Supporting Information

A 2D Layered Cobalt-Based Metal-Organic Framework for Photoreduction of CO_2 to Syngas with a Controllable Wide Ratio

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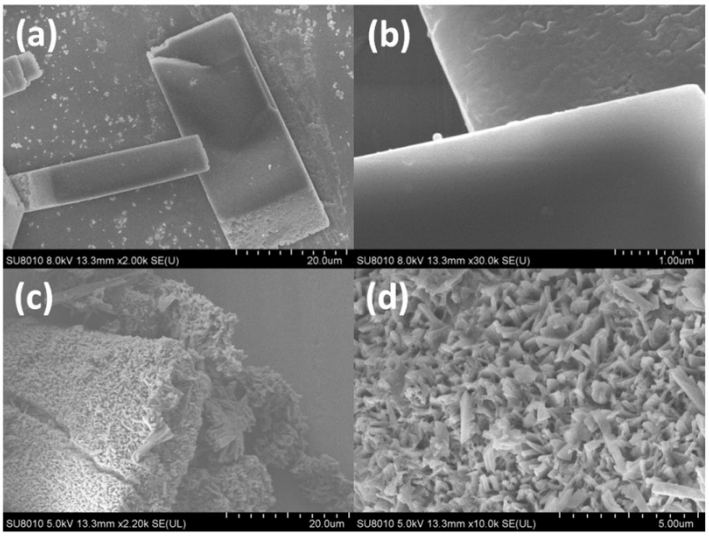

Figure S1. SEM images of Co-TBAPy before photocatalytic CO_2 reduction (a), (b); and after photocatalysis (c), (d).

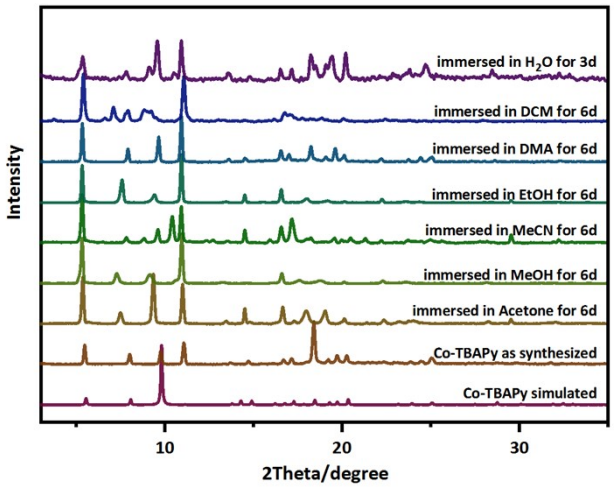

Figure S2. PXRD patterns of Co-TBAPy soaked in different solvents for a period of time.

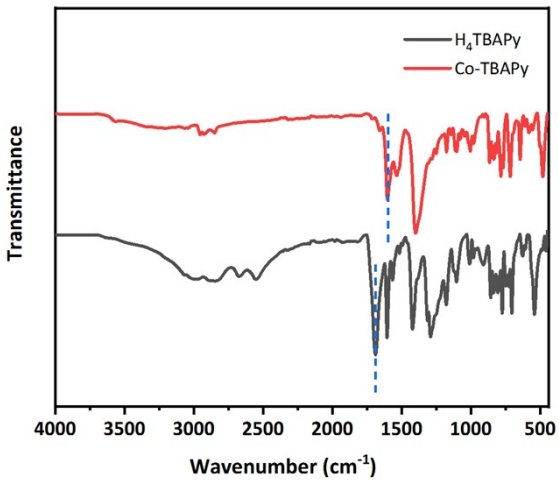

Figure S3. FT-IR specturms of Co-TBAPy and H_4TBAPy.

