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Supporting Information

A novel cobalt-anchored covalent organic framework for photocatalytic conversion of CO_2 into widely adjustable syngas

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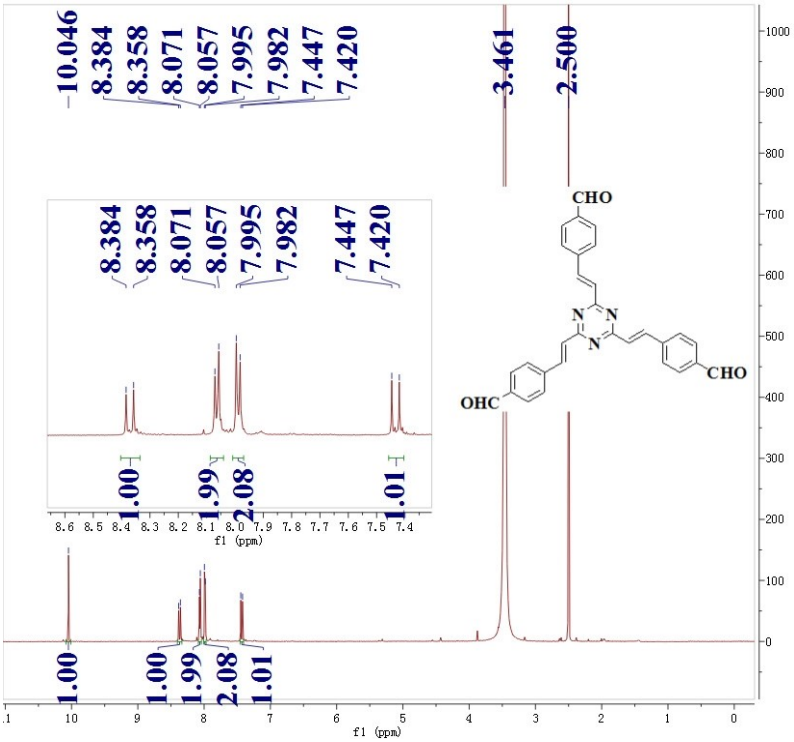

Fig. S1 ^{1}H NMR spectrum of TVBT.

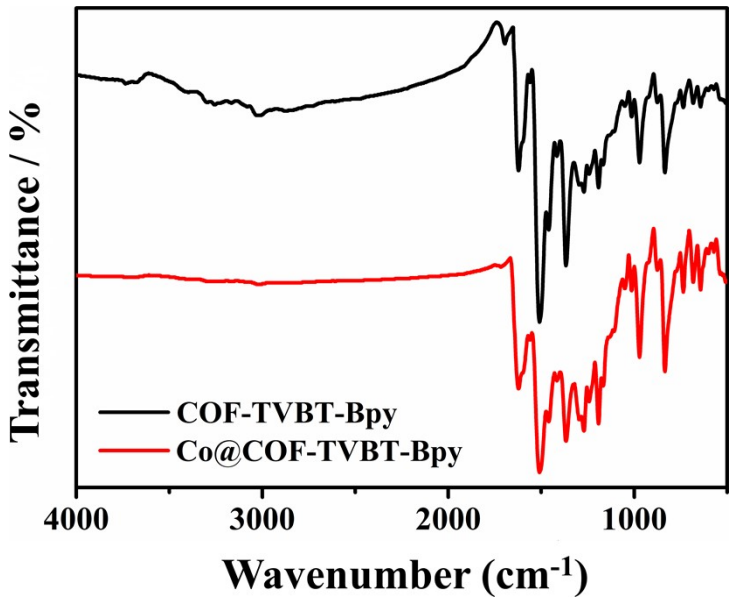

Fig. S2 FT-IR spectra of COF-TVBT-Bpy and Co@COF-TVBT-Bpy.

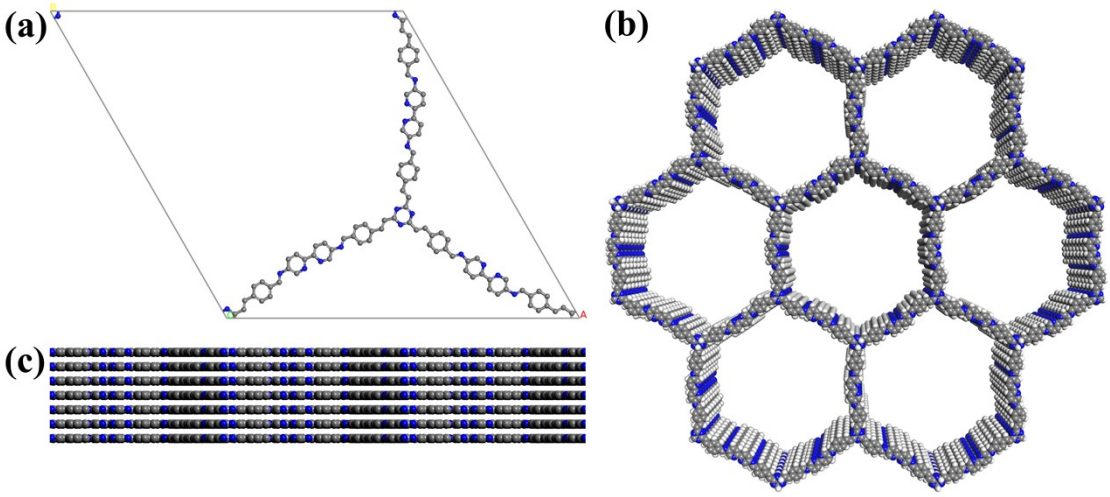

Fig. S3 AA-stacking modes of COF-TVBT-Bpy (a) Atomic coordinates; (b) Top view; (c) Side view.

