Supporting Information

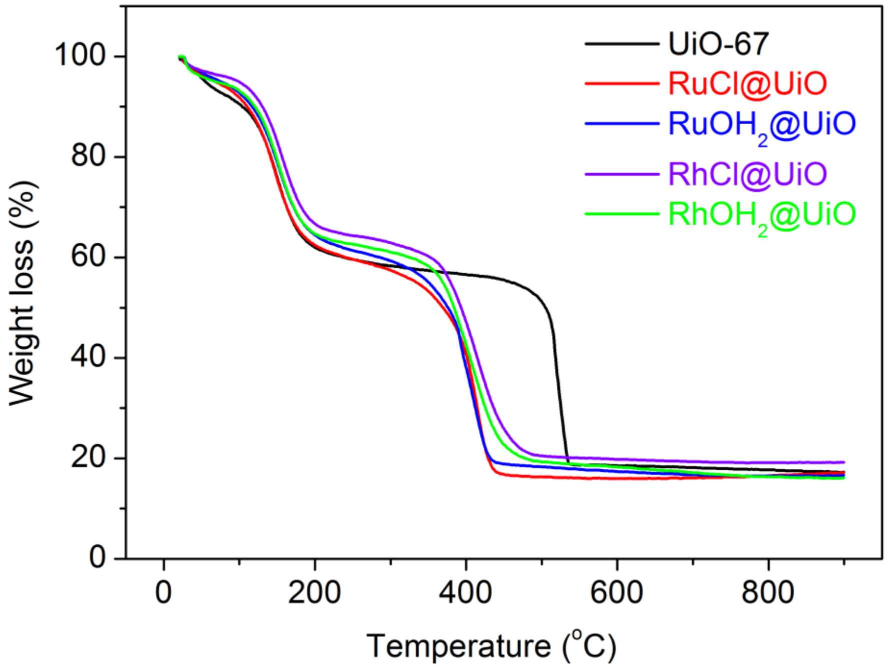

Fig. S1 TGA curves of UiO-67, RuCl@UiO, $RuOH_2$@UiO, RhCl@UiO and $RhOH_2$@UiO.

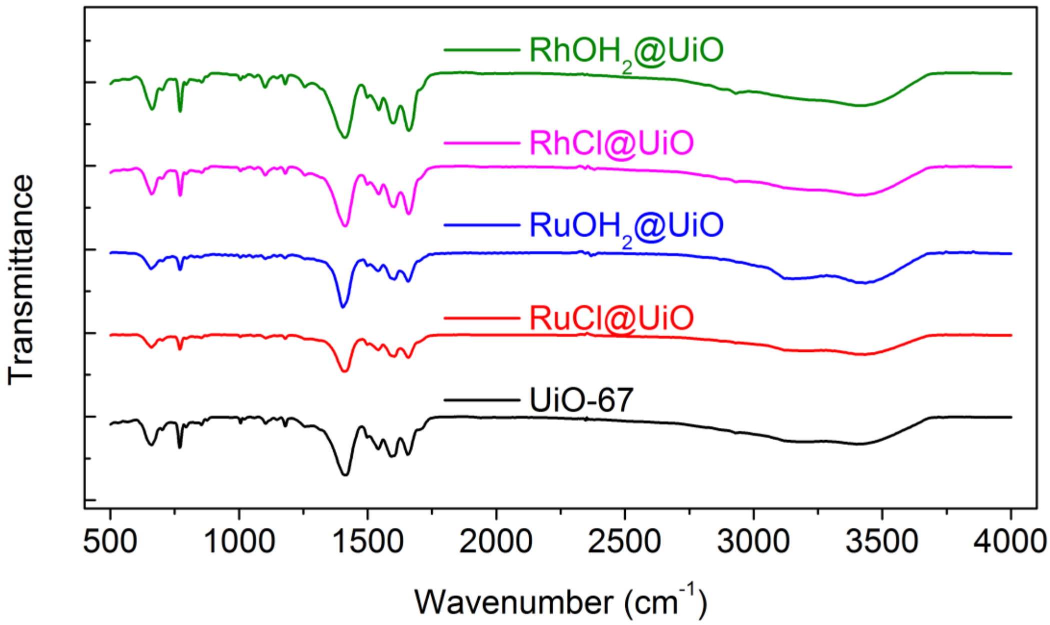

Fig. S2 FT-IR spectras of UiO-67, RuCl@UiO, $RuOH_2$@UiO, RhCl@UiO and $RhOH_2$@UiO.