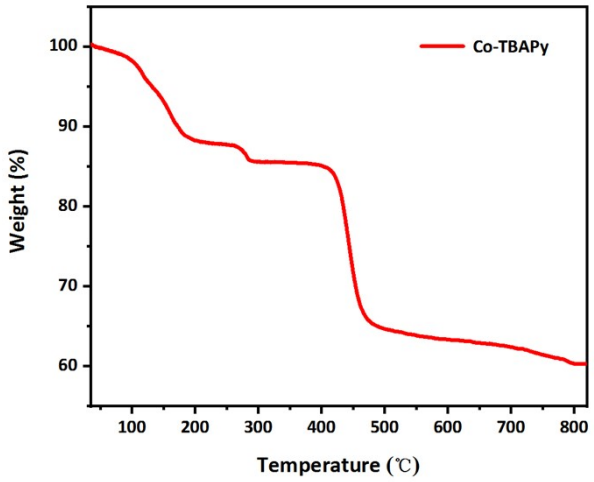

Figure S4. Thermogravimetric (TG) curve of Co-TBAPy.

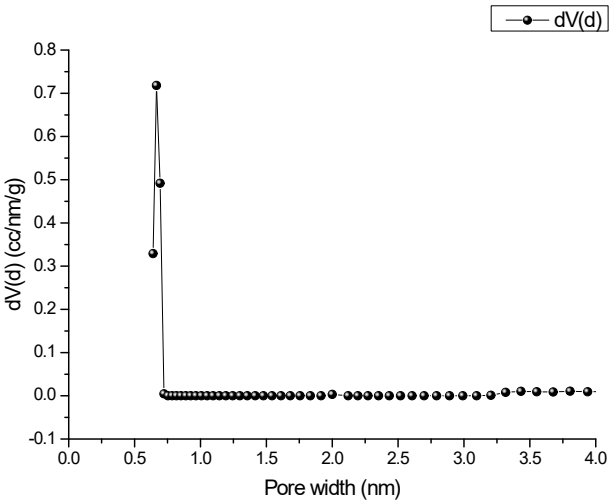

Figure S5. Pore size distribution curve of Co-TBAPy.

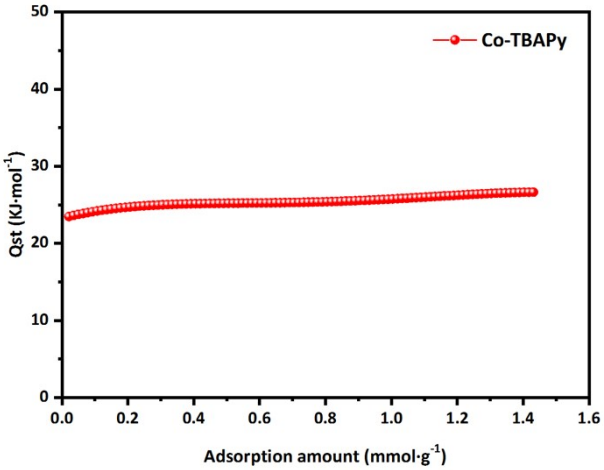

Figure S6. Adsorption enthalpy for carbon dioxide of Co-TBAPy.

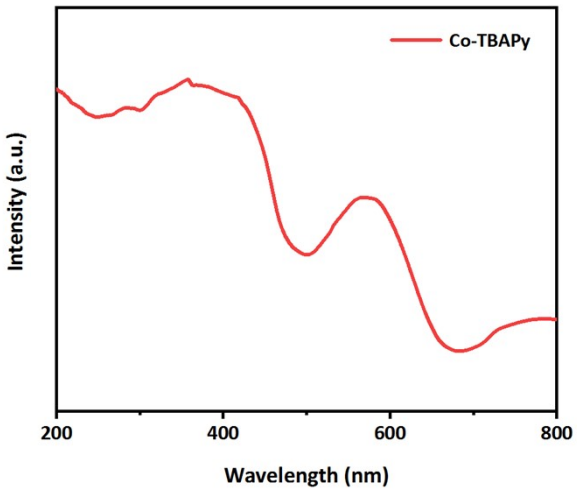

Figure S7. Ultraviolet-visible absorption (UV-Vis) spectrum of Co-TBAPy.