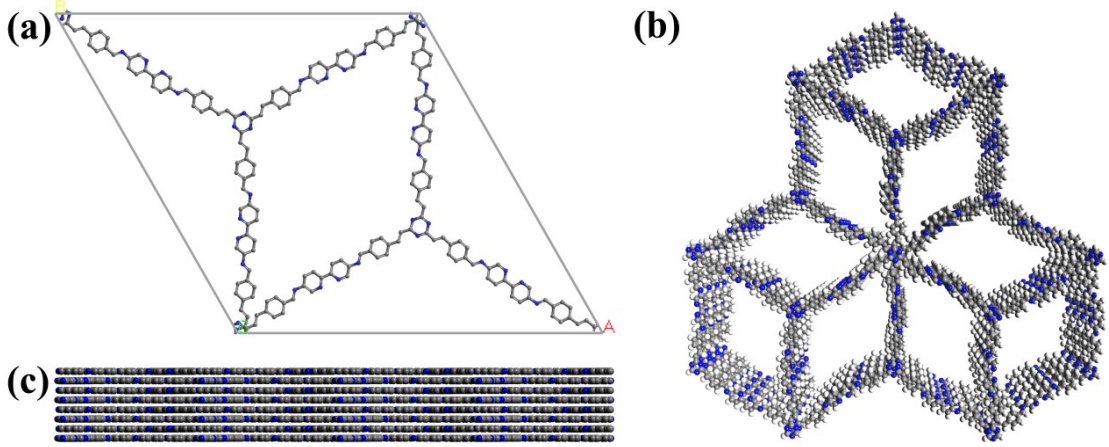

Fig. S4 AB-stacking modes of COF-TVBT-Bpy (a) Atomic coordinates; (b) Top view; (c) Side view.

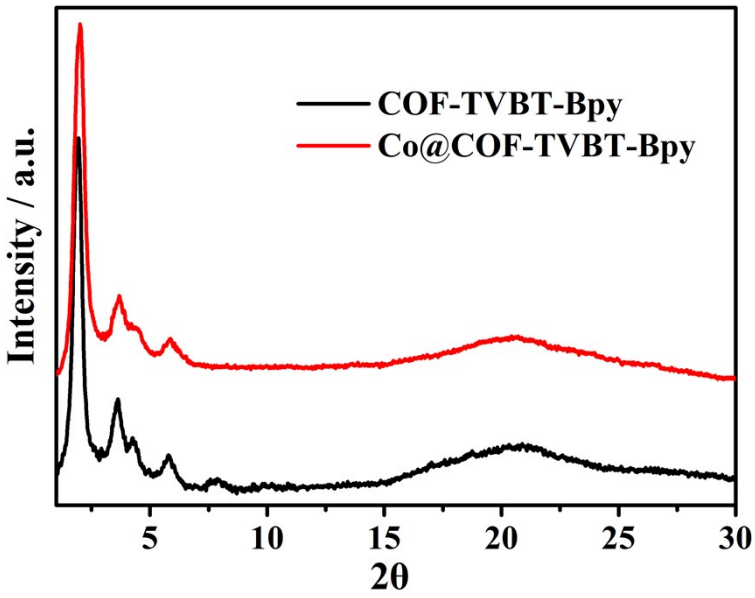

Fig. S5 PXRD patterns of COF-TVBT-Bpy and Co@COF-TVBT-Bpy.

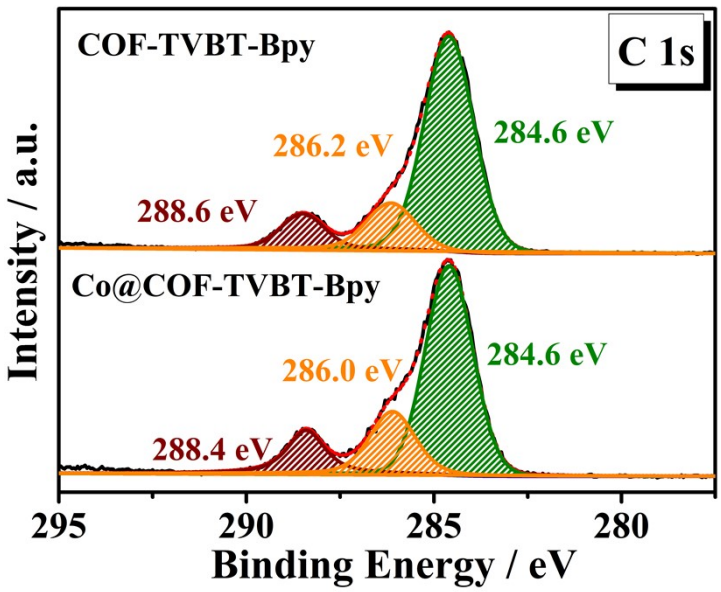

Fig. S6 C 1s XPS spectra of COF-TVBT-Bpy and Co@COF-TVBT-Bpy.