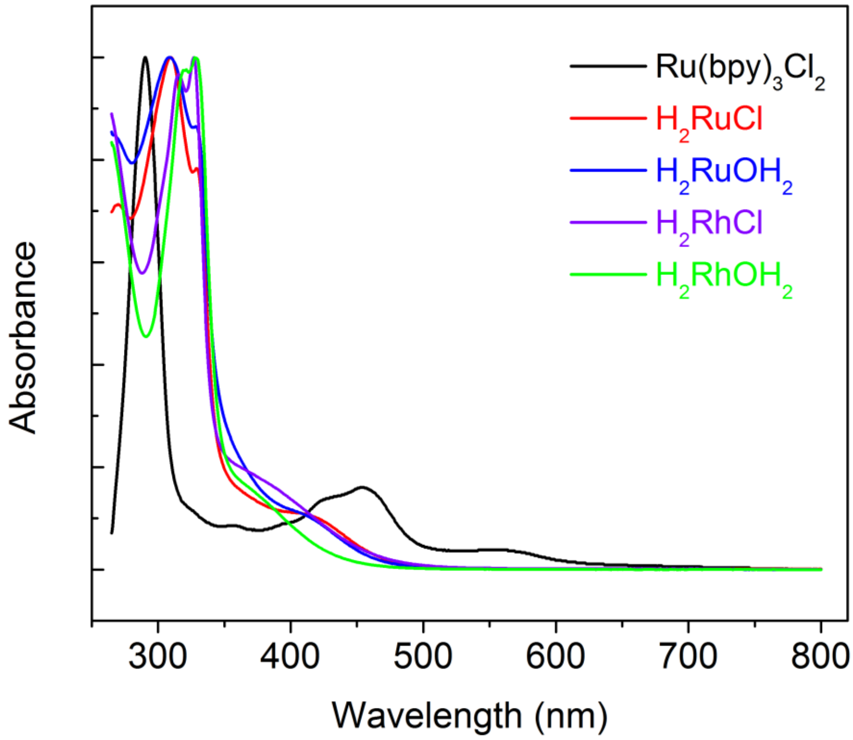

Fig. S3 UV-vis absorption spectra of $Ru(bpy)_3Cl_2$, H_2RuCl, H_2RuOH_2, H_2RhCl and H_2RhOH_2 in DMF solution (1×10^{-5} mol l^{-1}).

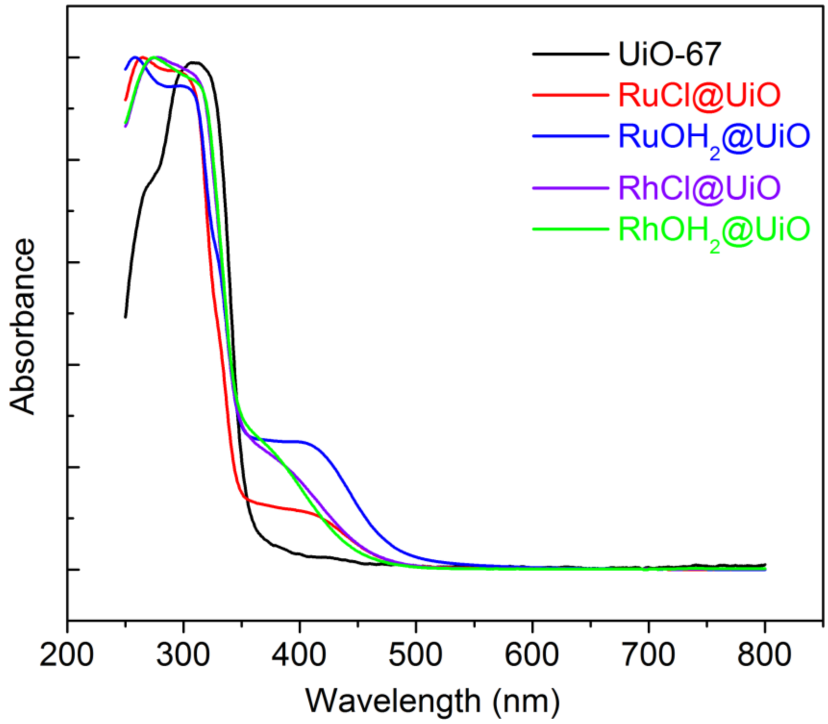

Fig. S4 Diffuse reflection UV-vis absorption spectra of UiO-67, RuCl@UiO, $RuOH_2$@UiO, RhCl@UiO and $RhOH_2$@UiO.

