

Supplementary Information

Iridium complex modified MOFs for enhancing photocatalytic hydrogen evolution

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Materials

Tetrakis(triphenylphosphine)palladium ($\geq 98.0\%$) was purchased from Bidepharm Corporation. $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ ($\geq 98.0\%$), 2-phenylpyridine (ppy, $\geq 98.0\%$), coumarin 6 (cmr, $\geq 98.0\%$), and 5,5'-Dibromo-2,2'-bipyridyl ($\geq 98.0\%$) were purchased from Aladdin Industrial Corporation. Chloro(1,5-cyclooctadiene)iridium(I) dimer ($\geq 98.0\%$), 4-methoxycarbonylphenylboronic acid ($\geq 98.0\%$), zirconium tetrachloride (ZrCl_4 , $\geq 99.0\%$), 2-aminoterephthalic acid (BDC- NH_2 , $\geq 98.0\%$), polyvinylpyrrolidone (PVP, $M_w=55000$), hexafluorophosphoric acid (HPF_6 , 60 wt.% aqueous solution), and chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 99.0%) were purchased from Energy Chemical Corporation. Acetic acid (A.R.), methanol (A.R.), ethylene glycol ethyl ether (A.R.), triethanolamine (A.R.), tetrahydrofuran (A.R.), acetone (A.R.), potassium carbonate (A.R.), triclosan (A.R.), ethylene glycol (A.R.), N, N-dimethylformamide (DMF) (A.R.), HCl (36 wt.% aqueous solution), and triethylamine (TEA) (A.R.) were purchased from Xilong Scientific Corporation. Potassium platinumchloride (K_2PtCl_4 , $\geq 99.9\%$) was purchased from Sigma Aldrich Corporation. All materials were used without further purification. Deionized water was used throughout all experiments.

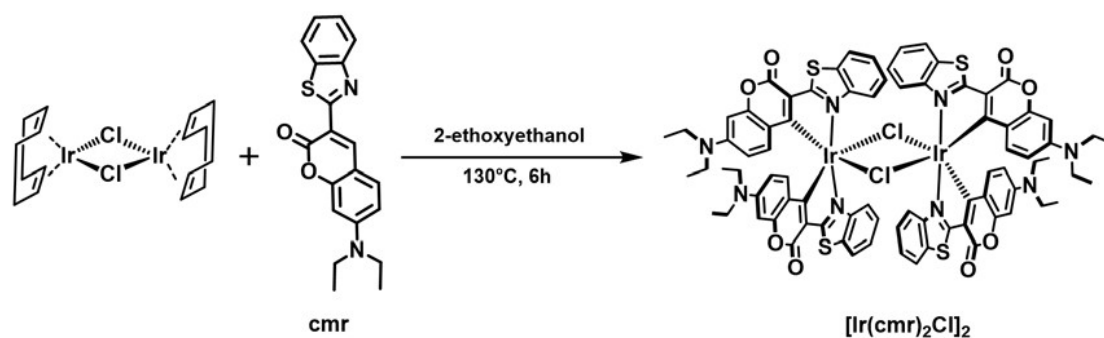


Fig. S 1 The synthesis route of iridium dichloro bridge compound $[\text{Ir}(\text{cmr})_2\text{Cl}]_2$.

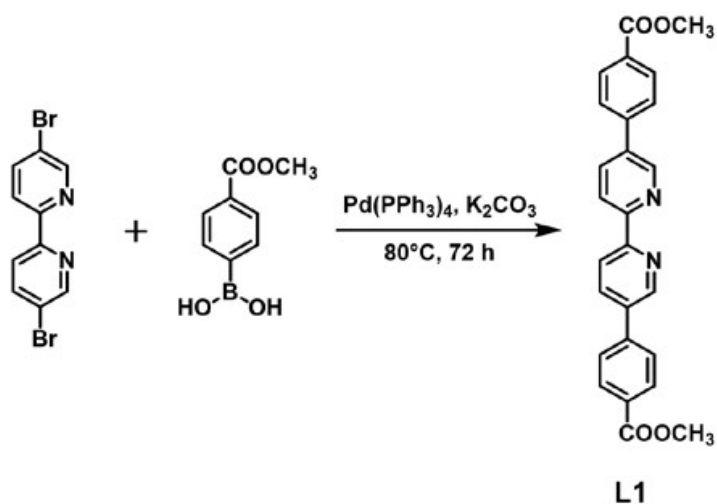


Fig. S 2 The synthetic route to the auxiliary ligand L1.