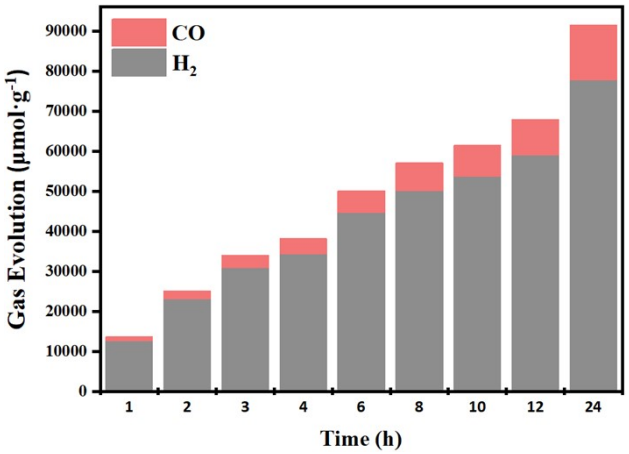

Figure S8. The H_2/CO ratio under the CO_2-saturated MeCN solution (5 mL) containing Co-TBAPy (5 μmol), $[Ru(bpy)_3]Cl_2$ (0.01 mmol), TEOA (1 mL) and H_2O (0.25 mL) at room temperature and irradiated by λ > 420 nm.

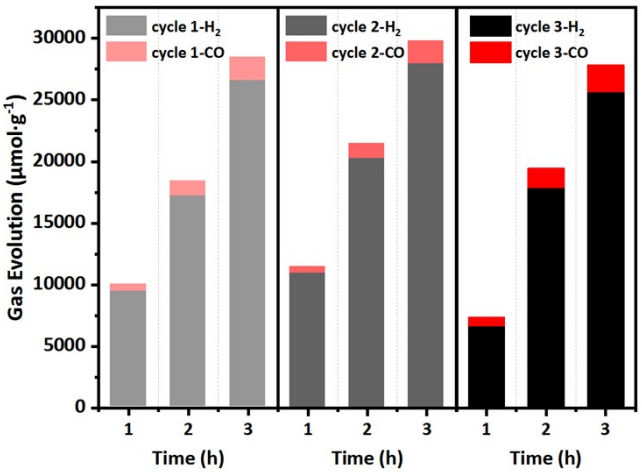

Figure S9. Amounts of CO and H_2 during three-run recycling experiments.

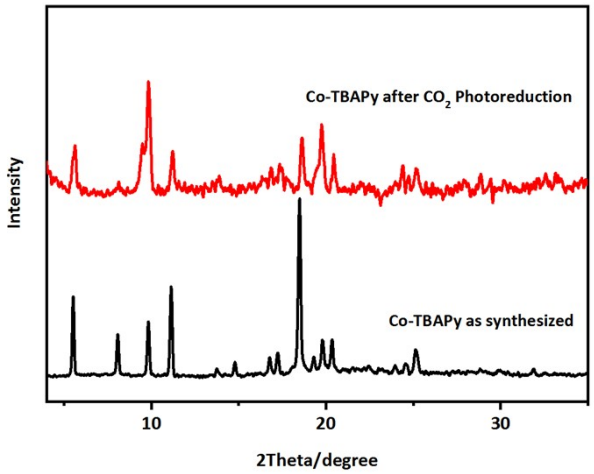

Figure S10. PXRD spectra of Co-TBAPy after photocatalytic CO_2 reduction compared with the as synthesized one.