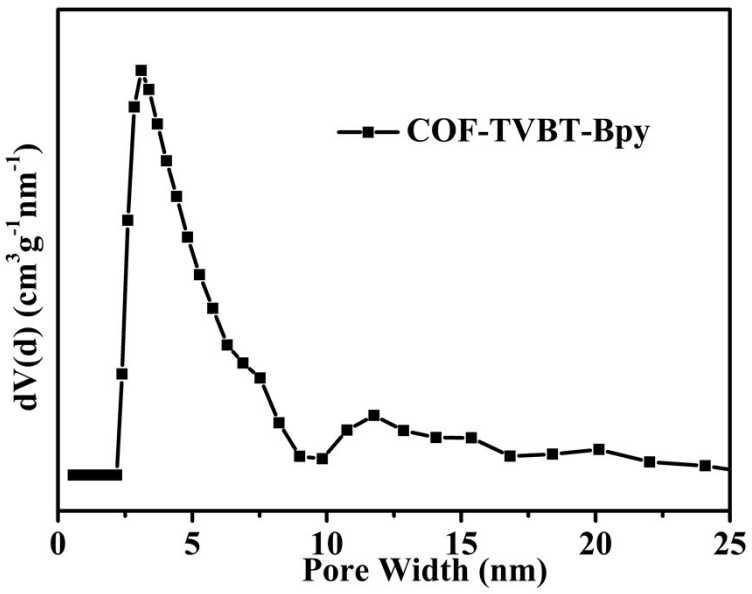

Fig. S7 The pore sizes of COF-TVBT-Bpy.

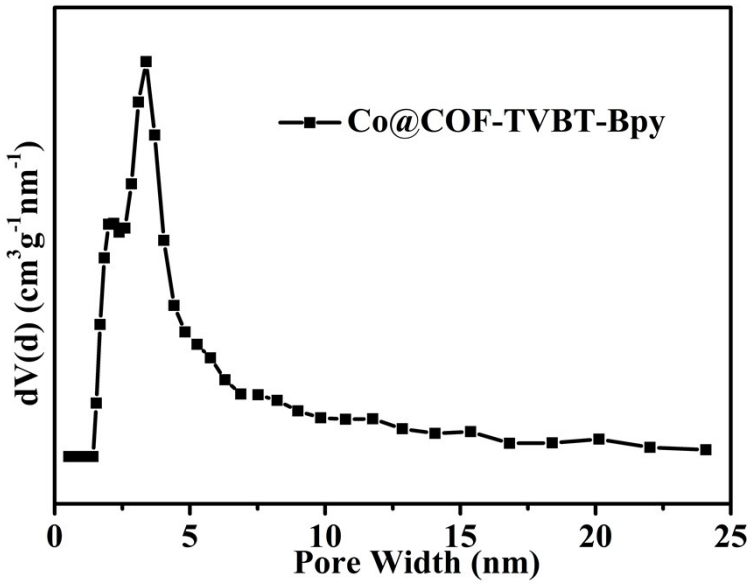

Fig. S8 The pore sizes of Co@COF-TVBT-Bpy.

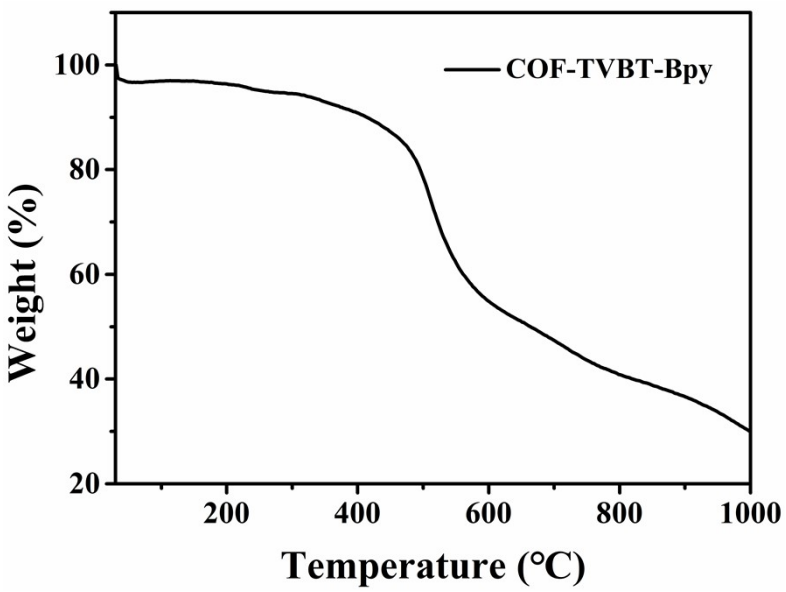

Fig. S9 TGA of COF-TVBT-Bpy.

