Supplementary Information (SI) for Inorganic Chemistry Frontiers.

Supporting Information

Temperature-driven growth of uranyl-organic frameworks for efficient photocatalytic CO_2 reduction

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1. Materials and Characterizations

All the chemicals were of analytical grade and purchased from commercial sources without any further purification. Powder X-ray diffraction (PXRD) patterns were collected on a MiniFlex 600X X-ray diffractometer in the range of 5-40°at room temperature. Thermogravimetric analysis (TGA) was performed on a Rigaku TG-DTA8122 Corporation analyzer heated from 30-800 °C under a dry nitrogen gas atmosphere. The Fourier transform infrared (FT-IR) spectra were examined in the range of 4000-400 cm^{-1} on a Shimadzu IRAffinity-1S FT-IR spectrophotometer. The scanning electron microscopy (SEM) was performed by Thermo Fisher. The gas products are identified by FULI GC9790II.

Caution! Uranyl nitrate hexahydrate $UO_2(NO_3)_2{\cdot}6H_2O$ is a radioactive and chemically toxic reactant, and precautions with suitable care and protection for handling such substances should be followed although it was used in the experiment. $UO_2(NO_3)_2{\cdot}6H_2O$ was dissolved in ultra-pure water (50 mL) to obtain a uranyl nitrate stock solution (0.50 M).

2. Crystallographic data

The crystallographic data and structural refinements of HNU-94-80 were collected at 100 K on a Bruker Apex CCD diffractometer with graphite monochromatic Ga-Kα radiation. All crystal structures are solved directly with the ShelXT[1] structure solution program using intrinsic phasing by the least square method based on F^2 using Olex2[2]. Except for some solvent molecules, other atoms are generated in the ideal geometric position. Topology analysis of

HNU-94-80 was performed using the TOPOS[3] program package.

3. Electrochemical test

Photo-electrochemical measurements were carried out on Shanghai Chenhua electrochemical workstation in 1 M Na_2SO_4 solution. Three-electrode configuration was used with ITO glass coated with the catalyst as the working electrode, AgCl electrode reference electrode, and Pt counter electrode. For the preparation of the working electrode, the as-synthesized photocatalyst sample (3 mg) were added to Nafion (20 μL), EtOH (200 μL) and H_2O (400 μL) for ultrasonic treatment for 6h, and the suspension thus obtained was evenly dropped on the surface of the ITO board, which was subsequently dried in a drying oven at 60°C.

4. Photocatalysis experiment

The photocatalytic reduction of carbon dioxide was conducted within a 150 mL quartz reactor. A 300 W xenon lamp, equipped with a filter ($\lambda \geq 420$ nm), served as the light source, and high-purity carbon dioxide was employed as the feedstock for the photocatalytic reaction. The reaction mixture consisted of $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (0.013 mmol, 10 mg) and HNU-94 (0.003 mmol, 5 mg), with acetonitrile (MeCN, 30 mL), water (7.5 mL), and triethanolamine (TEOA, 5 mL) as solvents. Initially, the catalyst was placed into the sealed quartz reactor. Subsequently, the reactor was evacuated using an online gas-closed system in tandem with a gas-circulated pump. Following this, high-purity carbon dioxide was introduced. After two rounds of gas purging to reach adsorption equilibrium, the xenon lamp was switched on for irradiation over a period of 2 hours, maintaining the temperature at 32°C. Every 20 min, a gas chromatography (GC) instrument was utilized to test and analyze gases such as carbon monoxide, methane, and hydrogen through the online system.

5. Figures and Tables

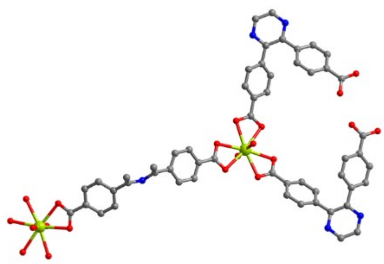

Figure S1. The asymmetric unit of HNU-94.