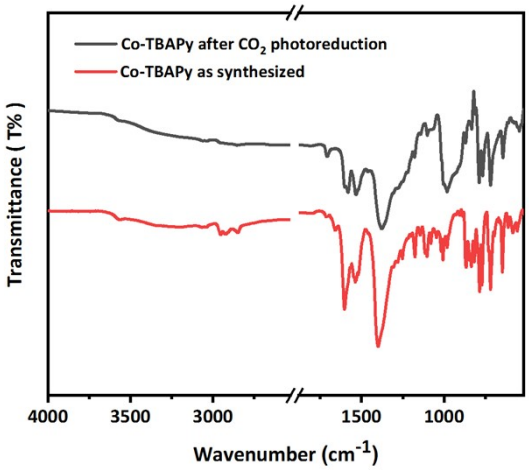

Figure S11. FT-IR spectra of Co-TBAPy after photocatalytic CO_2 reduction compared with the as synthesized one.

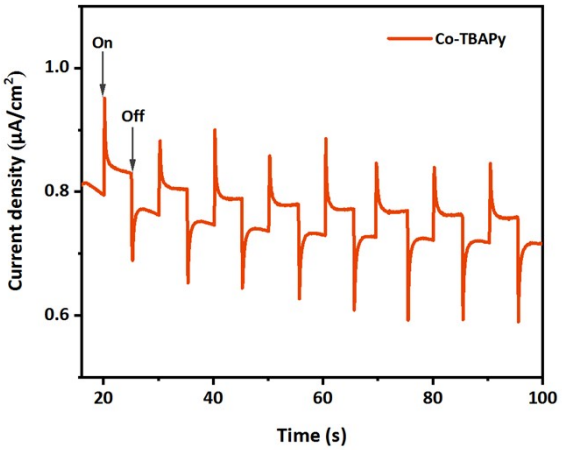

Figure S12. Photocurrent response curves of Co-TBAPy.

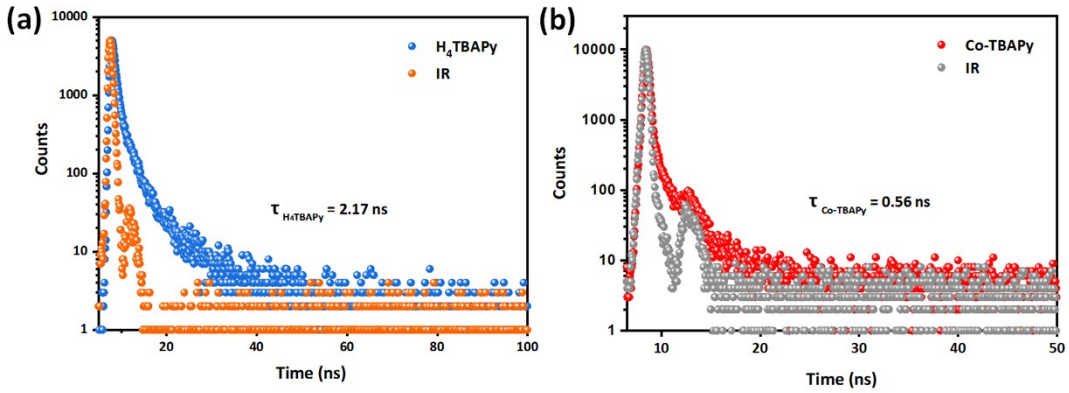

Figure S13. Time-resolved transient PL decay spectra of H_4TBAPy (a) and Co-TBAPy (b).

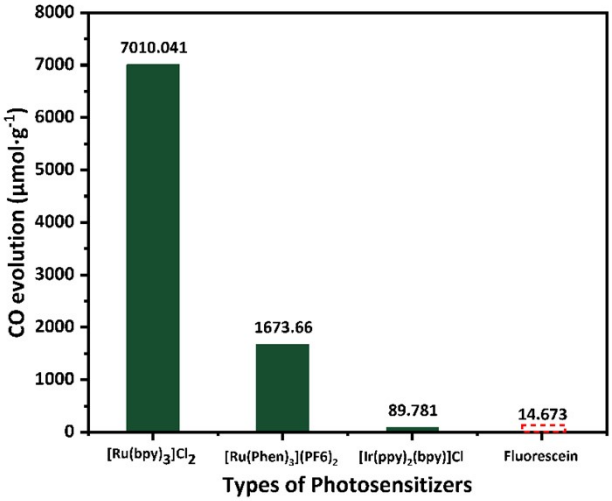

Figure S14. Amounts of CO detected using different types of photosensitizer.

