Supporting Information

Highly dispersed Co modified covalent organic frameworks as bridging cocatalysts for boosting CO_2 photoreduction over defective carbon nitride

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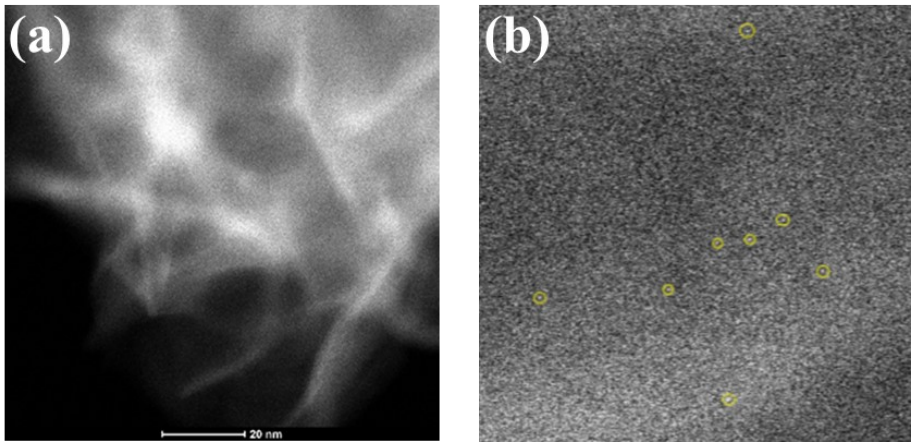

Figure s1. HAADF-STEM images of Co@TpTta.

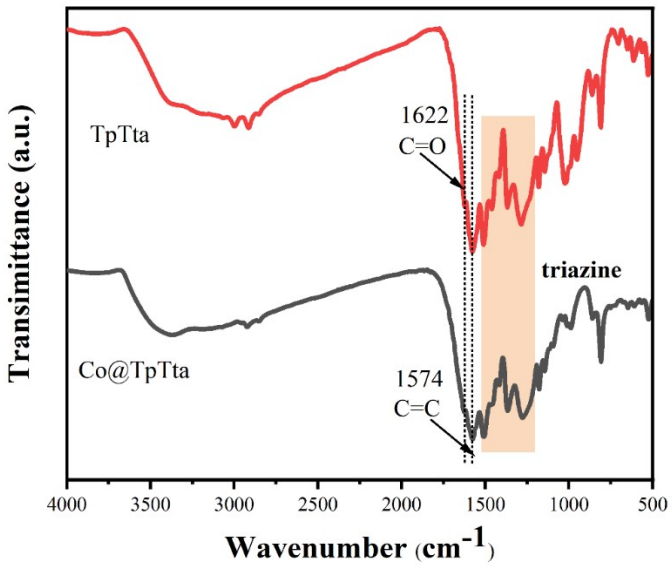

Figure s2. FTIR spectra of TpTta and Co@TpTta.

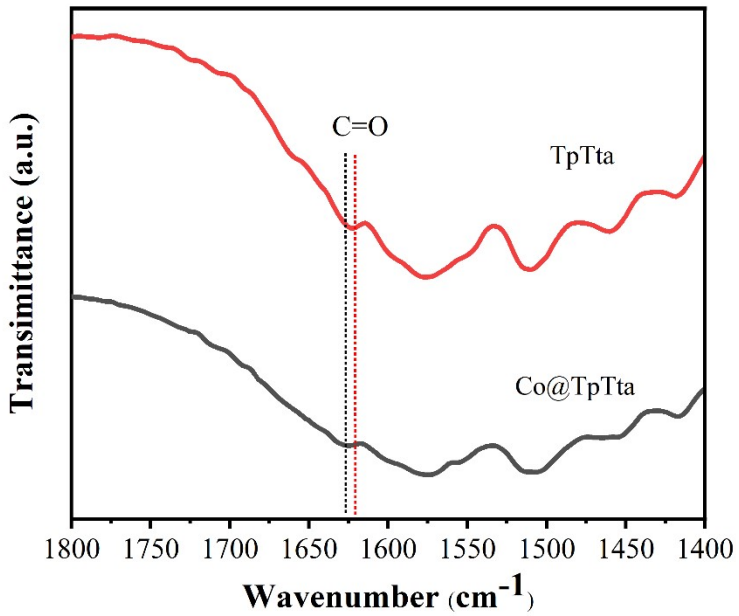

Figure s3. Enlarged FTIR spectra of TpTta and Co@TpTta.