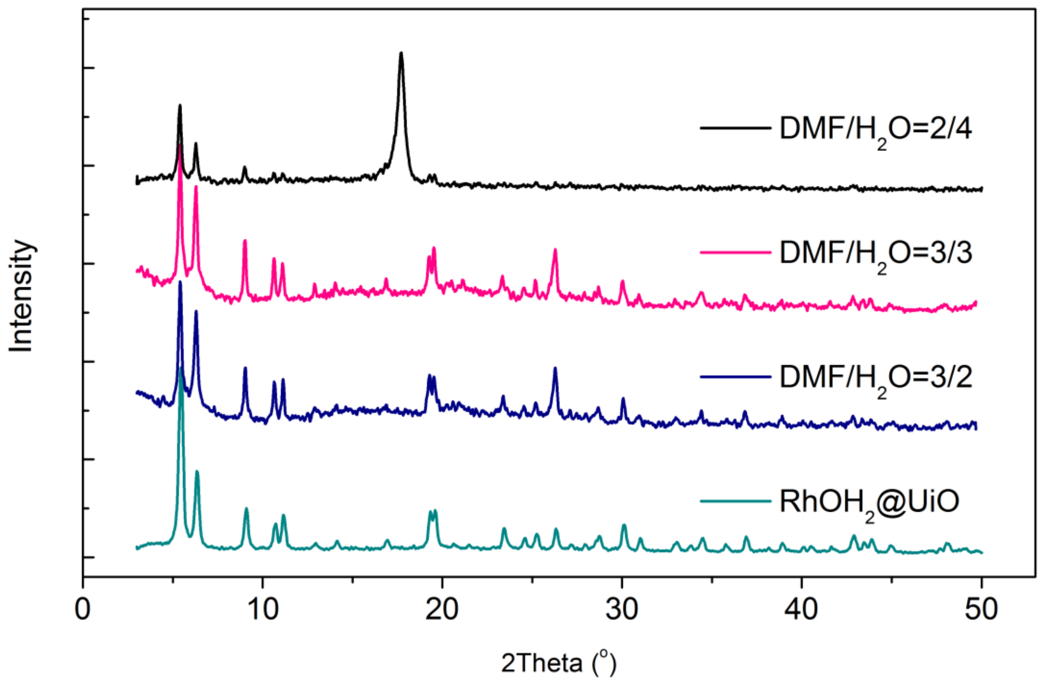

Fig. S5 PXRD patterns of $RhOH_2$@UiO before and after 174 h photocatalytic hydrogen evolution experiments in different DMF/H_2O solution.

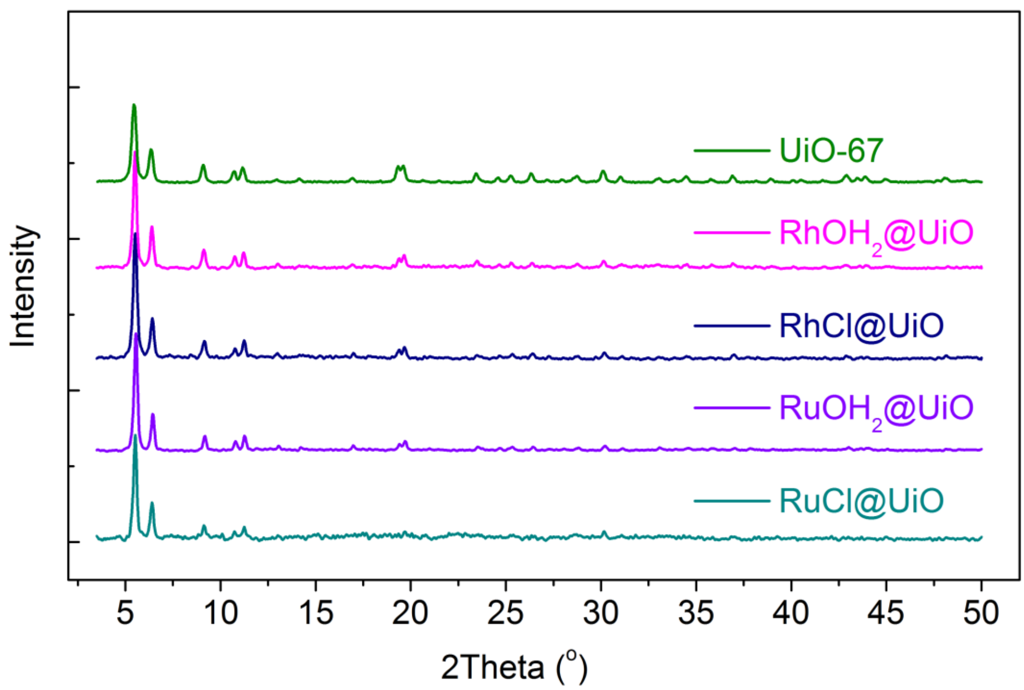

Fig. S6 PXRD patterns for PSE-MOFs after 6 h photocatalytic CO_2 reduction experiments.

