Supporting Information

Synthesis of Hybrid Nickel Boron-Oxo Clusters for Photocatalytic CO_2 Reduction

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1. Materials and Methods

All the reagents and solvents were commercially and used as received without further purification. Nickel(II) acetate, boronic acid, quinolineboronic acid, and **p**-methoxyphenyl boronic acid.and pyrazole were purchased from Adamas-beta. Ethanol (≥99.5%), Methanol and acetonitrile (≥ 99.5%) were acquired from Sinopharm Chemical Reagent Beijing. PXRD data were performed using a Rigaku Dmax2500 diffractometer with Cu Kα radiation (λ = 1.54056 Å) collected with the angular range (2θ) from 5° to 50° at room temperature. A UV-visible spectrophotometer (Lambda, PerkinElmer) was used to measure the absorption spectrum of the as-prepared samples. The TGA curve was recorded in the region of 30–800 °C using a heating rate of 10 °C min^{-1} in flowing N_2 atmosphere on a Mettler Toledo TGA/SDTA 851e analyzer. X-ray photoelectron spectroscopy (XPS) were recorded using ESCALAB 250Xi (Thermo Scientific) spectrometer equipped with an Al Ka as the X-ray excitation source, the C1s peak was uniformly calibrated to 284.8 eV.

2.Syntheses

Synthesis of the BOC-20：$Ni(Ac)_2$(50mg ,0.2mmol), 4-Methoxyphenylboronic acid(150mg,1mmol) and pyrazole (1.2g, 17.6 mmol) were dissolved in acetonitrile (5mL). The resultant solution was heated at 80 ℃ for 4~5 days. After cooling to the room temperature, dark blue crystals of **BOC-20** were obtained.

Synthesis of the BOC-21：$Ni(Ac)_2$(49mg,0.2mmol), Phenylboronic acid (120mg, 1mmol) , and pyrazole (1g, 14.7 mmol) were dissolved in acetonitrile (5mL). The resultant solution was heated at 80 ℃ for 5 days. After cooling to the room temperature, transparent blue crystals of **BOC-21** were obtained.

Synthesis of the BOC-22：$Ni(Ac)_2$(49mg,0.2mmol), boronic acid (92mg, 1.5 mmol) , 8-Quinoline boronic acid(86mg,0.5mmol) and pyrazole (1g, 14.7 mmol) were dissolved in acetonitrile (5mL). The resultant solution was heated at 80 ℃ for 5 days. After cooling to the room temperature, transparent blue crystals of **BOC-22** were obtained.

3.X-Ray crystallographic analysis

Crystallographic data of crystal was collected on Hybrid Pixel Array detector equipped with Cu-Kα radiation (λ = 1.5418Å) at about 293K and Mo-Kα radiation(λ = 0.7107Å). The structures were solved with the dual-direct methods using ShelXT and refined with the full-matrix least-squares technique based on F^2 with the SHELXL. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were added theoretically, riding on the concerned atoms and refined with fixed thermal factors. All absorption corrections were performed using the multi-scan program. A summary of crystallography data for are

listed in Table S1-S14.

Table S1 Summary of the compositions and characteristics of the structures in this work

Compounds	Composition	Sp.Gr.	a(Å)	b(Å)	c(Å)	V(Å^3)
BOC-20	Ni(II)[MeOPhB(Pz)$_3$]$_2$	$P2_1/c$	11.6960	8.6183	16.3091	1554.27
BOC-21	[H_3O]·{Ni(II) [(B_9O_{12})(OH)$_3$(Pz)$_3$]}	P-3	17.9516	17.9516	7.5179	2098.14
BOC-22	Ni(II)$_2$[B_3O_3(OH)$_2$Qi(Pz)$_2$]$_2$	$C2/c$	18.5688	16.7302	14.7104	4545.49

MeOPh=4-Methoxybenzene, Pz=pyrazole, B_3O_3=six-membered B_3O_3 ring,Qi=quinoline

Table S2 Crystal data and structure refinement for BOC-20、BOC-21、BOC-222

Compounds	BOC-20	BOC-21	BOC-22
Formula	$C_{32}H_{32}B_2N_{12}NiO_2$	$C_9H_{12}B_9N_6NiO_{15}$	$C_{36}H_{36}B_6N_{14}Ni_2O_{10}$
Formula weight	77.34	652.433	1007.07
Temperature/K	100.0(3)	99.97(19)	99.97(12)
Crystal system	monoclinic	trigonal	monoclinic
Space group	Pn	P-3	C2/c
a/Å	11.6960(5)	17.9516(8)	18.5688(4)
b/Å	8.6183(3)	17.9516(8)	16.7302(5)
c/Å	16.3091(7)	7.5179(3)	14.7104(3)
α/°	90	90	90
β/°	109.013(4)	90	95.928(2)
γ/°	90	120	90
Volume/Å^3	1554.26(11)	2098.14(16)	4545.5(2)
Z	18	1.8125	4
ρ_{calc}g/cm^3	1.487	0.936	1.583
μ/mm^{-1}	0.678	2.798	0.927
F(000)	722.0	583.6	2160.0
GoF（F^2）	1.048	1.675	1.000
R (F)[a]	0.0579	0.1489	0.0656
R_w (F_o^2)[b]	0.1481	0.4069	0.1484

Table S3 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for BOC-20. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)

Table S3 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for BOC-20. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Ni1	5063.3(8)	7382.8(7)	4933.1(7)	22.78(18)
O1	12326(4)	11983(6)	7164(3)	38.0(11)
N7	4740(4)	5177(6)	5340(3)	25.8(10)
N9	3220(4)	5558(5)	3561(3)	24.4(10)
N11	2423(4)	6977(6)	4622(3)	23.5(9)
N8	3607(4)	4528(5)	5055(3)	22.2(9)
N1	6765(4)	6874(5)	4887(3)	25.0(10)
N3	6500(4)	10324(5)	4899(3)	24.1(10)
N10	4185(5)	6542(6)	3676(3)	26.5(10)
N12	3369(4)	7960(6)	4969(3)	27.0(10)
N2	7697(4)	7854(6)	5281(3)	21.9(9)
N5	6884(4)	9195(5)	6353(3)	23.9(9)
N6	5922(4)	8204(6)	6198(3)	26.9(10)
N4	5381(5)	9606(6)	4539(3)	28.0(11)
C25	1398(8)	7620(8)	4704(6)	31.9(17)
C22	2967(6)	4845(7)	2788(4)	27.3(12)
C5	8779(5)	10298(6)	6061(4)	21.1(10)
C3	10769(6)	10149(7)	7195(4)	28.1(12)
C13	5545(6)	8314(7)	6888(4)	28.9(12)
O2	-2258(5)	2954(7)	2780(4)	48.2(12)
C4	9591(5)	9629(7)	6813(4)	26.5(12)
C21	3764(6)	5379(8)	2378(4)	33.9(14)
C2	11178(5)	11395(7)	6835(4)	28.0(12)
C26	1372(6)	4496(7)	3898(5)	35.2(15)
C10	7232(6)	5682(6)	4595(4)	31.0(13)
C24	1690(7)	9008(7)	5111(5)	35.6(15)
C23	2933(6)	9183(7)	5263(5)	32.4(13)
C11	7066(6)	9929(8)	7119(4)	28.3(12)
C17	5435(6)	4245(7)	5945(4)	30.1(13)
C9	8470(6)	5839(7)	4788(4)	28.8(12)
C12	6240(6)	9401(8)	7479(4)	34.1(14)
C18	4761(7)	3003(9)	6095(5)	45.1(18)
C16	4661(6)	10618(7)	4026(4)	29.3(12)
C20	4493(6)	6435(7)	2964(5)	32.3(13)
C6	9244(6)	11549(8)	5729(4)	33.7(14)
C1	13152(8)	11206(10)	7867(8)	55(2)