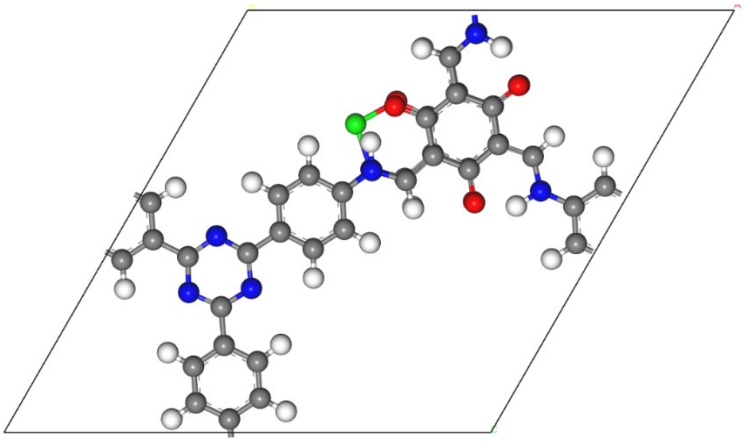

Figure s4. Possible coordination sites for Co in the TpTta COF framework: N-Co-O top view.

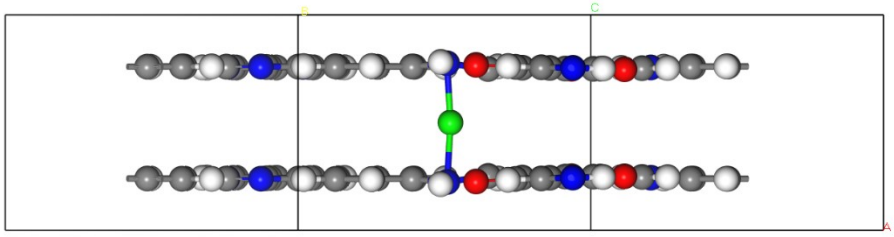

Figure s5. Possible coordination sites for Co in the TpTta COF framework: N-Co-N side view.

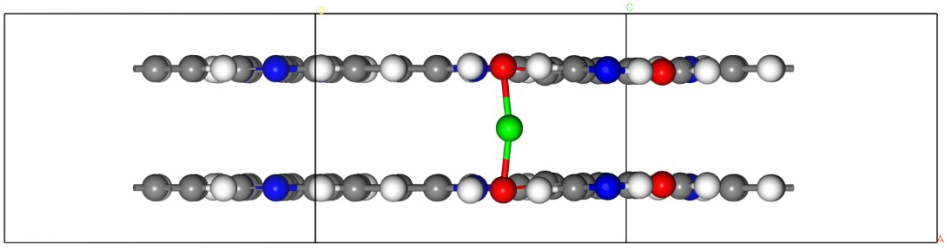

Figure s6. Possible coordination sites for Co in the TpTta COF framework: O-Co-O side view.

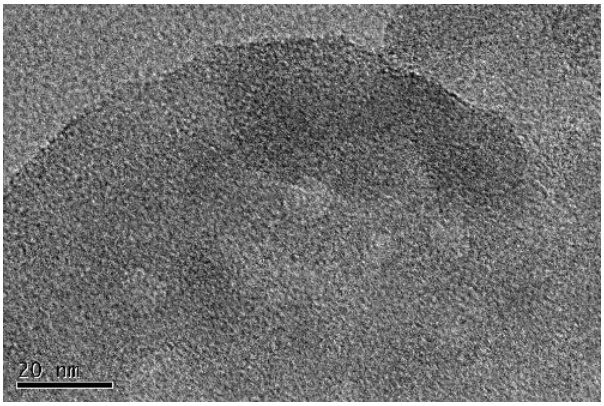

Figure s7. HRTEM image of NCN.