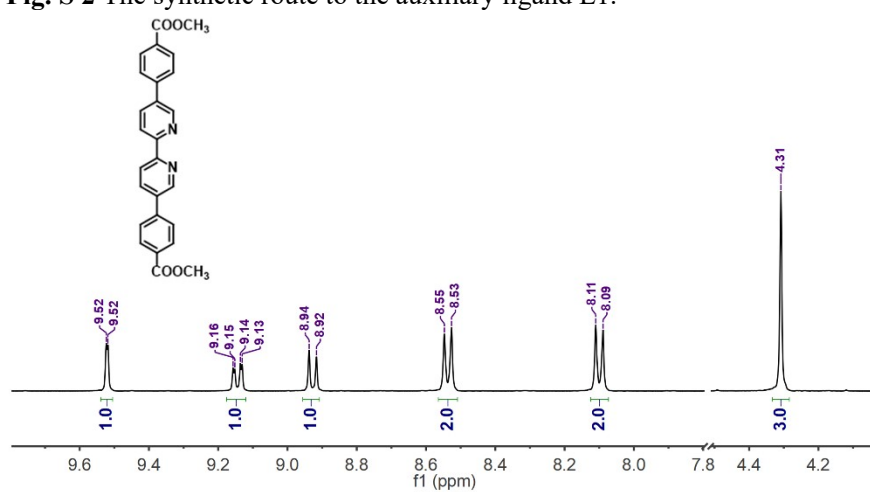


Fig. S 3 The ¹H NMR spectrum of auxiliary ligand L1.

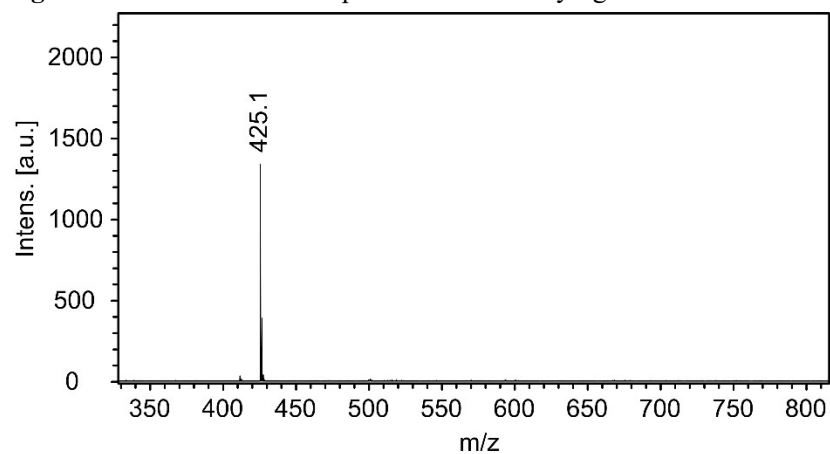


Fig. S 4 The mass spectra of auxiliary ligand L1.

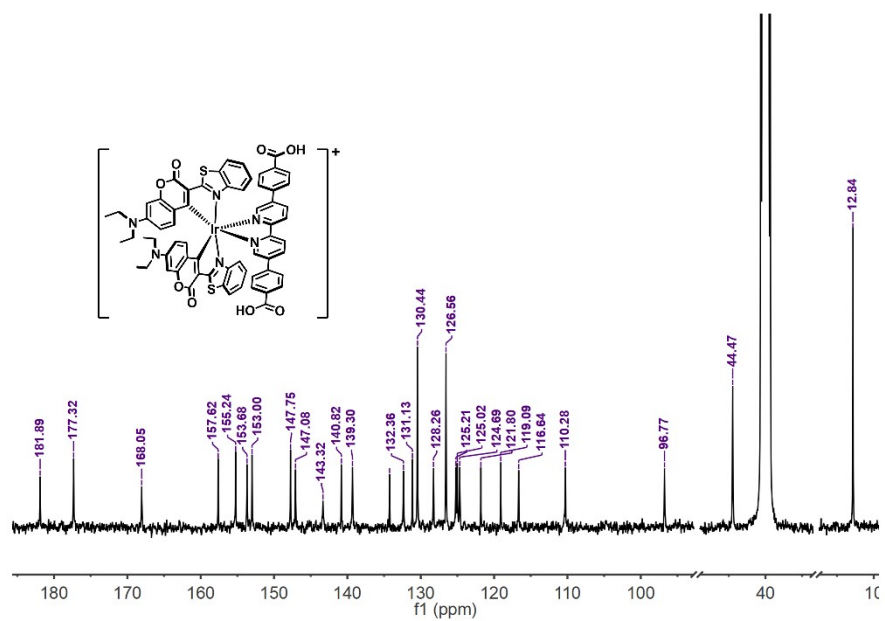


Fig. S 8 The ^{13}C NMR spectrum of auxiliary ligand cmrIr.