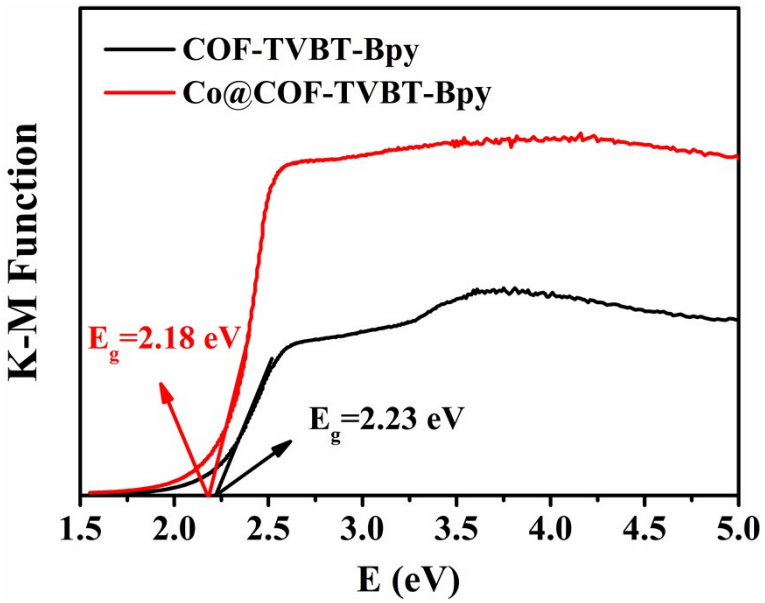

Fig. S10 Kubelka-Munk-transformed reflectance spectra of COF-TVBT-Bpy and Co@COF-TVBT-Bpy.

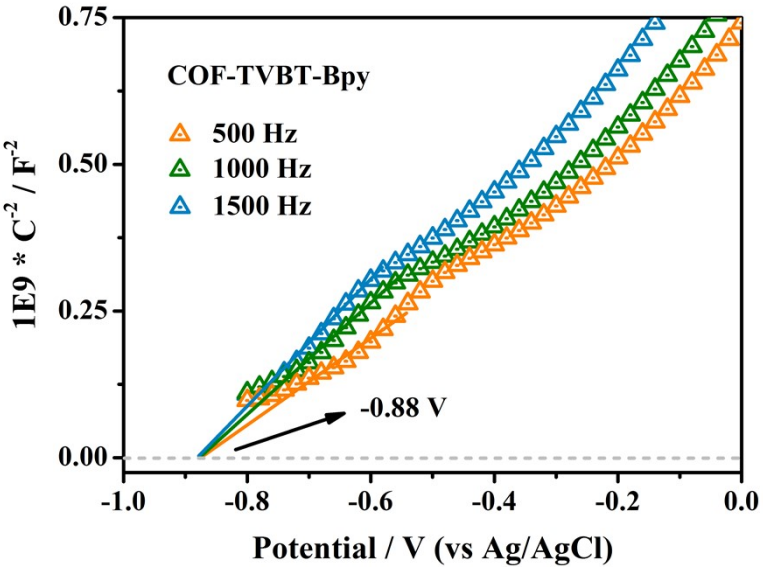

Fig. S11 Mott-Schottky plots of COF-TVBT-Bpy.

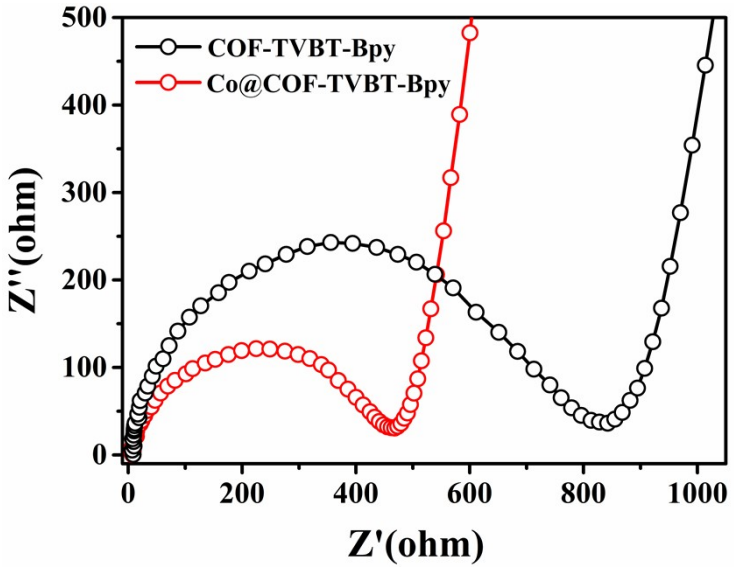

Fig. S12 Nyquist plots of COF-TVBT-Bpy and Co@COF-TVBT-Bpy.

Table S1 Summary of photocatalytic CO_2 reduction performance of metal-modified COF-based photocatalysts in pure CO_2.

Photocatalyst	Photosensitizer/ Sacrificial agent	Reaction solvent	Product yield/ $\mu mol \cdot g^{-1} \cdot h^{-1}$	AQE/ %	Ref.
Co@COF-TVBT-Bpy	$[Ru(bpy)_3]Cl_2$/TEOA	MeCN/H_2O	CO: 1132.7 H_2: 1158.4	1.18	This work
Bulk Co-FPy-COF	Dye[a)]/TEOA	MeCN/H_2O	CO: 393 H_2: 113	/	[S1]
Co-FPy-CON	Dye[a)]/TEOA	MeCN/H_2O	CO: 1683 H_2: 535	/	[S1]
Bulk COF367-Co	$[Ru(bpy)_3]Cl_2$/ Ascorbic acid	$KHCO_3$	CO: 124 H_2: 830	/	[S2]
COF367-Co NSs	$[Ru(bpy)_3]Cl_2$/ Ascorbic acid	$KHCO_3$	CO: 10162 H_2: 2875	/	[S2]
TFBD-COF-Co	$[Ru(bpy)_3]Cl_2$/TEOA	MeCN	CO: 360.9	/	[S3]
TFBD-COF-Co-SA	$[Ru(bpy)_3]Cl_2$/TEOA	MeCN	CO: 1480	/	[S3]
Co-COFs	$[Ru(bpy)_3]Cl_2$/TEOA	MeCN/H_2O	CO: 2375 H_2: 1750	/	[S4]
Ni-COFs	$[Ru(bpy)_3]Cl_2$/TEOA	MeCN/H_2O	CO: 5310 H_2: 291	/	[S4]
Fe-COFs	$[Ru(bpy)_3]Cl_2$/TEOA	MeCN/H_2O	CO: 1000 H_2: 4815	/	[S4]