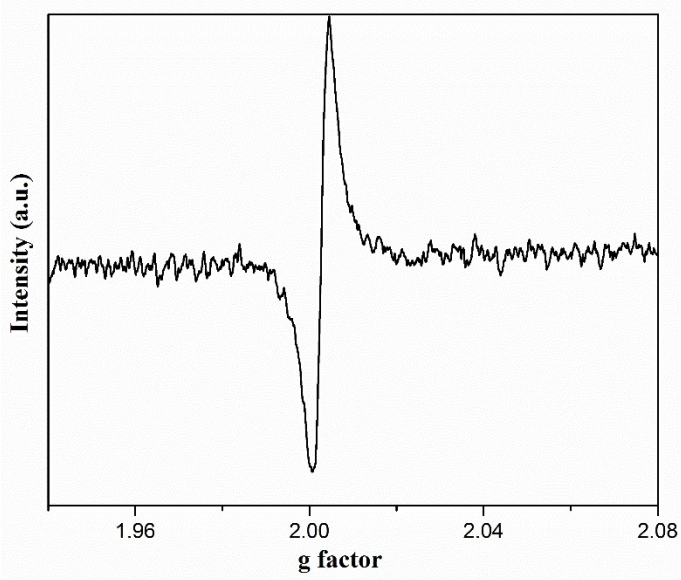

Figure s8. ESR spectrum of Co@TpTta/NCN.

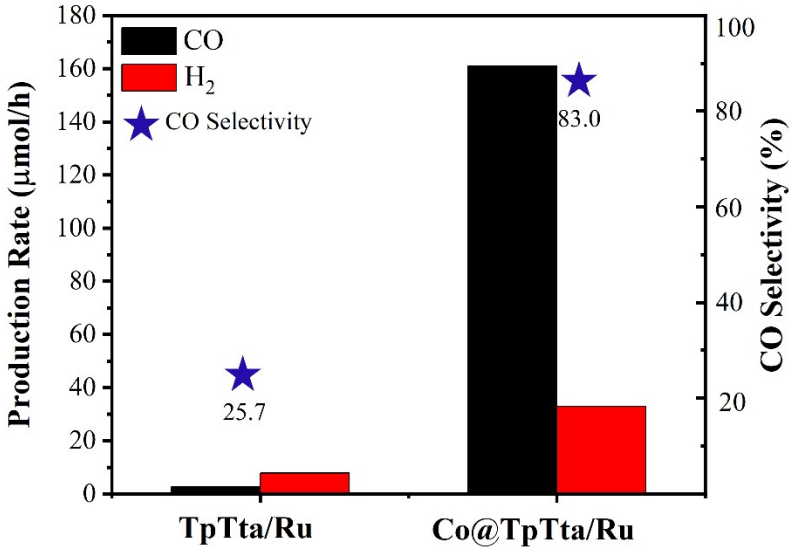

Figure s9. Photocatalytic yields of CO for TpTta/Ru and Co@TpTta/Ru.

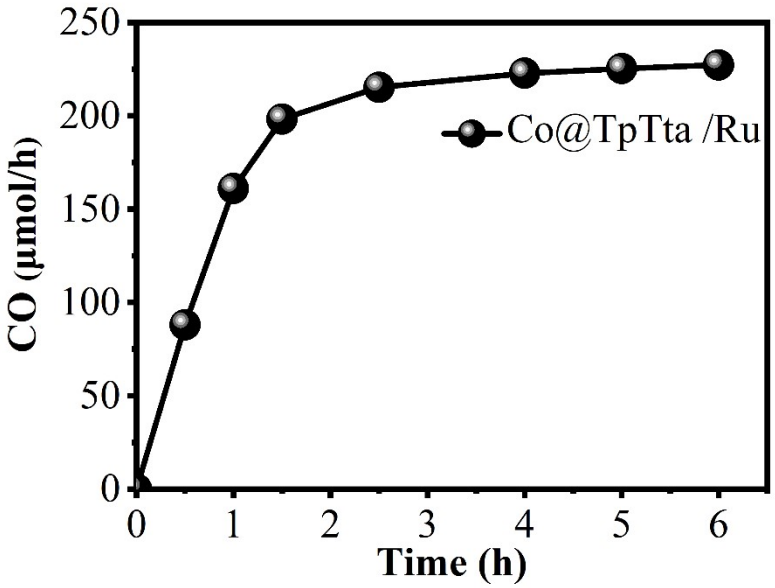

Figure s10. Co@TpTta/Ru for long-term photocatalytic CO_2 reduction reaction.