Table S3 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for BOC-20. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C15	5248(6)	12029(8)	4048(5)	37.2(14)
B1	7488(5)	9472(7)	5643(4)	21.4(12)
C8	8723(7)	7267(7)	5211(5)	23.4(13)
C19	3617(6)	3252(8)	5523(5)	41.9(17)
C14	6386(6)	11766(8)	4623(5)	42.5(17)
C28	-295(9)	2660(9)	3732(6)	41.4(19)
C30	-736(6)	4839(8)	2813(5)	36.1(14)
C7	10416(7)	12103(10)	6103(5)	38.2(16)
C27	894(7)	3171(9)	4113(5)	41.5(16)
C29	-1113(7)	3540(8)	3081(5)	39.4(15)
B2	2628(6)	5333(7)	4279(4)	22.9(12)
C32	-3120(7)	3871(10)	2098(7)	54(2)
C31	481(7)	5347(8)	3181(5)	39.5(15)

Table S4 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for BOC-21. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Ni1	6666(7)	3333(3)	3843(2)	22.6(7)
O9	5842(3)	2409(3)	2028(7)	24.8(13)
O13	5126(4)	3132(3)	977(7)	27.1(13)
O12	5388(4)	961(3)	1092(7)	26.9(13)
O14	4691(4)	1720(4)	28(8)	34.2(15)
O15	4177(5)	307(5)	-858(11)	42(2)
N6	5383(4)	3834(5)	3917(8)	28.7(16)
N5	5746(5)	3501(5)	5038(9)	29.4(16)
C9	4802(6)	3964(6)	4809(12)	39(2)
C8	4810(7)	3728(6)	6578(12)	41(2)
B7	5661(6)	3933(6)	1931(12)	26(2)
B8	5221(6)	2430(6)	1029(12)	26(2)
B9	4754(6)	1000(7)	92(12)	30(2)
C7	5400(6)	3448(6)	6650(11)	38(2)

Table S5 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for BOC-22. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*X*	*y*	*z*	U(eq)
Ni2	7308.3(2)	6825.6(2)	3547.0(2)	14.18(8)
O2	9094.8(8)	5443.0(10)	4688.8(11)	15.4(3)
O5	8288.4(9)	7547.9(10)	5541.9(11)	15.7(3)
O4	8095.2(8)	6395.0(9)	4542.9(11)	13.8(3)
O3	8887.2(9)	6300.9(10)	5964.2(11)	17.0(3)
O1	9946.9(9)	5554.2(11)	6028.1(12)	18.4(3)
N4	8505.0(10)	5847.0(11)	3152.7(13)	15.2(3)
N2	6529.8(11)	7088.0(12)	2447.7(14)	17.4(4)
N7	7588.5(11)	6443.7(12)	6082.3(14)	16.9(4)
N3	7995.2(11)	6321.4(12)	2691.6(13)	16.6(4)
N6	7228.7(11)	7042.4(12)	6489.3(15)	19.2(4)
N5	6742.7(11)	5739.6(12)	3834.0(14)	17.5(4)
N1	6083.0(11)	7735.2(13)	2395.2(15)	18.9(4)
C3	8971.9(13)	5581.8(15)	2561.8(17)	19.6(4)
C7	6582.9(13)	4307.5(14)	4111.2(17)	19.2(4)
C10	8081.1(13)	4125.0(14)	4300.1(16)	17.9(4)
C1	8158.1(14)	6369.6(15)	1812.1(17)	20.2(4)
C11	7818.2(12)	4902.9(13)	4178.7(15)	15.1(4)
C12	7044.7(12)	4990.2(13)	4038.0(16)	16.3(4)
C8	6896.7(15)	3530.1(15)	4251.8(18)	22.6(5)
C4	6026.1(13)	5817.5(16)	3758.2(19)	21.9(5)
C16	5610.7(14)	7710.3(16)	1631.2(18)	21.7(5)
C13	7299.0(14)	5726.5(15)	6265.1(18)	21.6(5)
C18	5747.2(14)	7021.8(16)	1155.9(18)	22.8(5)
C9	7632.6(14)	3439.5(15)	4320.4(18)	21.1(5)
C2	8769.5(14)	5914.0(16)	1694.3(18)	23.1(5)
C19	6326.4(14)	6653.4(15)	1685.8(18)	21.3(5)
C6	5824.7(14)	4415.3(16)	4017.7(19)	23.8(5)
C14	6733.1(16)	5844.8(17)	6793(2)	27.3(5)
C5	5543.0(14)	5172.8(17)	3850(2)	25.6(5)
B1	9304.5(14)	5759.0(15)	5548.5(18)	15.8(4)
C15	6709.5(16)	6680.2(17)	6915(2)	28.8(6)
B3	8236.8(13)	6664.9(15)	5484.2(18)	14.4(4)
B2	8386.6(13)	5654.8(15)	4192.0(18)	14.7(4)
C17	5027(4)	7403(5)	7132(5)	116(3)
N8	4858(11)	7736(11)	8997(13)	383(10)