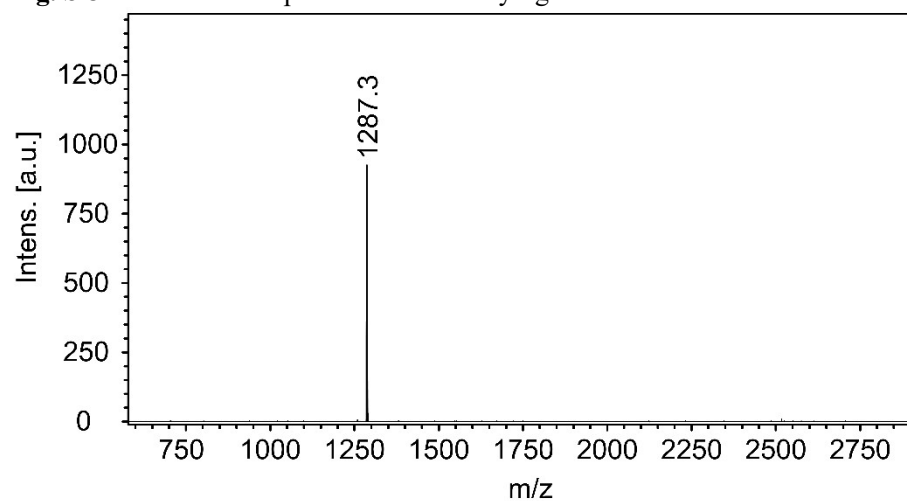


Fig. S 9 The mass spectra of auxiliary ligand cmrIr.

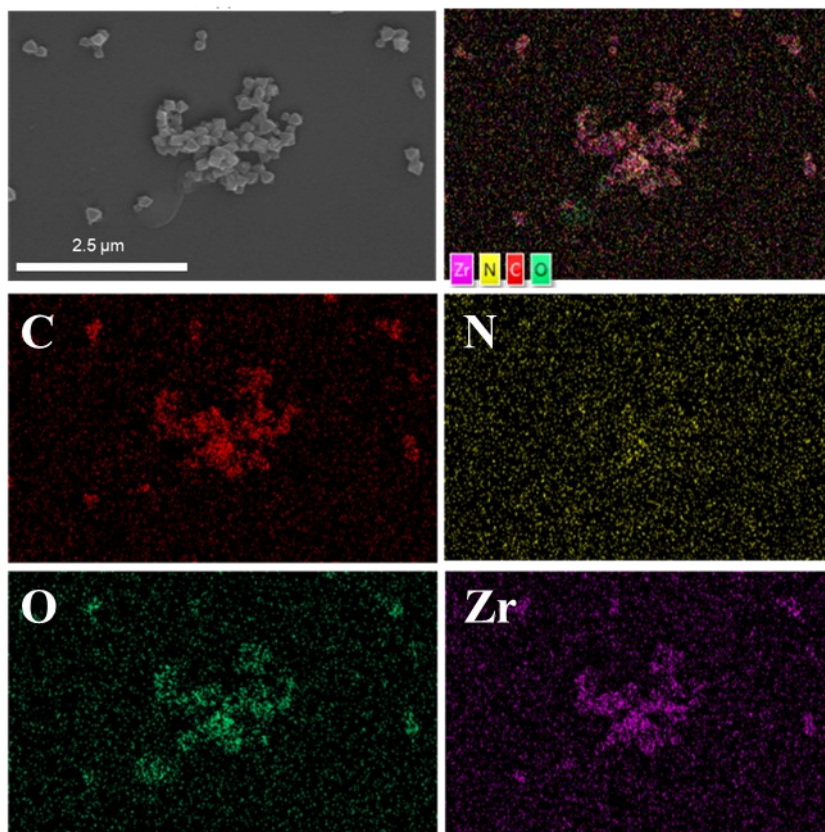


Fig. S 10 EDS image of W1.