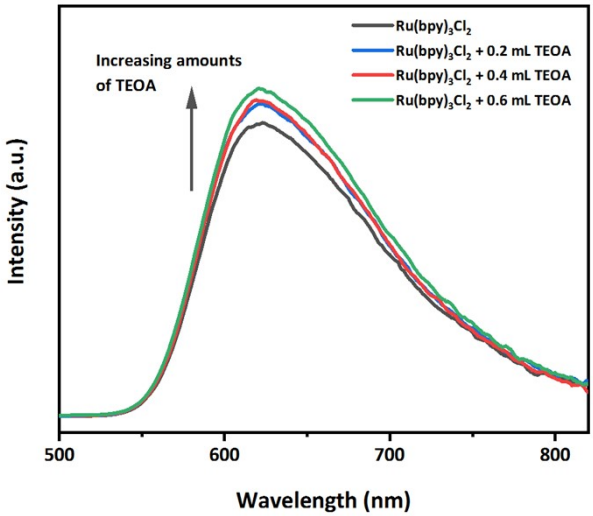

Figure S15. Steady state fluorescence spectra of $[Ru(bpy)_3]Cl_2$ upon the addition of increasing amounts of TEOA. (λ_{ex} = 395 nm)

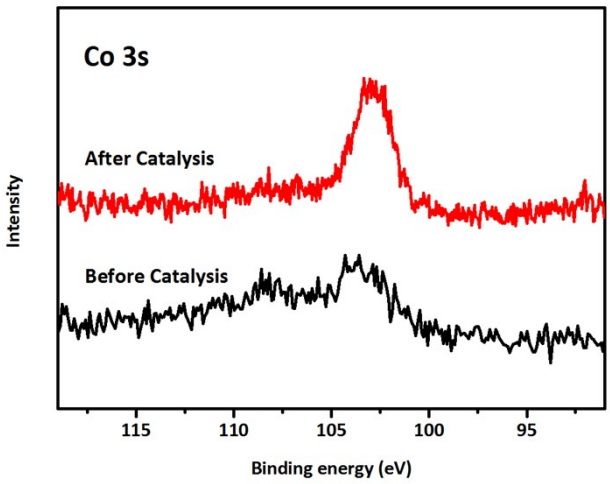

Figure S16. XPS spectrums of Co 3s orbit of Co-TBAPy before and after photocatalysis.

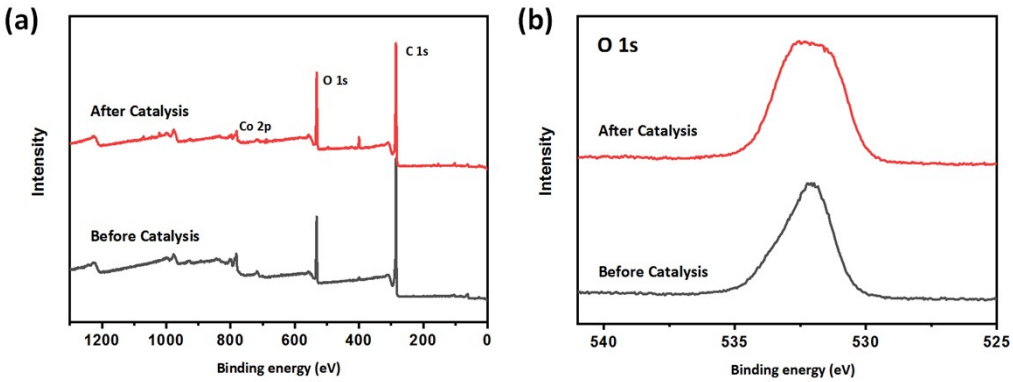

Figure S17. XPS spectrums of all elements (a) and O 1s orbit (b) of Co-TBAPy before and after photocatalysis.