Table S6 Anisotropic Displacement Parameters ($Å^2×10^3$) for BOC-20. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni1	17.4(3)	19.5(3)	30.8(3)	2.2(3)	6.90(19)	-2.5(3)
O1	25(2)	29(2)	53(3)	-3(2)	3(2)	-8.7(19)
N7	18(2)	23(2)	33(3)	-1.0(18)	4(2)	-3.6(16)
N9	17(2)	23(2)	31(2)	0.1(18)	4.9(18)	-2.0(16)
N11	17(2)	24(2)	29(2)	0(2)	6.8(18)	-2.2(19)
N8	18(2)	19(2)	27(2)	-1.4(16)	2.7(18)	-0.9(16)
N1	19(2)	23(3)	34(3)	-2.7(19)	9.7(19)	-5.9(19)
N3	22(2)	23(2)	28(2)	-1.5(18)	9(2)	2.1(16)
N10	25(2)	27(2)	30(2)	0.7(18)	12(2)	-2.6(17)
N12	20(2)	19(2)	38(3)	-4(2)	5(2)	-0.4(18)
N2	18(2)	19(2)	29(2)	-2.1(19)	7.7(18)	-0.4(18)
N5	20(2)	26(2)	26(2)	-0.2(18)	7.9(19)	-1.0(17)
N6	23(2)	27(2)	32(3)	0.6(18)	10(2)	-1.7(17)
N4	29(3)	25(2)	30(3)	0.2(19)	11(2)	-3.7(19)
C25	23(4)	39(4)	36(4)	4(3)	13(3)	5(2)
C22	24(3)	33(3)	24(3)	2(2)	6(2)	3(2)
C5	21(2)	19(2)	23(2)	-1.0(18)	7(2)	-0.6(18)
C3	28(3)	23(3)	31(3)	1(2)	6(2)	-1(2)
C13	24(3)	34(3)	31(3)	6(2)	12(2)	1(2)
O2	33(3)	45(3)	61(3)	0(3)	8(2)	-8(2)
C4	24(3)	24(3)	30(3)	-1(2)	8(2)	-2(2)
C21	32(3)	44(4)	25(3)	4(3)	9(3)	5(3)
C2	21(3)	24(3)	36(3)	-8(2)	5(2)	-2(2)
C26	43(4)	30(3)	42(4)	-17(3)	27(3)	-17(3)
C10	36(3)	19(3)	40(3)	-2(2)	16(3)	-4(2)
C24	36(4)	25(3)	53(4)	5(3)	24(3)	8(2)
C23	30(3)	22(3)	46(4)	-3(2)	14(3)	3(2)
C11	21(3)	33(3)	26(3)	-4(2)	1(2)	2(2)
C17	21(3)	29(3)	36(3)	-2(2)	3(2)	0(2)
C9	30(3)	22(3)	38(3)	-5(2)	17(3)	-2(2)
C12	30(3)	44(3)	31(3)	3(2)	13(3)	10(2)
C18	40(4)	36(4)	44(4)	16(3)	-6(3)	-9(3)
C16	28(3)	30(3)	28(3)	-4(2)	6(2)	-5(2)
C20	30(3)	34(3)	37(3)	9(3)	16(3)	3(2)
C6	26(3)	38(3)	33(3)	12(2)	4(2)	-2(2)
C1	29(4)	42(4)	74(7)	5(4)	-8(4)	-7(3)
C15	29(3)	25(3)	49(4)	10(3)	1(3)	3(2)
B1	17(3)	18(3)	28(3)	-4(2)	6(2)	-1.1(19)

Table S6 Anisotropic Displacement Parameters ($Å^2×10^3$) for BOC-20. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

C8	19(3)	20(2)	35(3)	-3(2)	14(3)	-4(2)
C19	30(3)	33(3)	51(4)	16(3)	-3(3)	-11(3)
C14	29(3)	28(3)	61(5)	4(3)	2(3)	-6(2)
C28	41(4)	44(4)	39(4)	1(3)	12(3)	-8(3)
C30	23(3)	34(3)	43(4)	-2(3)	-1(3)	5(2)
C7	28(3)	36(3)	53(4)	11(3)	16(3)	-5(3)
C27	37(4)	43(4)	43(4)	9(3)	12(3)	-4(3)
C29	36(4)	40(4)	43(4)	-12(3)	15(3)	-5(3)
B2	20(3)	22(3)	25(3)	-2(2)	5(2)	-1(2)
C32	30(4)	47(4)	68(6)	-2(4)	-8(4)	-4(3)
C31	37(4)	32(3)	47(4)	2(3)	10(3)	-1(3)

Table S7 Anisotropic Displacement Parameters ($Å^2×10^3$) for BOC-21. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni1	28.9(8)	28.9(8)	9.8(9)	14.5(4)	-0	0
O9	31(3)	28(3)	17(3)	16(2)	-3(2)	3(2)
O13	35(3)	27(3)	20(3)	16(3)	-1(2)	-1(2)
O12	32(3)	24(3)	22(3)	12(2)	-4(2)	1(2)
O14	42(4)	30(3)	29(3)	17(3)	-13(3)	-6(2)
O15	44(4)	33(4)	54(5)	23(4)	-22(3)	-15(4)
N6	33(4)	39(4)	17(3)	21(3)	7(3)	1(3)
N5	40(4)	36(4)	15(3)	21(3)	2(3)	0(3)
C9	50(6)	45(6)	32(5)	31(5)	11(4)	-7(4)
C8	55(6)	49(6)	31(5)	35(5)	16(4)	6(4)
B7	30(5)	26(5)	15(4)	9(4)	4(3)	-1(3)
B8	32(5)	35(5)	16(4)	21(4)	-2(4)	0(4)
B9	24(5)	35(5)	22(5)	8(4)	-7(4)	-5(4)
C7	55(6)	40(5)	18(4)	23(5)	11(4)	6(4)

Table S8 Anisotropic Displacement Parameters ($Å^2×10^3$) for BOC-22. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni2	15.35(14)	12.24(12)	14.75(13)	-0.45(10)	0.55(9)	3.83(10)
O2	13.5(7)	15.5(7)	17.0(7)	-2.0(6)	0.5(5)	5.0(5)