sp^2c-COF_{dpy}-Co	TEOA	H_2O	CO: 1000	1.2	[S5]
DQTP COF-Co	$[Ru(bpy)_3]Cl_2$/TEOA	MeCN	CO: 1020	/	[S6]
DQTP COF-Zn	$[Ru(bpy)_3]Cl_2$/TEOA	MeCN	HCOOH:152.5	/	[S6]
$ZnFe_2O_4$/FeP-CTFs	$[Ru(bpy)_3]Cl_2$/TEOA	MeCN	CO: 178	0.112	[S7]
TTCOF-Zn	/	H_2O	CO: 2.1	/	[S8]
TTCOF-Ni	/	H_2O	CO: 1.4	/	[S8]
Ni-TpBpy	$[Ru(bpy)_3]Cl_2$/TEOA	MeCN/H_2O	CO: 811.4	0.3	[S9]
Ni-PCD@TD-COF	$[Ru(bpy)_3]Cl_2$/TEOA	MeCN/H_2O	CO: 478	0.31	[S10]
PD-COF-23-Ni	TEOA	MeCN/H_2O	CO: 40	0.079	[S11]
Ni@PI-COF-TT	TEOA	MeCN	CO: 483	0.55	[S12]
Ni@TPHH-COF	$[Ru(bpy)_3]Cl_2$/TEOA	MeCN/H_2O	CO: 1270	/	[S13]
Re-COF	TEOA	MeCN	CO: 750	/	[S14]
Re-Bpy-sp^2c-COF	TEOA	MeCN	CO: 1040 H_2: 244	0.5	[S15]
Re-CTF-py	TEOA	MeCN	CO: 353.05	/	[S16]
Ru/TpPa-1	TEOA	MeCN	HCOOH:108.8	/	[S17]
Ru@TpBpy	TEOA	MeCN	HCOOH: 172	/	[S18]

[a] Dye is $Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$.

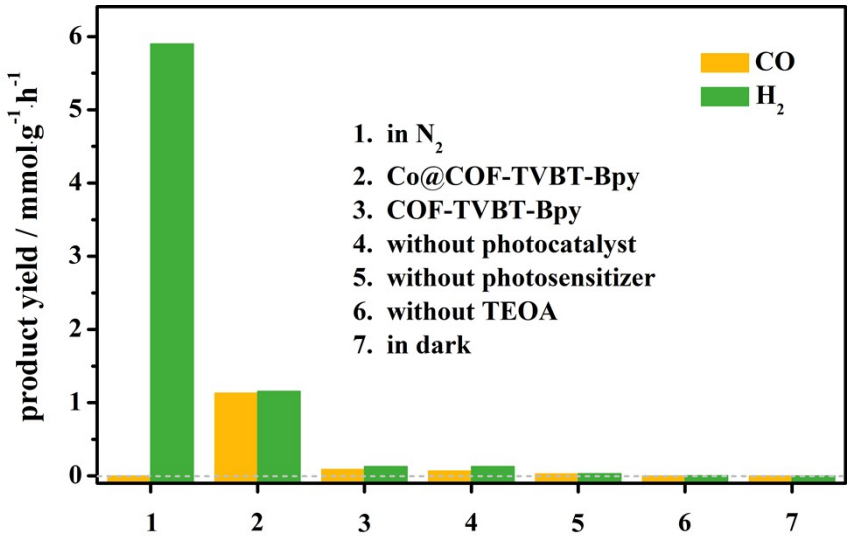

Fig. S13 Photocatalytic CO_2 reduction under various reaction conditions.

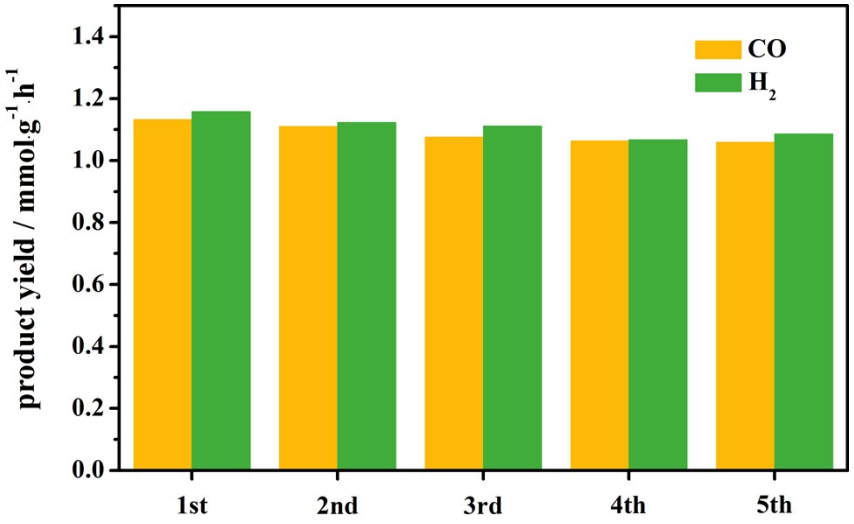

Fig. S14 Reusability test of Co@COF-TVBT-Bpy in photocatalytic reaction.