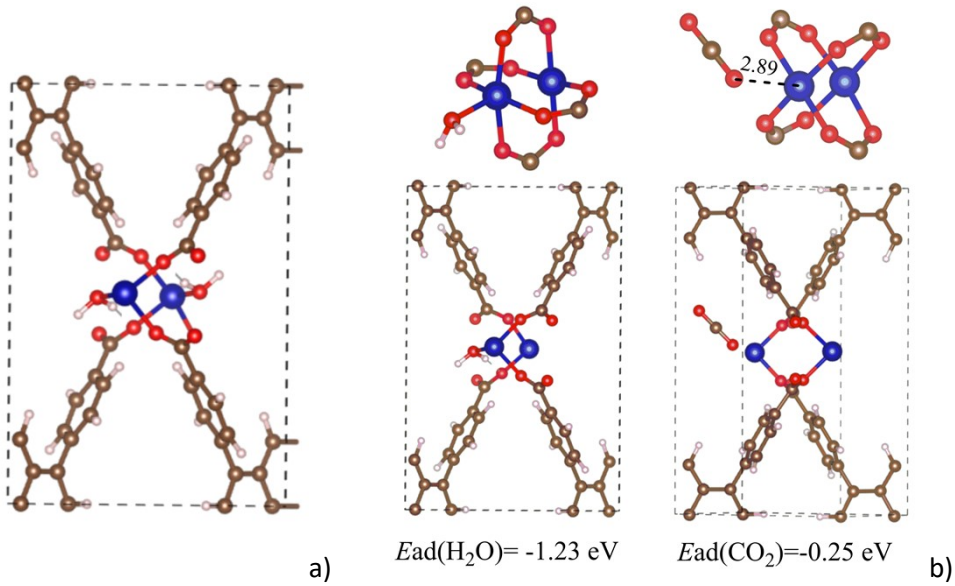

Figure S18. (a) The simulated configuration of Co-TBAPy. (b) The adsorption configuration of H_2O or CO_2 on Co-TBAPy. Color representation: brown, C; red, O; blue, Co; white, H.

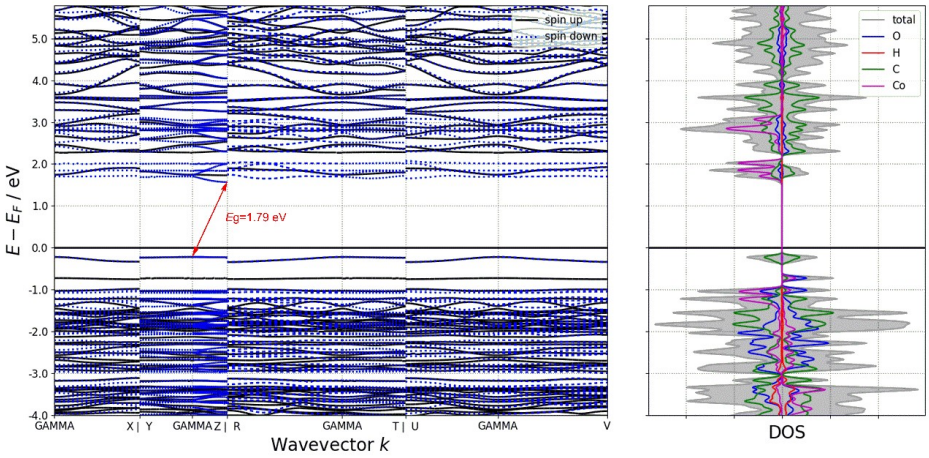

Figure S19. Band structure and density of states for Co-TBAPy.