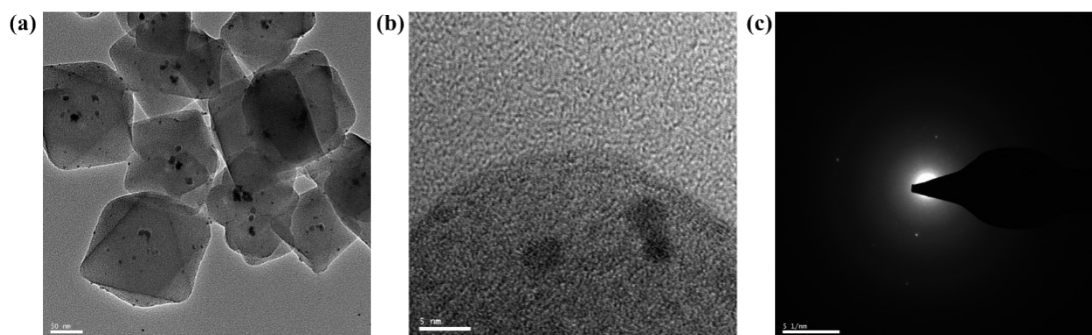


Fig. S 11 (a)TEM image of W2, (b)high-resolution transmission electron microscopy image of W2, (c) selected area electron diffraction image.

Table S 1 Iridium and platinum content of the sample

	Ir (wt%)	Pt (wt%)
W1	-	1.66
W2	0.24	1.41
cmrIr	22.10	-

Table S 2 Elemental content of the sample surface

XPS Contents (at.%)

	C 1s	N 1s	O 1s	S 2p	Zr 3d	Ir 4f
W1	58.7	17.7	20.1	-	3.5	-
cmrIr	73.1	8.7	12.8	2.9	-	2.5
W2	54.9	5.8	34.2	0.6	4.3	0.2

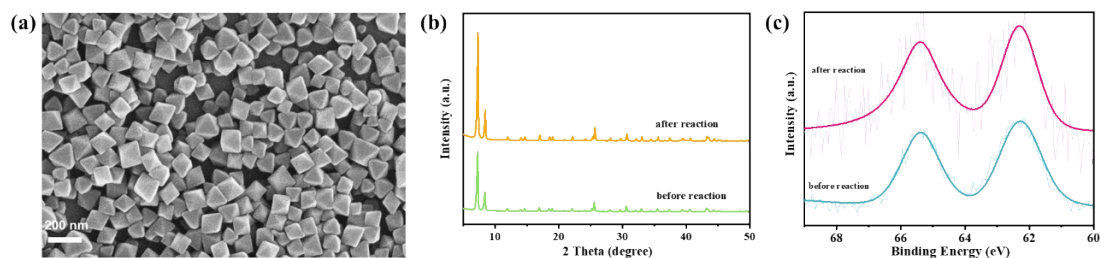


Fig. S 12 SEM (a), XRD (b) and XPS (c) images or spectra of W2 after cyclic stability testing.

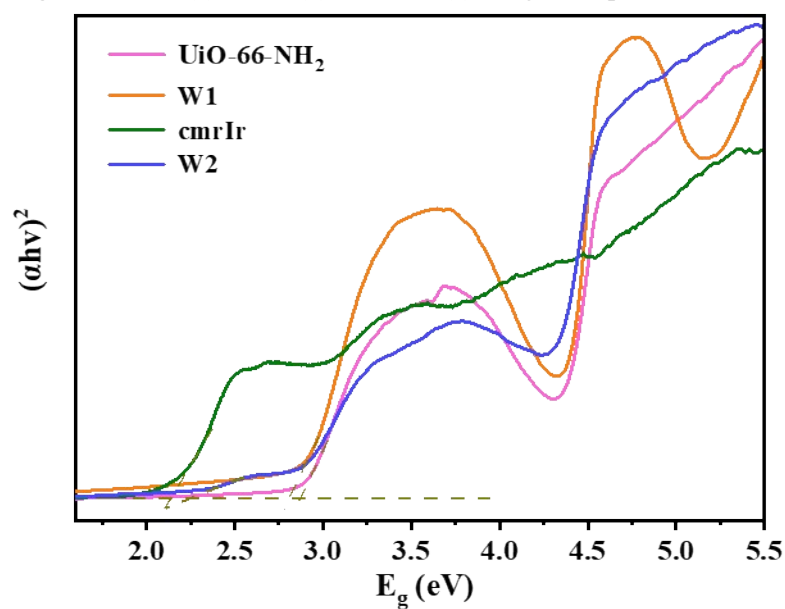


Fig. S 13 Energy bands of UiO-66-NH₂, W1, cmrIr and W2 calculated from Tauc plots derived from solid-state UV-vis absorption spectra.