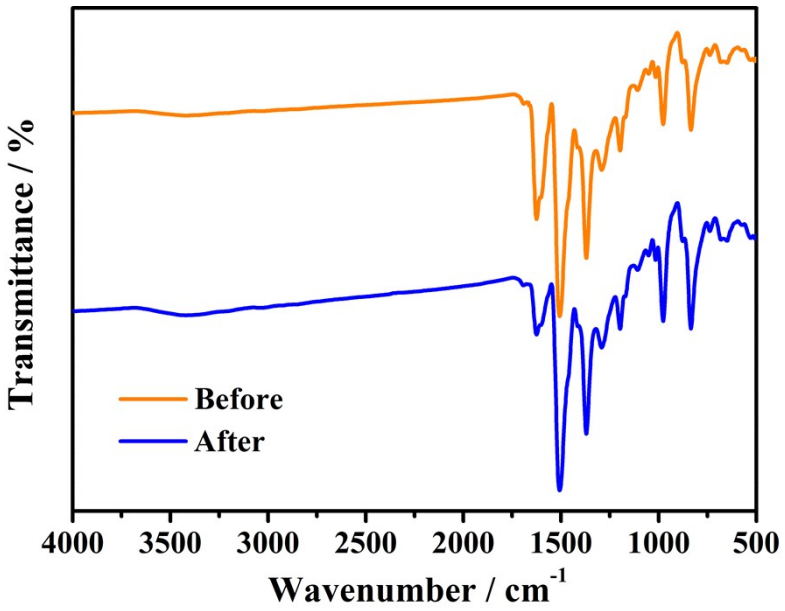

Fig. S15 FT-IR spectra of Co@COF-TVBT-Bpy before and after photocatalytic cycling reactions.

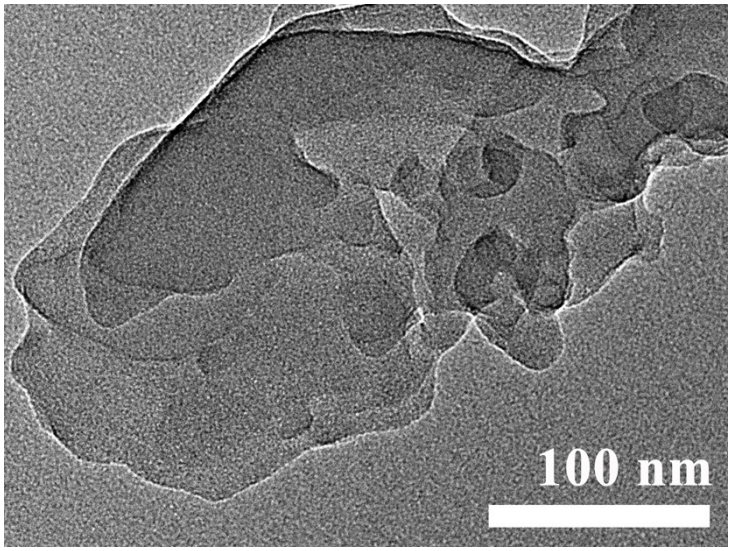

Fig. S16 TEM image of Co@COF-TVBT-Bpy after photocatalytic cycling reaction.

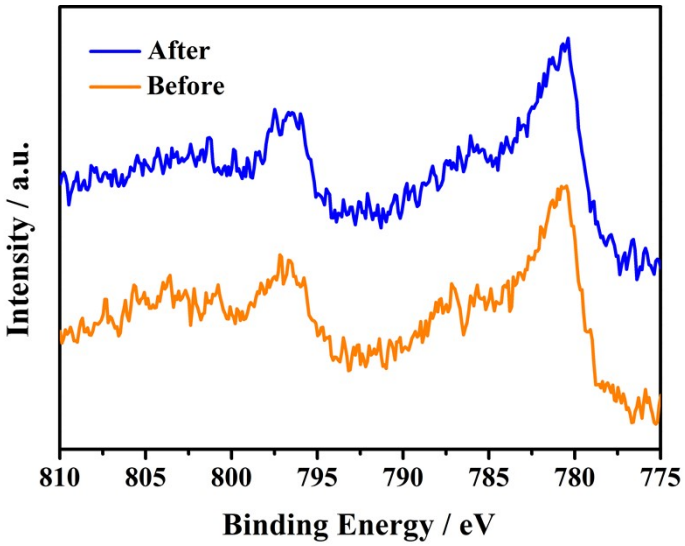

Fig. S17 The high-resolution XPS spectrum of Co 2p of Co@COF-TVBT-Bpy before and after photocatalytic cycling reactions.