Table S8 Anisotropic Displacement Parameters ($Å^2×10^3$) for BOC-22. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O5	16.9(7)	12.2(7)	17.7(7)	-1.0(6)	1.1(6)	2.2(5)
O4	14.0(7)	14.3(7)	12.8(7)	-1.4(5)	0.2(5)	4.7(5)
O3	17.4(8)	17.4(8)	15.7(7)	-2.6(6)	-0.9(6)	6.3(6)
O1	15.8(8)	18.2(8)	20.5(8)	-5.0(6)	-1.6(6)	6.2(6)
N4	15.0(8)	13.3(8)	17.4(9)	0.1(6)	2.5(6)	4.1(6)
N2	19.1(9)	14.6(8)	18.0(9)	0.6(7)	-1.2(7)	4.9(7)
N7	18.7(9)	14.4(8)	17.6(9)	-1.3(7)	2.3(7)	2.1(7)
N3	19.8(9)	15.7(8)	14.1(8)	1.0(6)	0.5(7)	5.9(7)
N6	21.4(10)	16.9(9)	20.0(9)	0.8(7)	5.7(7)	3.1(7)
N5	16.3(9)	15.4(8)	20.5(9)	-1.6(7)	0.6(7)	2.7(7)
N1	19.4(10)	16.9(9)	19.8(10)	-1.1(7)	-0.8(7)	5.9(7)
C3	19.5(11)	19.6(11)	20.5(11)	-0.8(8)	5.1(8)	4.9(8)
C7	20.1(11)	16.5(10)	20.9(11)	0.7(8)	1.8(8)	-0.9(8)
C10	19.8(11)	15.2(9)	18.3(10)	0.4(8)	-0.4(8)	2.6(8)
C1	24.3(12)	19.4(10)	16.6(10)	0.3(8)	0.6(8)	6.8(8)
C11	15.0(10)	14.9(9)	15.2(9)	-0.9(7)	0.8(7)	1.2(7)
C12	18.3(11)	14.5(9)	16.1(10)	-2.2(7)	1.5(8)	1.7(7)
C8	27.3(13)	16.2(10)	24.3(12)	0.3(9)	2.7(9)	-3.9(9)
C4	17.4(11)	19.2(11)	28.7(13)	0.3(9)	1.3(9)	1.9(8)
C16	19.3(11)	25.0(12)	20.1(11)	3.3(9)	-1.9(8)	5.9(9)
C13	28.7(13)	14.7(10)	21.8(11)	0.9(8)	5.1(9)	-1.1(9)
C18	22.2(12)	26.4(12)	18.6(11)	-1.8(9)	-3.4(9)	0.6(9)
C9	25.5(12)	13.9(9)	23.3(11)	-0.5(8)	-0.1(9)	3.1(8)
C2	26.6(12)	24.9(12)	18.7(11)	-0.4(9)	6.3(9)	7.3(9)
C19	23.0(12)	18.0(11)	22.6(12)	-2.8(8)	0.5(9)	3.4(8)
C6	19.6(12)	21.4(11)	30.9(13)	1.5(10)	4.7(9)	-2.7(9)
C14	33.7(14)	22.5(12)	27.8(13)	-1.1(10)	13.6(11)	-5.2(10)
C5	16.0(11)	24.5(12)	36.7(15)	3.0(10)	4.0(10)	-1.2(9)
B1	15.9(11)	12.2(10)	18.9(11)	-0.2(8)	0.4(9)	2.0(8)
C15	32.8(15)	23.4(13)	32.7(15)	0.6(10)	15.7(11)	-1.2(10)
B3	13.8(11)	12.9(10)	16.3(11)	-0.3(8)	1.3(8)	2.5(8)
B2	14.3(11)	14.1(10)	15.3(11)	-0.6(8)	-0.6(8)	4.1(8)
C17	66(4)	159(7)	126(7)	-56(5)	18(5)	7(5)

Table S9 Bond Lengths for BOC-20

Atom	Atom	Length/Å	Atom	Atom	Length/Å

Table S9 Bond Lengths for BOC-20

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ni1	N7	2.088(5)	N6	C13	1.339(8)
Ni1	N1	2.063(5)	N4	C16	1.308(8)
Ni1	N10	2.100(5)	C25	C24	1.357(11)
Ni1	N12	2.062(5)	C22	C21	1.391(10)
Ni1	N6	2.101(5)	C5	C4	1.407(8)
Ni1	N4	2.092(5)	C5	C6	1.394(8)
O1	C2	1.371(7)	C5	B1	1.608(8)
O1	C1	1.404(10)	C3	C4	1.388(9)
N7	N8	1.373(7)	C3	C2	1.382(9)
N7	C17	1.325(8)	C13	C12	1.399(10)
N9	N10	1.375(7)	O2	C29	1.364(9)
N9	C22	1.346(8)	O2	C32	1.466(10)
N9	B2	1.554(8)	C21	C20	1.393(10)
N11	N12	1.362(7)	C2	C7	1.378(10)
N11	C25	1.366(10)	C26	C27	1.366(9)
N11	B2	1.569(8)	C26	B2	1.571(9)
N8	C19	1.337(8)	C26	C31	1.483(11)
N8	B2	1.565(8)	C10	C9	1.385(10)
N1	N2	1.363(7)	C24	C23	1.401(10)
N1	C10	1.323(8)	C11	C12	1.362(10)
N3	N4	1.393(7)	C17	C18	1.397(10)
N3	B1	1.559(7)	C9	C8	1.395(9)
N3	C14	1.314(8)	C18	C19	1.375(10)
N10	C20	1.326(9)	C16	C15	1.391(9)
N12	C23	1.327(8)	C6	C7	1.390(10)
N2	B1	1.564(8)	C15	C14	1.375(9)
N2	C8	1.341(9)	C28	C27	1.397(12)
N5	N6	1.369(7)	C28	C29	1.398(12)
N5	C11	1.354(8)	C30	C29	1.329(10)
N5	B1	1.559(8)	C30	C31	1.422(10)

Table S10 Bond Lengths for BOC-21

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ni1	O9	2.085(5)	O12	B9	1.394(11)
Ni1	$O9^{1}$	2.085(5)	O14	B8	1.373(11)
Ni1	$O9^{2}$	2.085(5)	O14	B9	1.353(12)

Table S10 Bond Lengths for BOC-21

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ni1	N5	2.033(7)	O15	B9	1.358(12)
Ni1	N5[1]	2.033(7)	N6	N5	1.371(9)
Ni1	N5[2]	2.033(7)	N6	C9	1.355(11)
O9	B7[1]	1.469(11)	N6	B7	1.556(10)
O9	B8	1.361(10)	N5	C7	1.343(10)
O13	B7	1.458(10)	C9	C8	1.398(13)
O13	B8	1.352(11)	C8	C7	1.382(14)
O12	B7[1]	1.450(11)			

Table S11 Bond Lengths for BOC-22

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ni2	O5[1]	2.0830(16)	N6	C15	1.336(3)
Ni2	O4	2.0736(15)	N5	C12	1.384(3)
Ni2	N2	2.0856(19)	N5	C4	1.328(3)
Ni2	N3	2.043(2)	N1	C16	1.342(3)
Ni2	N6[1]	2.069(2)	C3	C2	1.390(4)
Ni2	N5	2.147(2)	C7	C12	1.430(3)
O2	B1	1.372(3)	C7	C8	1.422(3)
O2	B2	1.475(3)	C7	C6	1.409(4)
O5	B3	1.471(3)	C10	C11	1.385(3)
O4	B3	1.435(3)	C10	C9	1.411(3)
O4	B2	1.454(3)	C1	C2	1.387(3)
O3	B1	1.365(3)	C11	C12	1.435(3)
O3	B3	1.461(3)	C11	B2	1.632(3)
O1	B1	1.360(3)	C8	C9	1.366(4)
N4	N3	1.354(3)	C4	C5	1.410(4)
N4	C3	1.350(3)	C16	C18	1.371(4)
N4	B2	1.576(3)	C13	C14	1.372(4)
N2	N1	1.354(3)	C18	C19	1.397(4)
N2	C19	1.341(3)	C6	C5	1.374(4)
N7	N6	1.363(3)	C14	C15	1.399(4)
N7	C13	1.343(3)	C17	C17[2]	1.082(14)
N7	B3	1.593(3)	C17	N8[2]	1.76(2)
N3	C1	1.341(3)			