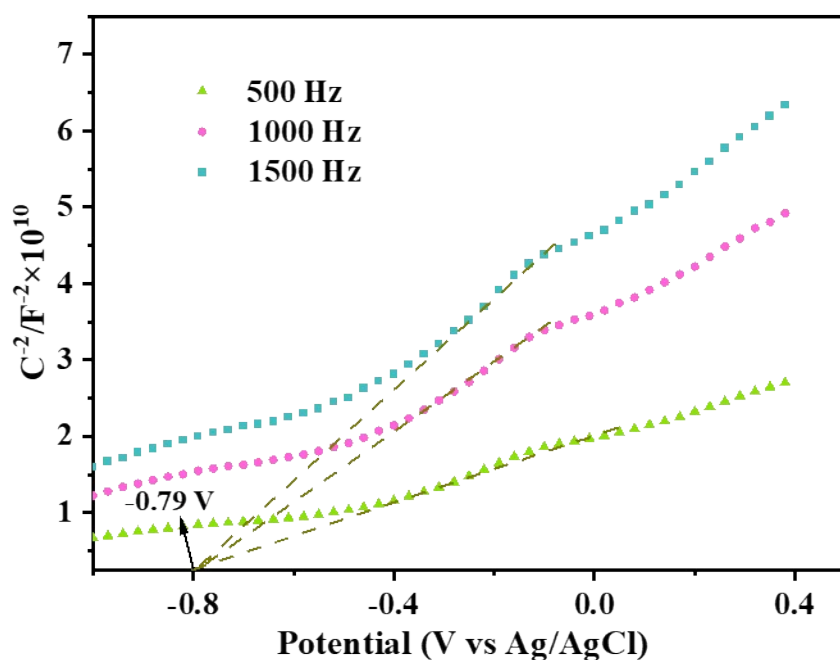


Fig. S 14 Mott-Schottky Curve of UiO-66-NH₂.

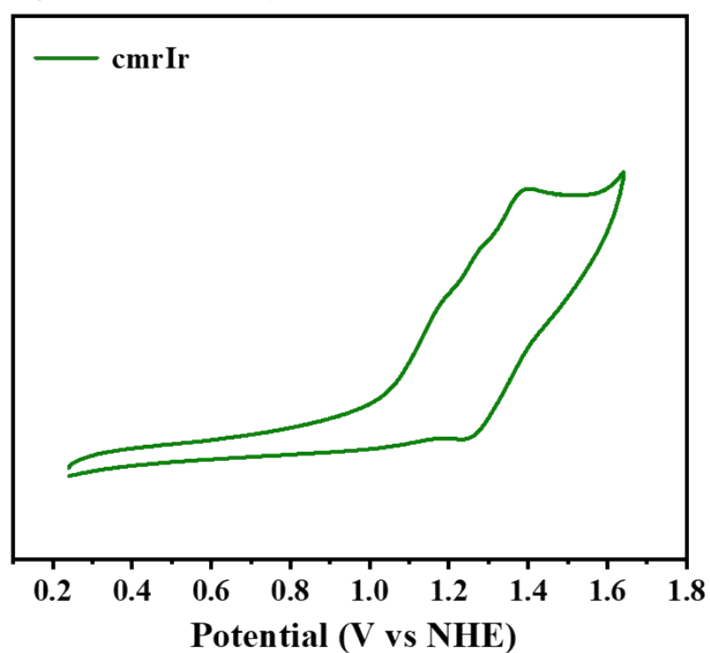


Fig. S 15 Oxidation potential plots of cmrIr measured by cyclic voltammetry.

Table S 3 Electrochemical data for the complex cmrIr.

	E_{ox}^{a} (V)	E_{g}^{b} (eV)	$E_{\text{red}}^{\text{c}}$ (V)	E_{0-0}^{d} (eV)	$E_{\text{ox}}^{*\text{e}}$ (V)	$E_{\text{red}}^{*\text{f}}$ (V)
cmrIr	1.16	2.20	-1.04	2.44	-1.28	1.40

^a Oxidation potential obtained from cyclic voltammetry experimental testing, which has been converted to a standard hydrogen electrode potential; ^b Band gap value calculated from the band edges of the liquid's UV-vis absorption spectrum; ^c $E_{\text{red}} = E_{\text{ox}} - E_{\text{g}}$; ^d E_{0-0} is calculated from the intersection of the normalized absorption and emission spectra,

$$E_{0-0} = 1240/\lambda; \quad {}^e E_{\text{ox}}^* = E_{\text{ox}} - E_{0-0}; \quad {}^f E_{\text{red}}^* = E_{\text{red}} + E_{0-0}$$