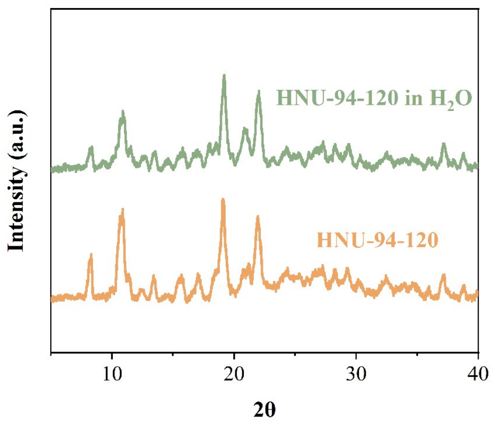

Figure S2. PXRD of HNU-94-120 after 48 h immersion in H_2O.

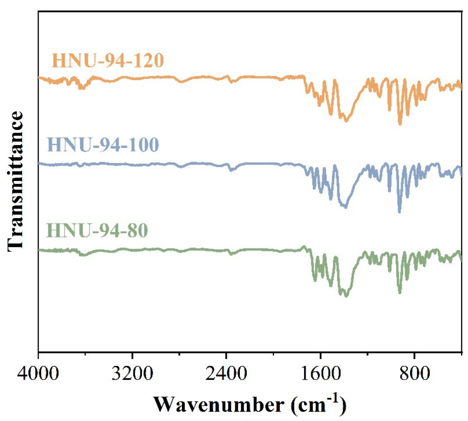

Figure S3. The FT-IR curves for HNU-94-80, HNU-94-100 and HNU-94-120.

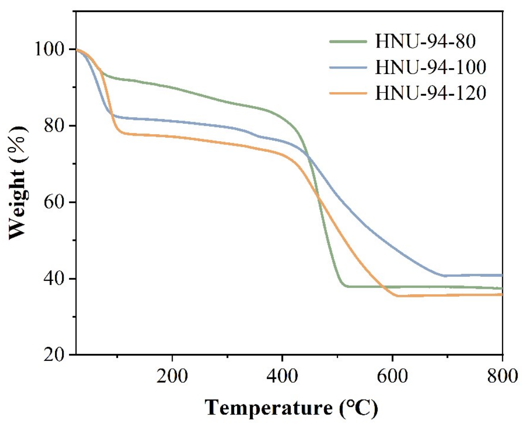

Figure S4. The TGA for HNU-94-80, HNU-94-100 and HNU-94-120

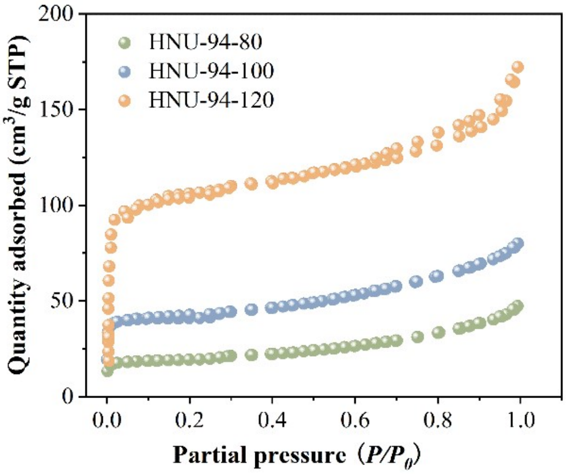

Figure S5. N_2 sorption isotherms of the HNU-94-80, HNU-94-100 and HNU-94-120.