Table S12 Bond Angles for BOC-20.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N7	Ni1	N10	85.10(19)	C24	C25	N11	108.4(7)
N7	Ni1	N6	94.2(2)	N9	C22	C21	108.8(6)
N7	Ni1	N4	179.2(3)	C4	C5	B1	117.5(5)
N1	Ni1	N7	95.44(19)	C6	C5	C4	114.7(5)
N1	Ni1	N10	93.5(2)	C6	C5	B1	127.6(5)
N1	Ni1	N6	87.07(19)	C2	C3	C4	119.4(6)
N1	Ni1	N4	85.0(2)	N6	C13	C12	110.5(6)
N12	Ni1	N7	86.3(2)	C29	O2	C32	115.2(6)
N12	Ni1	N1	178.3(2)	C3	C4	C5	123.2(6)
N12	Ni1	N10	86.7(2)	C22	C21	C20	104.0(6)
N12	Ni1	N6	92.7(2)	O1	C2	C3	123.5(6)
N12	Ni1	N4	93.2(2)	O1	C2	C7	116.7(6)
N6	Ni1	N10	179.1(2)	C7	C2	C3	119.8(6)
N4	Ni1	N10	95.5(2)	C27	C26	B2	133.7(7)
N4	Ni1	N6	85.3(2)	C27	C26	C31	112.0(6)
C2	O1	C1	117.9(6)	C31	C26	B2	114.3(5)
N8	N7	Ni1	121.2(3)	N1	C10	C9	111.5(5)
C17	N7	Ni1	131.2(4)	C25	C24	C23	105.2(6)
C17	N7	N8	107.2(5)	N12	C23	C24	110.5(6)
N10	N9	B2	121.5(5)	N5	C11	C12	108.8(6)
C22	N9	N10	109.2(5)	N7	C17	C18	110.5(6)

Table S13 Bond Angles for BOC-21.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
$O9^{1}$	Ni1	O9	81.8(2)	C9	N6	N5	110.2(7)
$O9^{2}$	Ni1	O9	81.8(2)	B7	N6	N5	116.4(6)
$O9^{2}$	Ni1	$O9^{1}$	81.8(2)	B7	N6	C9	133.3(8)
$N5^{1}$	Ni1	$O9^{1}$	95.8(2)	N6	N5	$Ni1^{1}$	113.1(5)
$N5^{2}$	Ni1	O9	161.4(2)	C7	N5	$Ni1^{1}$	140.3(7)
$N5^{2}$	Ni1	$O9^{1}$	79.6(2)	C7	N5	N6	106.4(7)
N5	Ni1	O9	95.8(2)	C8	C9	N6	107.0(8)
$N5^{1}$	Ni1	O9	79.6(2)	C7	C8	C9	105.8(8)
N5	Ni1	$O9^{1}$	161.4(2)	O13	B7	$O9^{2}$	112.8(7)
$N5^{2}$	Ni1	$O9^{2}$	95.8(2)	$O12^{2}$	B7	$O9^{2}$	111.2(7)
$N5^{1}$	Ni1	$O9^{2}$	161.4(2)	$O12^{2}$	B7	O13	108.7(7)
N5	Ni1	$O9^{2}$	79.6(2)	N6	B7	$O9^{2}$	103.4(6)
$N5^{2}$	Ni1	N5	101.9(2)	N6	B7	O13	110.2(6)

Table S13 Bond Angles for BOC-21.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N5[2]	Ni1	N5[1]	101.9(2)	N6	B7	O12[2]	110.5(7)
N5[1]	Ni1	N5	101.9(2)	O13	B8	O9	121.8(8)
B7[1]	O9	Ni1	108.3(4)	O14	B8	O9	118.3(7)
B8	O9	Ni1	127.2(5)	O14	B8	O13	119.9(7)
B8	O9	B7[1]	124.4(7)	O14	B9	O12	121.8(8)
B8	O13	B7	125.3(7)	O15	B9	O12	120.3(9)
B9	O12	B7[1]	120.5(7)	O15	B9	O14	117.9(8)
B9	O14	B8	121.2(7)	C8	C7	N5	110.5(8)

Table S14 Bond Angles for BOC-22

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O5[1]	Ni2	N2	90.55(7)	N4	C3	C2	108.2(2)
O5[1]	Ni2	N5	89.80(7)	C8	C7	C12	119.4(2)
O4	Ni2	O5[1]	96.41(6)	C6	C7	C12	119.3(2)
O4	Ni2	N2	171.24(7)	C6	C7	C8	121.2(2)
O4	Ni2	N5	84.17(7)	C11	C10	C9	123.6(2)
N2	Ni2	N5	90.56(8)	N3	C1	C2	110.4(2)
N3	Ni2	O5[1]	172.58(7)	C10	C11	C12	116.5(2)
N3	Ni2	O4	81.01(7)	C10	C11	B2	119.6(2)
N3	Ni2	N2	92.71(8)	C12	C11	B2	123.96(19)
N3	Ni2	N6[1]	94.12(8)	N5	C12	C7	119.7(2)
N3	Ni2	N5	96.84(8)	N5	C12	C11	119.9(2)
N6[1]	Ni2	O5[1]	79.05(7)	C7	C12	C11	120.4(2)
N6[1]	Ni2	O4	93.81(7)	C9	C8	C7	120.1(2)
N6[1]	Ni2	N2	92.73(8)	N5	C4	C5	123.9(2)
N6[1]	Ni2	N5	168.40(8)	N1	C16	C18	107.6(2)
B1	O2	B2	120.65(18)	N7	C13	C14	109.0(2)
B3	O5	Ni2[1]	119.88(14)	C16	C18	C19	105.0(2)
B3	O4	Ni2	127.10(13)	C8	C9	C10	119.7(2)
B3	O4	B2	123.86(17)	C1	C2	C3	104.8(2)
B2	O4	Ni2	107.92(13)	N2	C19	C18	110.8(2)
B1	O3	B3	122.63(18)	C5	C6	C7	119.4(2)
N3	N4	B2	115.63(17)	C13	C14	C15	104.3(2)
C3	N4	N3	109.65(19)	C6	C5	C4	118.6(2)
C3	N4	B2	134.36(19)	O3	B1	O2	122.1(2)
N1	N2	Ni2	125.53(16)	O1	B1	O2	121.5(2)
C19	N2	Ni2	129.24(16)	O1	B1	O3	116.4(2)