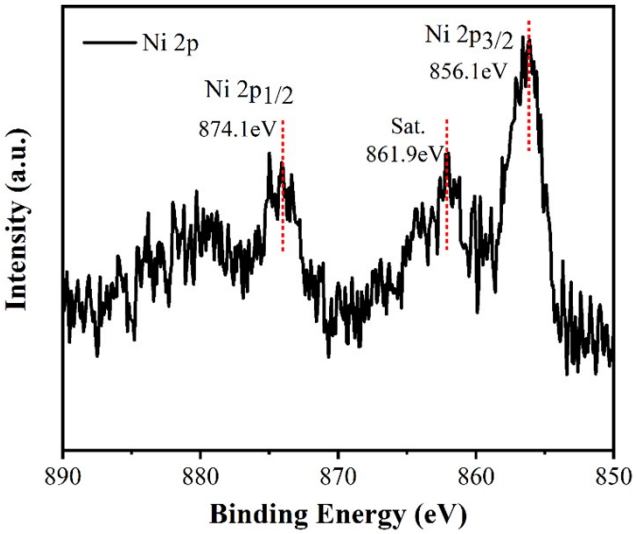

Figure s11. Ni 2p XPS spectrum of Ni@TpTta.

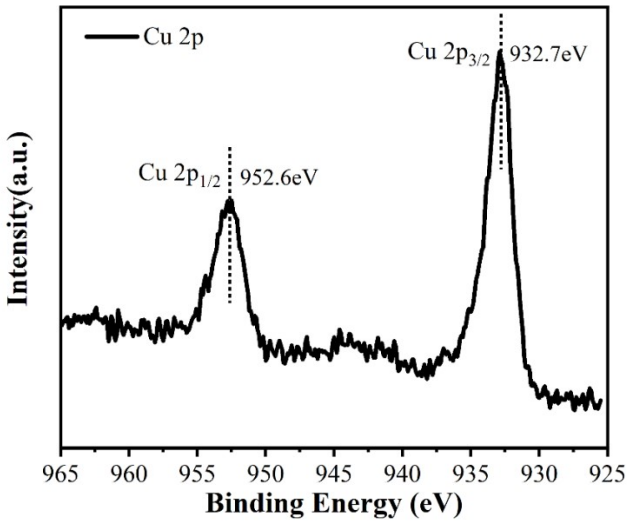

Figure s12. Cu 2p XPS spectrum of Cu@TpTta.

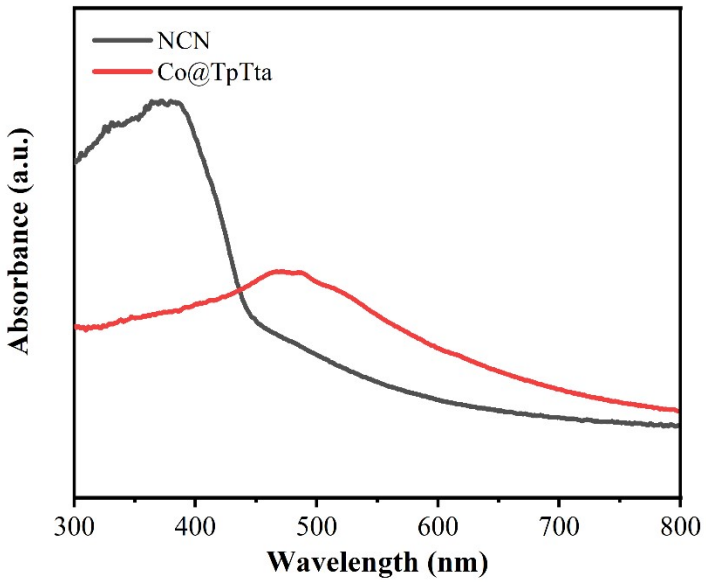

Figure s13. Uv-vis plots of NCN and Co@TpTta.