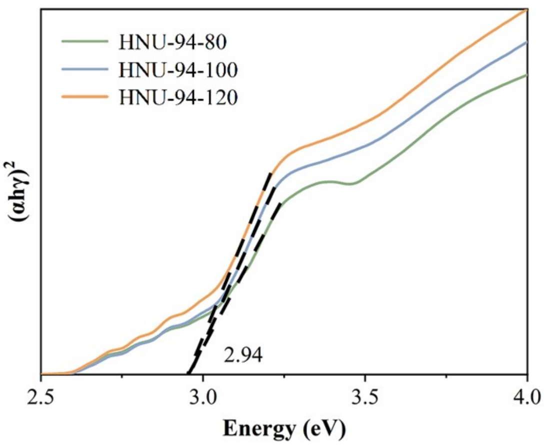

Figure S6. Band gap energy analysis for HNU-94-80, HNU-94-100 and HNU-94-120.

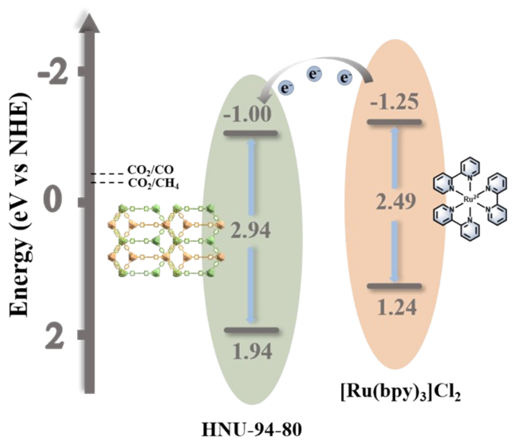

Figure S7. Schematic diagram of HNU-94-80 electron transfer.

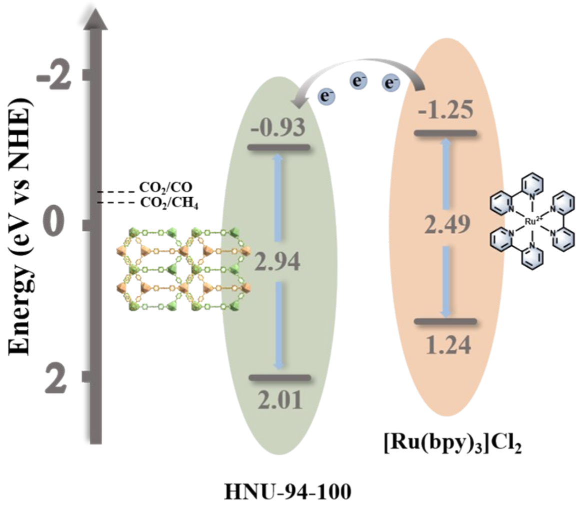

Figure S8. Schematic diagram of HNU-94-100 electron transfer.

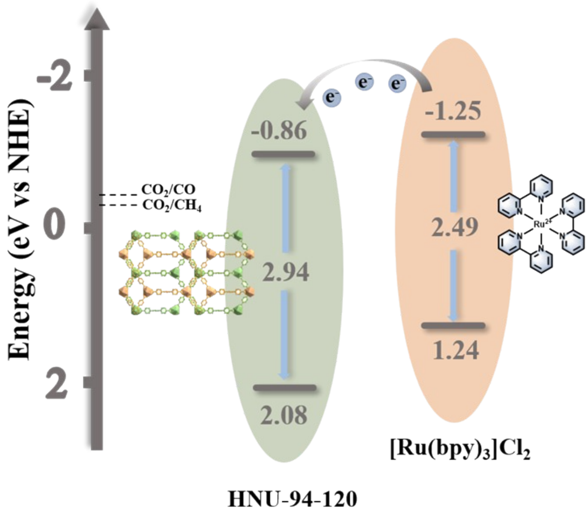

Figure S9. Schematic diagram of HNU-94-120 electron transfer.