Table S14 Bond Angles for BOC-22

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C19	N2	N1	105.11(19)	N6	C15	C14	110.8(2)
N6	N7	B3	119.69(18)	O5	B3	N7	104.30(17)
C13	N7	N6	109.8(2)	O4	B3	O5	111.71(19)
C13	N7	B3	130.5(2)	O4	B3	O3	112.80(18)
N4	N3	Ni2	112.65(14)	O4	B3	N7	111.66(18)
C1	N3	Ni2	139.93(16)	O3	B3	O5	109.85(18)
C1	N3	N4	106.96(18)	O3	B3	N7	106.06(18)
N7	N6	Ni2[1]	115.43(15)	O2	B2	N4	108.23(18)
C15	N6	Ni2[1]	137.73(18)	O2	B2	C11	111.40(18)
C15	N6	N7	106.1(2)	O4	B2	O2	111.96(18)
C12	N5	Ni2	126.99(16)	O4	B2	N4	104.78(17)
C4	N5	Ni2	113.92(16)	O4	B2	C11	112.88(19)
C4	N5	C12	119.0(2)	N4	B2	C11	107.14(18)
C16	N1	N2	111.5(2)	C17[2]	C17	N8[2]	161.6(7)

Table S15 Striking contrast between BOC-22 and other known boron-based catalysts (after 7hours)[1-3].

catalysts	solvent conditions	gas atmosphere	Gas evolution （μmol/g）
BOC-22	acetonitrile/H_2O (v/v= 4 : 1)	atmosphere of CO_2	CO:792 CH_4:101 H_2:57
PTC-391-Cu[1]	acetonitrile/H2O (v/v= 4 : 1)	atmosphere of CO_2	CO:668 H_2:82
BIF-29[2]	acetonitrile/H_2O (v/v= 4 : 1)	atmosphere of CO_2	CO:3334 H_2:702
BIF-101[3]	acetonitrile/H_2O (v/v= 4 : 1)	atmosphere of CO_2	CO:5830 H_2:1100

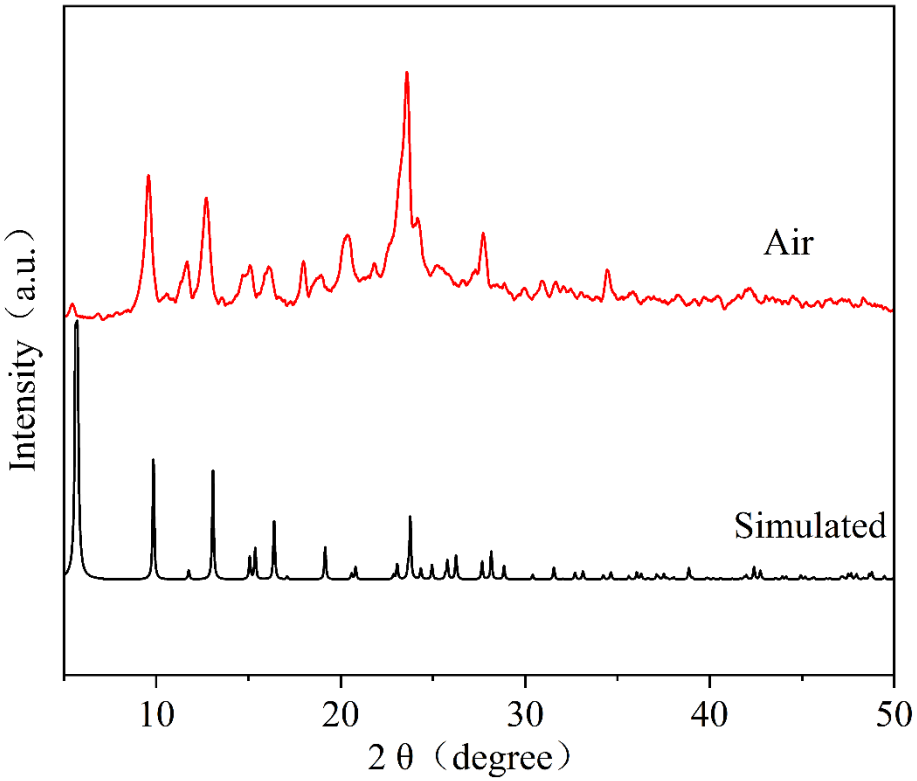

Figure S1. Calculated and experimental powder X-ray diffraction patterns of BOC-21 in air

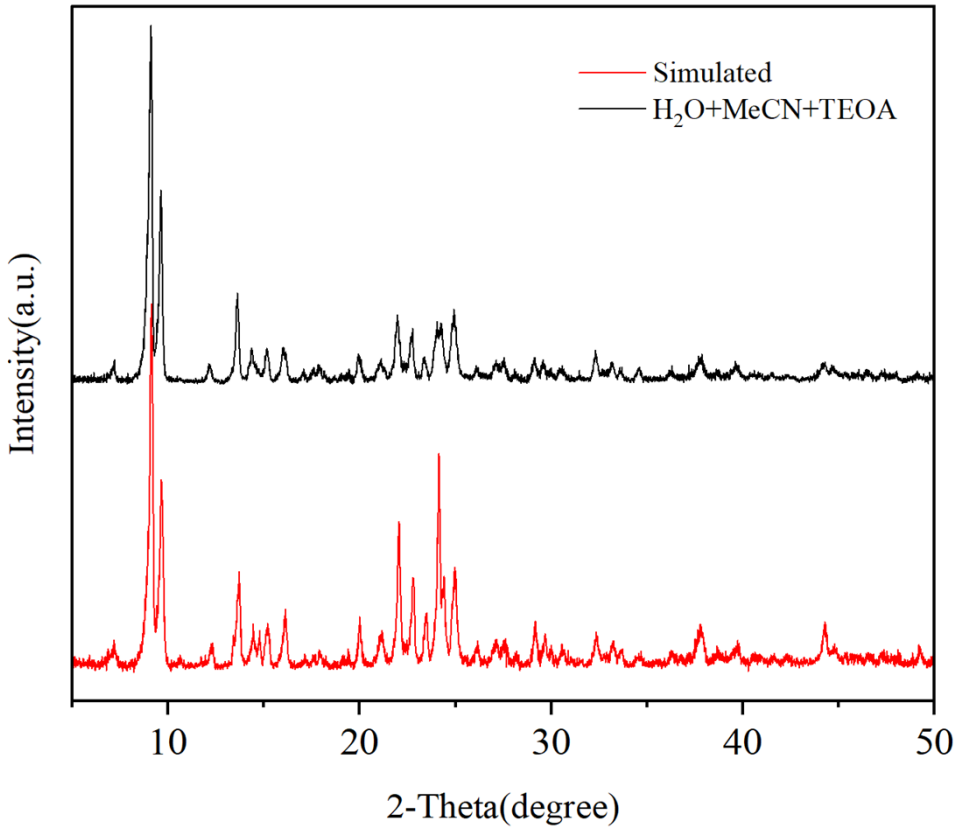

Figure S2. Calculated and experimental powder X-ray diffraction patterns of BOC-22 Under photocatalytic conditions