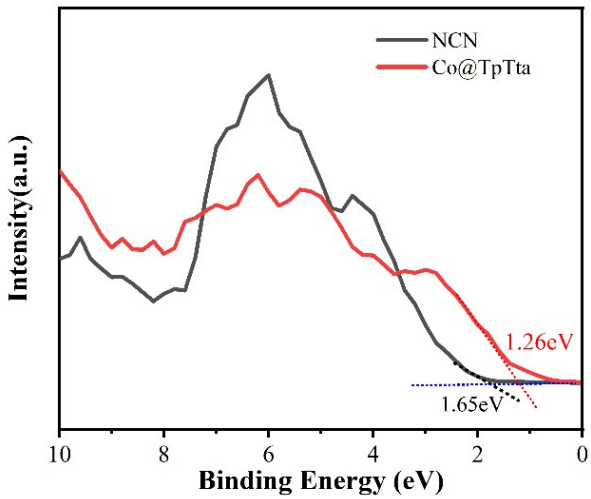

Figure s14. VB XPS spectra of NCN and Co@TpTta.

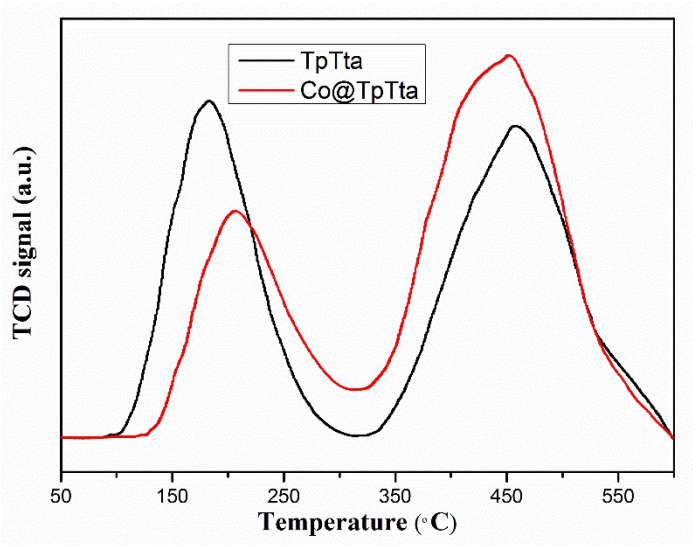

Figure s15. CO_2-TPD curves of TpTta and Co@TpTta.

Table s1. The formation energy as function of the position according to Figure s4-s6.

	E_{COF+Co}	E_{COF}	μ_{Co}	μ_H	n_H	ΔE_{form}
OCoO	-129775.201	-92212.572	-37563.455	-15.433	0	0.826
OCoN	-129760.050				1	0.544
NCoN	-129743.728				2	1.433

Table s2. Comparison of photocatalytic CO_2 activities in the C_3N_4 systems.

catalysts	Sacrificial agent	Light source	CO production yield (μmol/h)	Selectivity (%)	Ref
Co-POM/carbon nitride hybrids	MeCN: TEOA (4:1, v/v)	300 W Xe lamp (400 nm>λ>800 nm)	17.0	80.0	[1]
g-CNU-CoTDPP	MeCN: TEOA (4:1, v/v)	5 W white-light LED lamp	57.0	79.0	[2]
Co-PYN5@g-C_3N_4	MeCN: TEOA (4:1, v/v)	Hg lamp (λ>400 nm)	0.6	96.0	[3]
Coqpy@mpg-C_3N_4	MeCN	100 W Xe lamp (λ>400nm)	8.0	98.0	[4]
CoPc@P-g-C_3N_4	-	300 W Xe lamp (λ>420nm)	12.3	92.2	[5]
Co-MOF/g-C_3N_4	-	300 W Xe lamp (λ>420nm)	6.8	55.2	[6]
TCOH-CN	-	300 W Xe lamp (λ>420nm)	11.2	90.0	[7]
mpg-CN_x|CoPPc	MeCN:TEOA (4:1, v/v)	100mW·cm^{-2} Xe lamp (λ>400nm)	20.8	85.0	[8]
Co@TpTta/NCN	TEOA	300 W Xe lamp (λ>400 nm)	37.3	98.8	This work

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[8] Roy S, Reisner E. Visible-light-driven CO_2 reduction by mesoporous carbon nitride modified with polymeric cobalt phthalocyanine. Angewandte Chemie International Edition, 2019, 58 (35): 12180~12184.