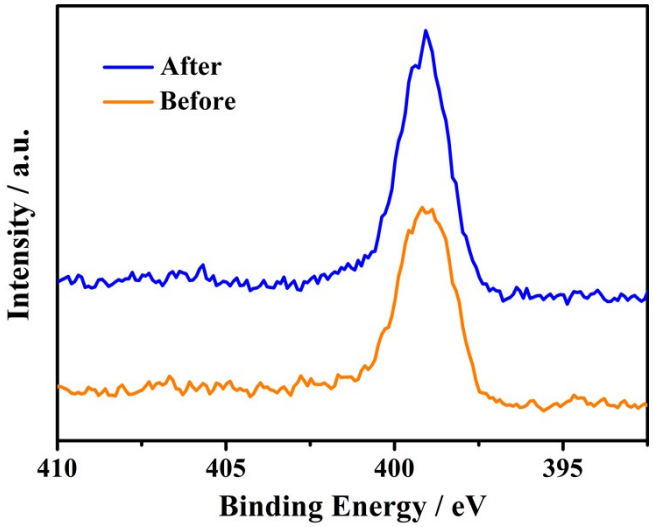

Fig. S18 The high-resolution XPS spectrum of N 1s of Co@COF-TVBT-Bpy before and after photocatalytic cycling reactions.

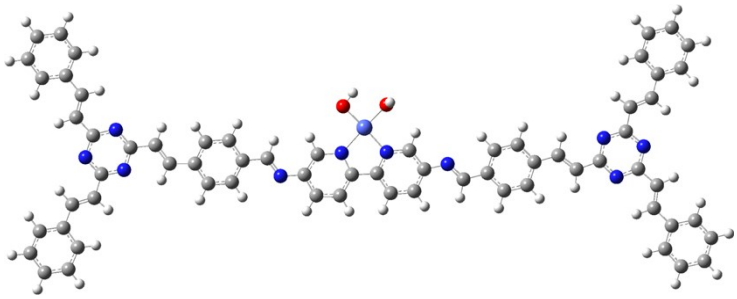

Fig. S19 Computational model of Co@COF-TVBT-Bpy. Carbon (grey), Hydrogen (white), Nitrogen (dark blue), Cobalt (blue) and Oxygen (red).

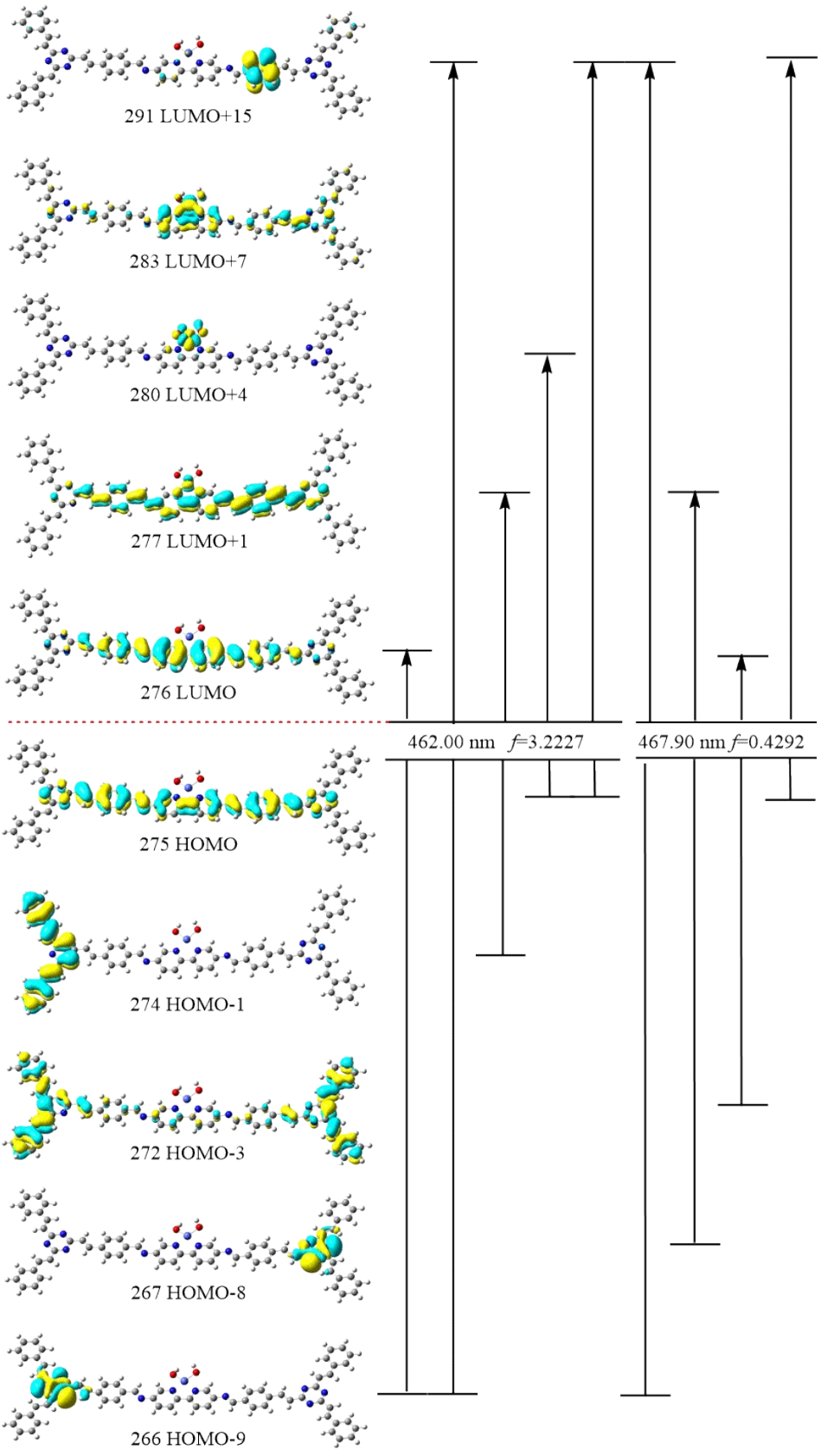

Fig. S20 Orbital composition analysis image of Co@COF-TVBT-Bpy. Carbon (grey), Hydrogen (white), Nitrogen (dark blue), Cobalt (blue) and Oxygen (red).