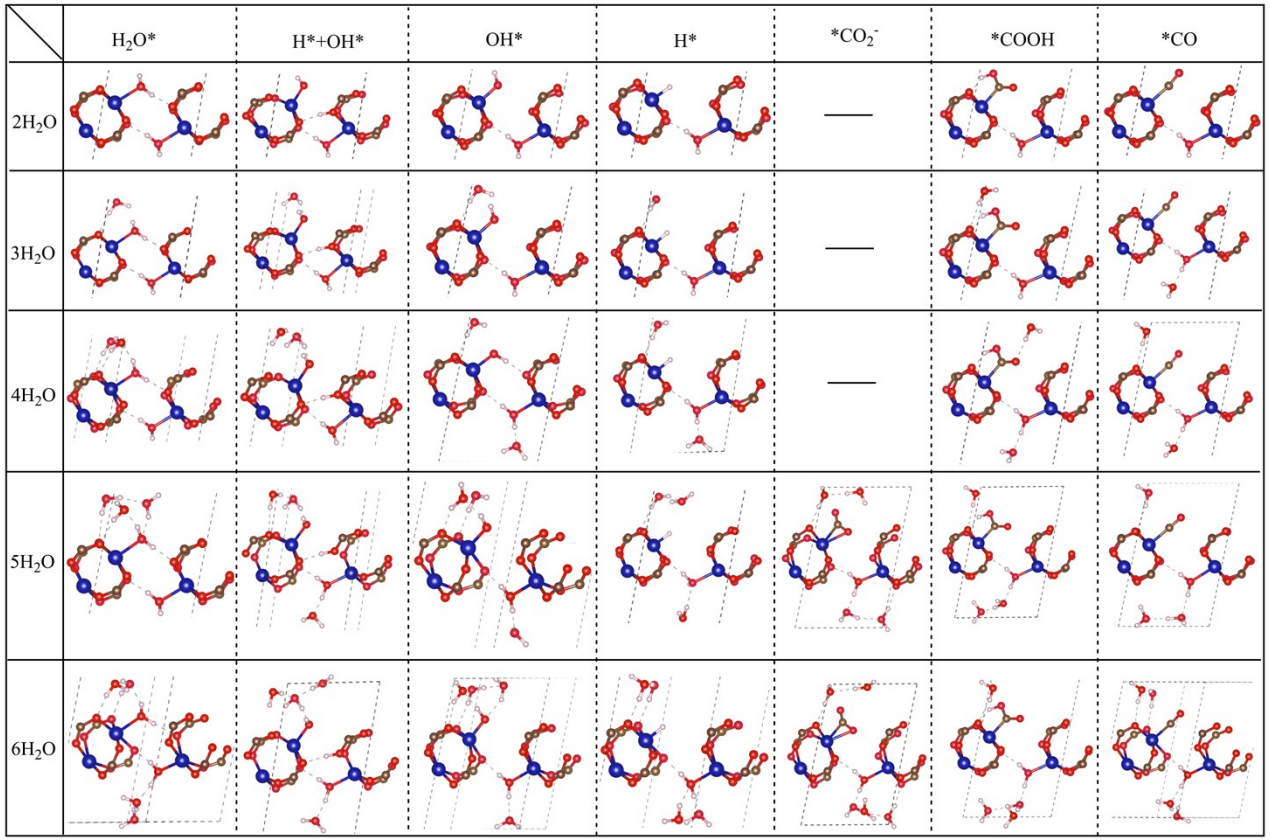

Figure S20. The intermediates along HER and CO_2RR pathways.

Table S1. Crystal data and structure refinement parameters for Co-TBAPy.

Co-TBAPy	
Empirical formula	$C_{22}CoO_5H_{0.5}$
Formula weight	403.65
Temperature/K	273.15
Crystal system	triclinic
Space group	*P*-1
a/Å	6.786(18)
b/Å	10.87(2)
c/Å	15.75(3)
α/°	87.31(6)
β/°	87.77(11)
γ/°	77.39(10)
Volume/Å^3	1132(4)
Z	2
ρ_{calc} (g/cm^3)	1.184
μ/mm^{-1}	0.989
Reflections collected	1624
Independent reflections	1582
Goodness-of-fit on F^2	1.725
Final *R* indexes [*I*>=2σ (I)]	R_1 = 0.2009, wR_2 = 0.4172
Final R indexes [all data]	R_1 = 0.3024, wR_2 = 0.4447