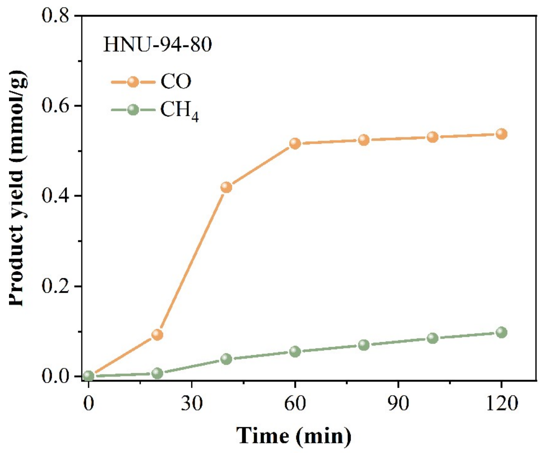

Figure S10. Time-course profiles of CO and CH_4 catalyzed by HNU-94-80.

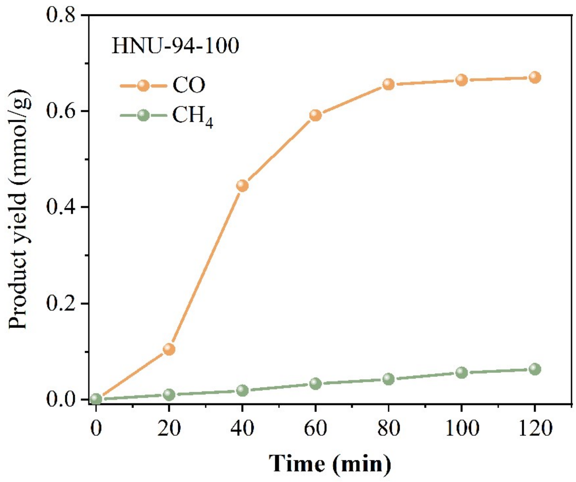

Figure S11. Time-course profiles of CO and CH_4 catalyzed by HNU-94-100.

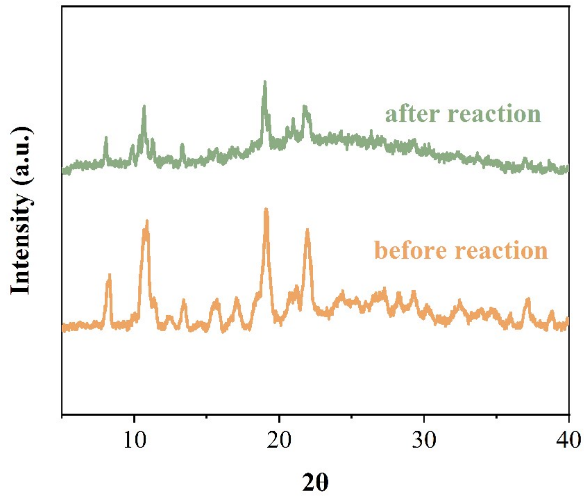

Figure S12. PXRD of HNU-94-120 before and after photocatalytic reaction.

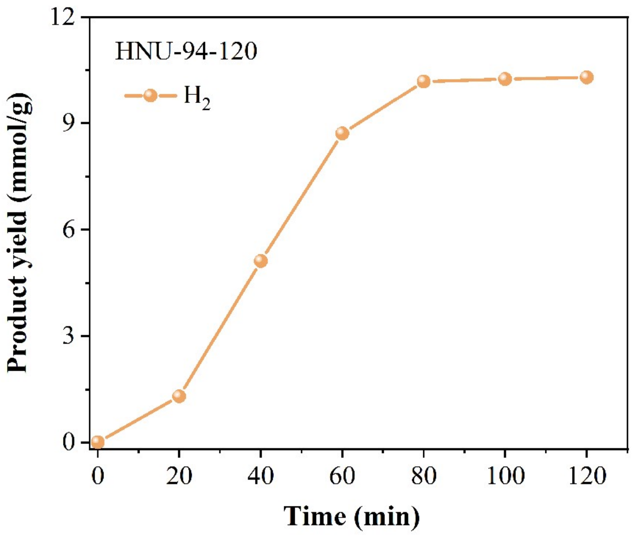

Figure S13. Time-course profiles of H_2 catalyzed by HNU-94-120.

Table S1 Crystal data of HNU-94-80.