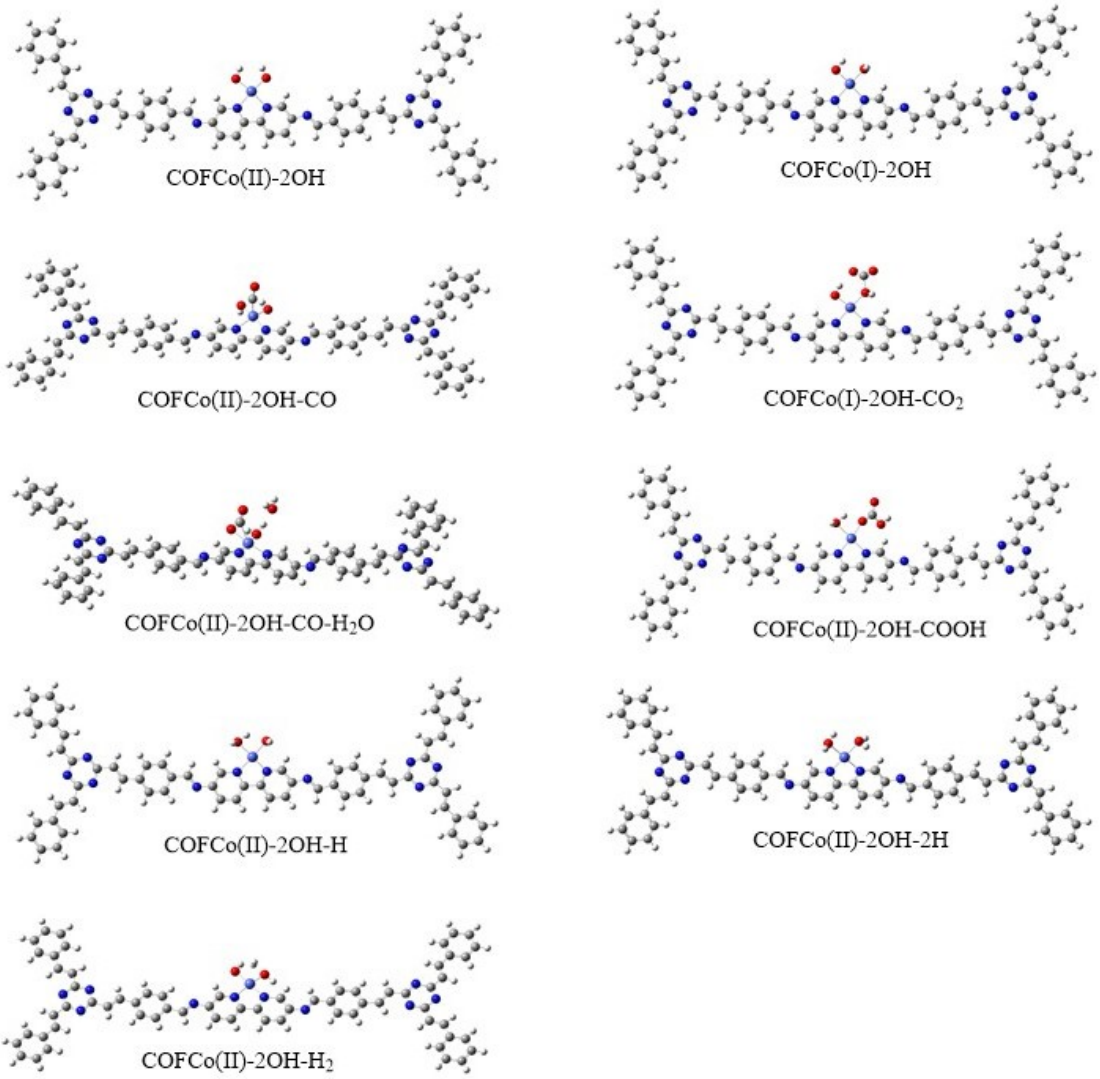

Fig. S21 Adsorption model diagrams of Co@COF-TVBT-Bpy. Carbon (grey), Hydrogen (white), Nitrogen (dark blue), Cobalt (blue) and Oxygen (red).

Table S2 The energy of CO formation process.

Model	ΔE (eV)	ΔG (eV)
[Co(II)@COF]	0.000	0.000
[Co(I)@COF]	0.152	0.164
[Co(I)@COF-CO_2]	-0.200	0.005
[Co(II)@COF-COOH]	-0.981	-1.381
[Co(II)@COF-CO-H_2O]	-1.358	-2.306
[Co(II)@COF-CO] + [H_2O]	-1.240	-1.887

Table S3 The energy of H_2 formation process.

Model	ΔE (eV)	ΔG (eV)
[Co(II)@COF]	0.000	0.000
[Co(I)@COF]	0.152	0.164
[Co(II)@COF-H]	-0.269	-0.884
[Co(II)@COF-2H]	-0.957	-2.105
[Co(II)@COF-H_2]	-1.435	-2.151

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