Table S2. The research of photocatalytic reaction conditions.[a]

Entry	CO [μmol]	H_2 [μmol]	TON [b]
1	37.13	52.06	17.84
2[c]	n.d.[d]	n.d.	n.d.
3[e]	1.10	5.06	1.23
4[f]	n.d.	n.d.	n.d.
5[g]	n.d.	n.d.	n.d.
6[h]	0.02	2.24	0.45
7[i]	1.72	32.84	6.91

a. Reaction conditions: $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (0.01 mmol), Co-TBAPy (0.005 mmol, activated), acetonitrile (MeCN, 3.5 mL), H_2O (0.5 mL), TEOA (1 mL), CO_2 (1 atm), LED Lamp, λ > 420 nm, 25 °C, 10 h. b. Turnover number (mol amount of CO and H_2)/(mol amount of Co-TBAPy). c. Without Light. d. Not detectable. e. Without Co-TBAPy. f. Without $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$. g. Without the TEOA. h. Replacing the CO_2 with N_2. i. Low concentration of CO_2. (5% CO_2, 95% N_2).

Table S3. Comparison of the photocatalytic CO_2 reduction performance of analogous MOF-based catalysts, homogeneous complexes and semiconductor materials.

MOFs	**Conditions**							
	Quantity [μmol]	Light [nm]	Time [h]	CO [μmol]	H_2 [μmol]	TON [b]	Syngas ratio (CO/H_2)	Reference
Co-TBAPy	5	λ>420 nm	10	37.13	52.06	17.84	0.14-1.65	This work
Co_6-MOF	5	λ>420 nm	3	39.36	28.13	13.5	—	Ref. 1
Co-MOF-74	0.8	λ>420 nm	0.5	11.7	7.3	23.8	—	Ref. 2
Co-ZIF-9	4	λ>420 nm	2	20.8	3.3	6	—	Ref. 3
$(Co/Ru)_{2.4}$-UiO-67(bpydc)	1 mg	λ=450 nm, LED	16	4.52	9.12	—	0.33-0.53	Ref. 4
BIF-101	24.6	λ>420 nm	10	583	110	28.2	0.5-1	Ref. 5
$[Co_5(btz)_6(NO_3)_4(H_2O)_4]$	0.08	λ>420 nm	70	79.2	140.6	2748	0.06-0.5	Ref. 6
CoAl-LDH/MoS_2	0.2-1.5 $mg{\cdot}mL^{-1}$	λ>400 nm	1	—	—	—	0.07-0.77	Ref. 7

Ref. 1: J. Zhao, Q. Wang, C. Sun, T. Zheng, L. Yan, M. Li, K. Shao, X. Wang and Z. Su, *J. Mater. Chem. A,* 2017, **5**, 12498.

Ref. 2: S. B. Wang, W. S. Yao, J. L. Lin, Z. X. Ding and X. C. Wang, *Angew. Chem. Int. Ed.,* 2014, **53**, 1034.

Ref. 3: S. B. Wang, J. L. Lin and X. C. Wang, *Phys. Chem. Chem. Phys.,* 2014, **16**, 14656.

Ref. 4: M. Liu, Y. F. Mu, S. Yao, S. Guo, X. W. Guo, Z. M. Zhang, T. B. Lu, *Appl. Catal. B: Environ.,* 2019, **245**, 496.

Ref. 5: Q. L. Hong, H. X. Zhang and J. Zhang, *J. Mater. Chem. A,* 2019, **7**, 17272.

Ref. 6: M. Sun，C. Wang，C. Y. Sun，M. Zhang，Z. M. Su. *J. Catal.*, 2020, **385**, 70.

Ref. 7: C. H. Qiu, X. J, Hao, L. Tan, X. Wang, W. J. Cao, J. Y. Liu, Y. F. Zhao and Y. F. Song. *Chem. Commun*., 2020, **56**, 5354.