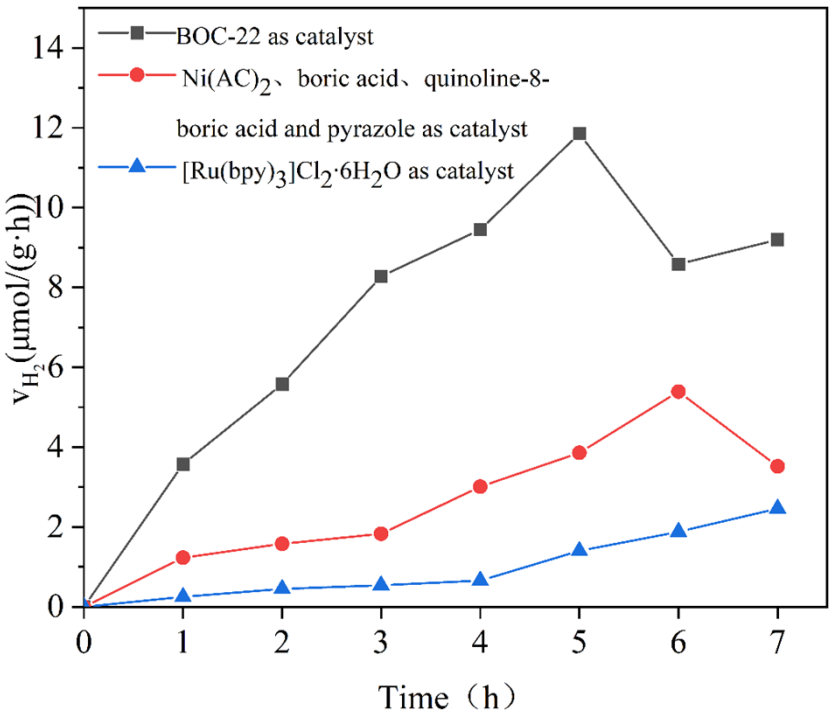

Figure S3. Time-dependent H_2 evolution over BOC-22 (10 mg) under visible-light ($\lambda > 420$ nm) irradiation in the presence of $[Ru(bpy)_3]Cl_2$ (10 mg) and TEOA (0.5 mL) in an acetonitrile/water (4:1, v/v) solution (10 mL).

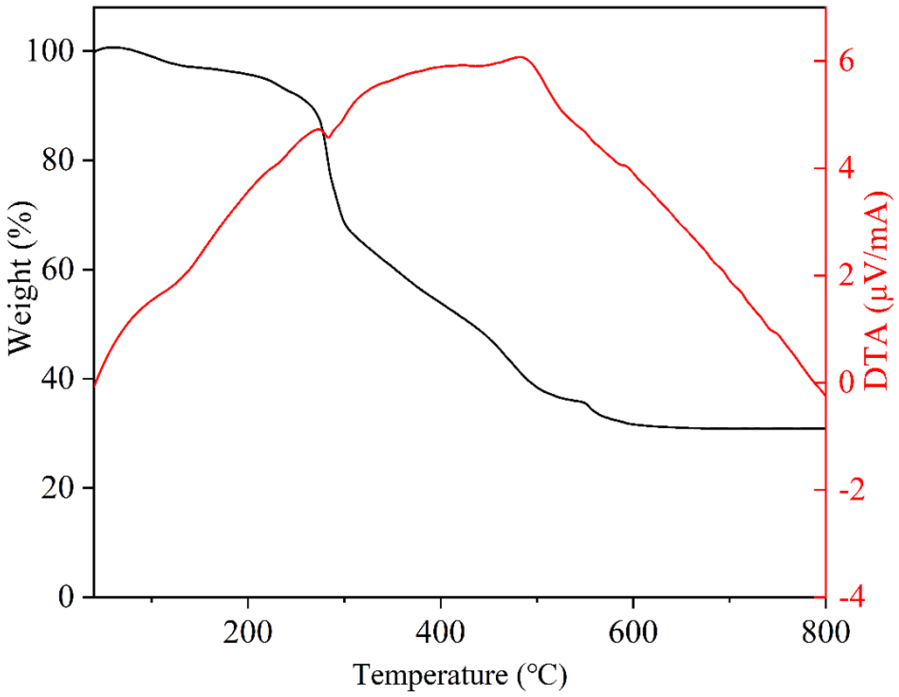

Figure S4. TG-DTA curves of BOC-22.

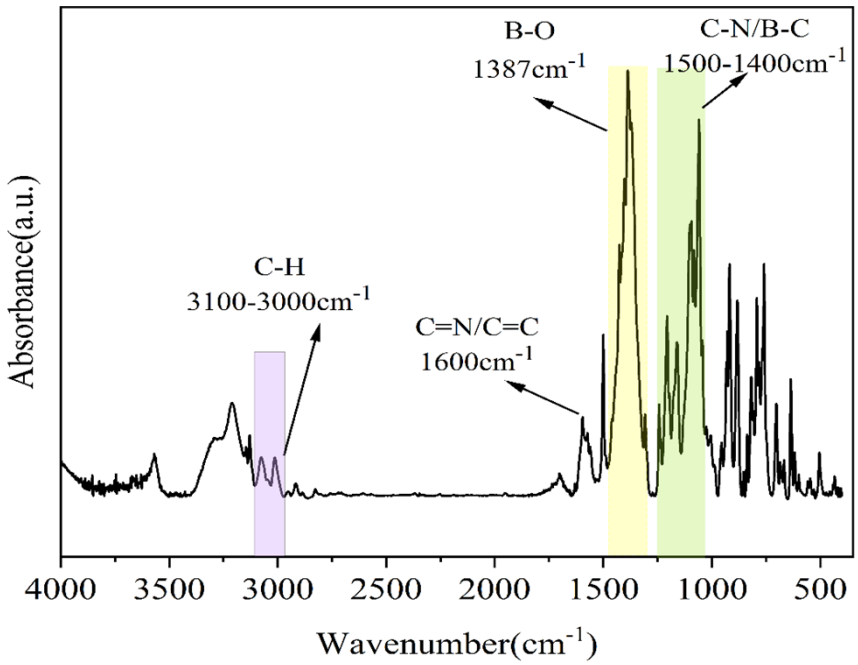

Figure S5. IR spectrum of BOC-22.

