1.96
7	Me	Zr-TTF-L ₁ -L ₃	Light, 20°C	99	86.1	10.9
8	Me	Zr-TTF-L ₁ -L ₃	Dark, 55°C	64	55.7	6.96
9	Et	Zr-TTF-L ₁ -L ₃	Light, 20°C	98	85.8	10.7
10	t-BuO	Zr-TTF-L ₁ -L ₃	Light, 20°C	91	79.1	9.89
11	PhO	Zr-TTF-L ₁ -L ₃	Light, 20°C	91	79.1	9.89
12	Bu	Zr-TTF-L ₁ -L ₃	Light, 20°C	81	70.2	8.78
13	Ph ^[d]	Zr-TTF-L ₁ -L ₃	Light, 20°C	90	78.3	2.61
14	Cy ^[e]	Zr-TTF-L ₁ -L ₃	Light, 20°C	73	63.5	1.59

^[a] Reaction condition: epoxides (2 mmol), MOF catalysts (0.023 mmol based on Zr), 360 mW·cm⁻², 8 h, 1 bar CO₂. Cyclic carbonate yield was calculated from the ¹H-NMR spectra using mesitylene as the internal standard (Fig. S12-20).

^[b] Turnover number: product (mmol) / Zr (mmol).

^[c] Turnover frequency: product (mmol) / Zr (mmol) / time (h).

^[d] Reaction time is 30 h.

^[e] Cyclohexene oxide as the reactant, reaction time is 40 h.

References

1. Su, J.; Yuan, S.; Wang, T.; Lollar, C. T.; Zuo, J.-L.; Zhang, J.; Zhou, H.-C. Zirconium Metal–Organic Frameworks Incorporating Tetrathiafulvalene Linkers: Robust and Redox-Active Matrices for in Situ Confinement of Metal Nanoparticles. *Chem. Sci.* 2020, 11 (7), 1918–1925.