	HNU-94-80
Empirical formula	$C_{48}H_{24}N_3O_{16}U_2$
Formula weight	1374.76
Temperature/K	100
Crystal system	monoclinic
Space group	C2/c
a/Å	17.8388(13)
b/Å	56.143(4)
c/Å	18.6016(14)
α/°	90
β/°	116.072(3)
γ/°	90
Volume/Å^3	16734(2)
Z	8
ρcalcg/cm^3	1.091
μ/mm^{-1}	8.365
F(000)	5160.0
Reflections collected	155999
Independent reflections	14743 [R_{int} = 0.0703, R_{sigma} = 0.0381]
Data/restraints/parameters	14743/24/625
Goodness-of-fit on F2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0407, wR_2 = 0.1138
Final R indexes [all data]	R_1 = 0.0465, wR_2 = 0.1168

Table S2. Bond lengths [Å] and angles [deg] for HNU-94-80.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
U1	O16	1.774(6)	U2	O121	2.473(4)
U1	O15	1.768(6)	U2	O111	2.475(4)
U1	O3	2.466(4)	U2	O14	1.768(4)
U1	O4	2.440(4)	U2	O71	2.470(3)
U1	O5	2.449(5)	U2	O81	2.456(4)
U1	O6	2.479(4)	U2	O13	1.758(4)
U1	O9	2.423(4)	U2	O1	2.486(4)
U1	O10	2.461(4)	U2	O2	2.439(4)

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
O16	U1	O3	89.6(2)	O15	U1	O16	178.5(2)
O16	U1	O4	92.5(2)	O15	U1	O3	91.6(2)
O16	U1	O5	91.8(2)	O15	U1	O4	88.9(2)
O16	U1	O6	90.23(19)	O15	U1	O5	88.4(2)
O16	U1	O9	93.2(2)	O15	U1	O6	88.73(19)
O16	U1	O10	89.1(2)	O15	U1	O9	86.4(2)
O3	U1	O6	170.85(13)	O15	U1	O10	89.47(19)
O4	U1	O3	52.45(15)	O5	U1	O3	118.05(14)
O4	U1	O5	65.61(14)	O5	U1	O6	52.81(13)
O4	U1	O6	118.42(14)	O5	U1	O10	121.42(12)
O4	U1	O10	172.74(14)	O9	U1	O3	67.74(13)
O9	U1	O4	119.83(14)	O9	U1	O10	52.99(12)
O9	U1	O5	172.38(17)	O10	U1	O3	120.53(13)
O9	U1	O6	121.40(12)	O10	U1	O6	68.62(12)

Table S3 Photocatalytic efficiency of HNU-94 compared to other MOFs.

MOFs	Light [nm]	Time [h]	CO [mmol g^{-1}]	Ref
HNU-94-120	λ≥420	2	2.57	This work
HNU-94-100	λ≥420	2	0.67	This work
HNU-94-80	λ≥420	2	0.53	This work
V_{18}-Co	λ≥420	1	1.037	4
V_{18}-Mn	λ≥420	9	5.74×10^{-3}	4
BPAN-Co-1	λ≥420	1	1.927	5
NNU-55-Ni	λ≥420	16	4.265	6
$Ni_{0.75}Mg_{0.25}$-MOF-74	λ≥420	1	0.64	7
Co-OAc	λ≥420	1	2.3257	8
UiO-Co-N_3	λ≥420	2	0.3586	9
UCu1	λ≥420	3	1.0782	10
UCu2	λ≥420	3	1.4448	10
MR-$N_{0.2}C_{0.8}O$	λ≥400	4	1.11	11
U-B-Co	λ≥400	1	3.41	12
IHEP-101	λ≥420	3	1.374	13

Table S4 The research of reaction conditions of HNU-94-120

	CO [mmol g^{-1}]	CH_4 [mmol g^{-1}]
Without the H_2O	0.45	0.02
Without the MeCN	0.16	0
Without the TEOA	0	0
CH_3OH instead of CH_3CN	0.78	0

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