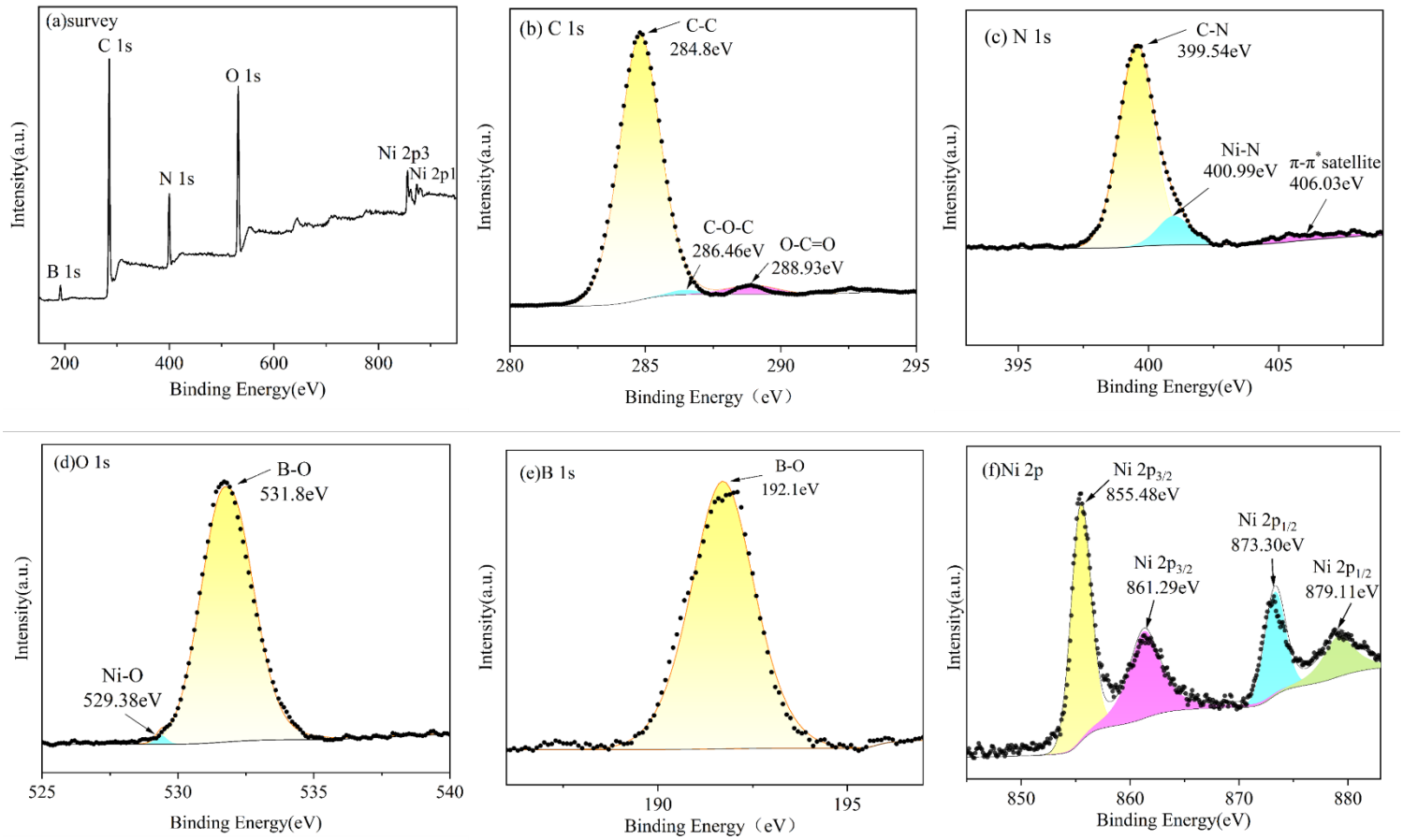

Figure S6. (a) Survey XPS analysis of BOC-22; High-resolution XPS analysis of BOC-22 (b) C 1s, (c) N 1s, (d) O 1s, (e) B 1s, and (f) Ni 2p.

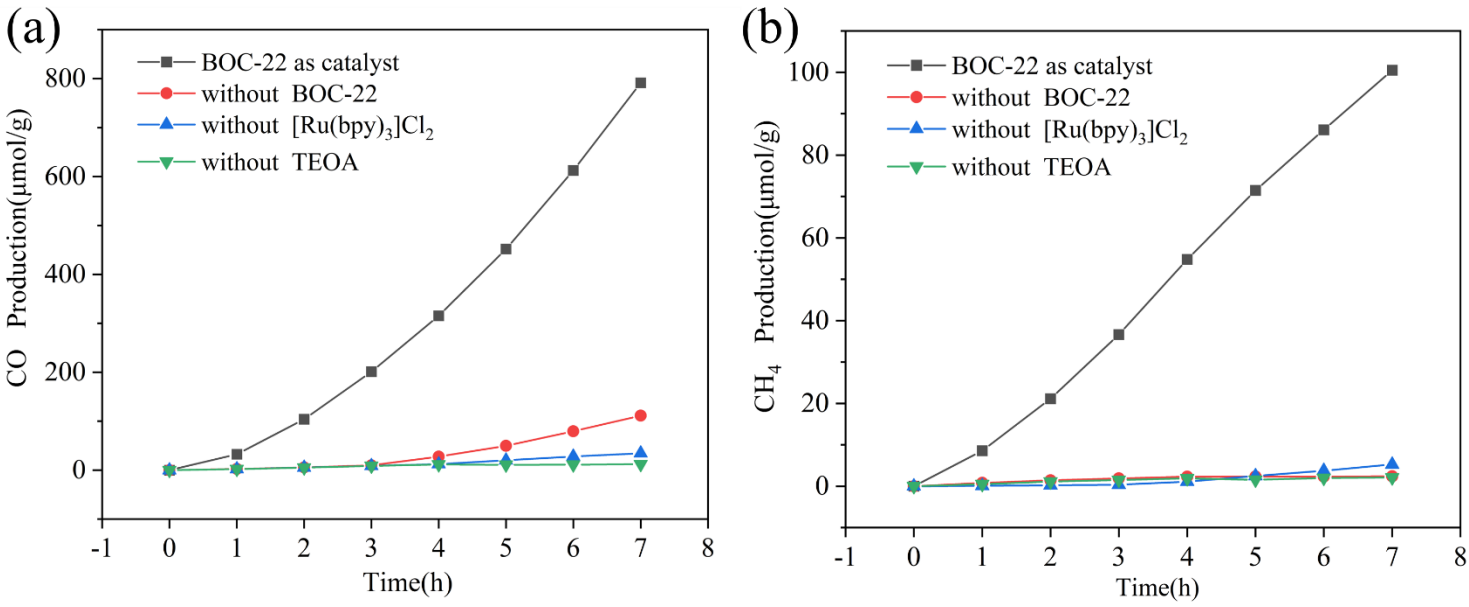

Figure S7. CO(a) and CH_4(b) production under various conditions(include tests on the intrinsic photocatalytic performance of BOC-22 in the absence of a photosensitizer, and experiments without the addition of $[Ru(bpy)_3]Cl_2$ and TEOA.)

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