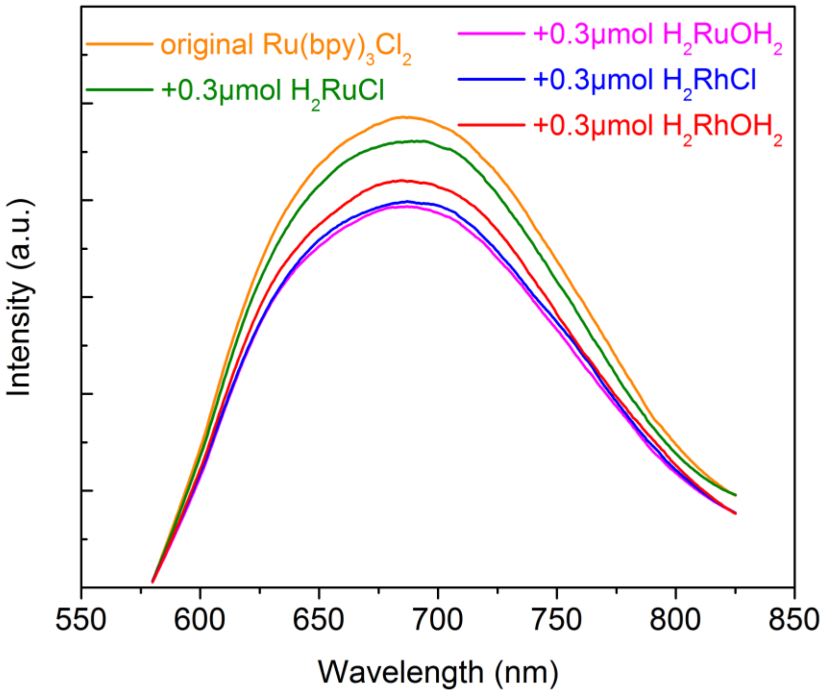

Fig. S7 Photoluminescence spectra of (Ru(bpy)$_3$Cl$_2$, 4 mg) in a mixed solution of 5mL DMF/H_2O (v/v, 4/1). And changing spectra after 0.3 μmol H_2RuCl, H_2RuOH$_2$, H_2RhCl or H_2RhOH$_2$ was added into the solution, respectively.

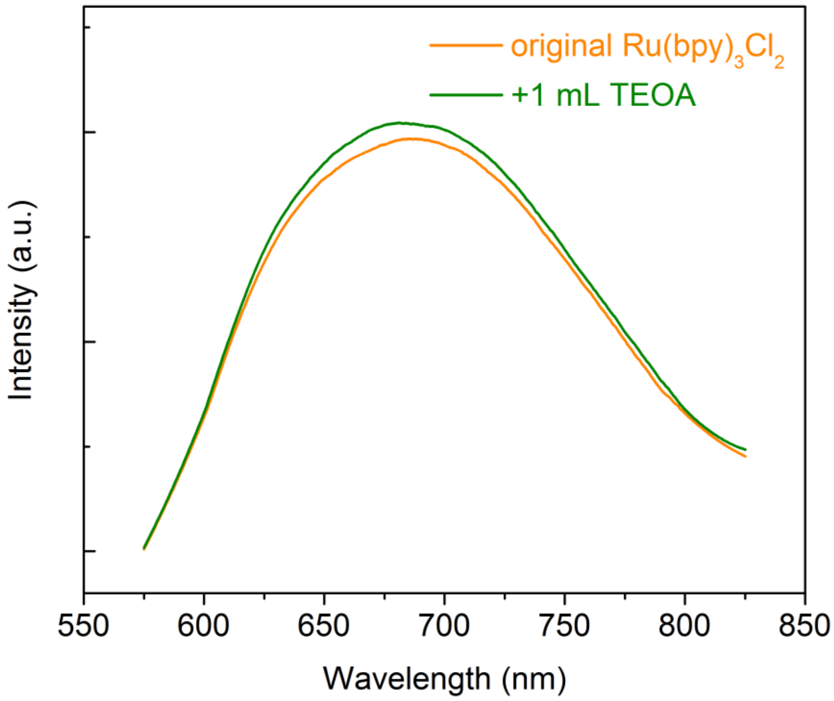

Fig. S8 Photoluminescence spectra of (Ru(bpy)$_3$Cl$_2$, 4 mg) in a mixed solution of 5 mL DMF/H_2O (v/v, 4/1). And changing spectra after 0.2 and 1 mL TEOA was added into the solution.

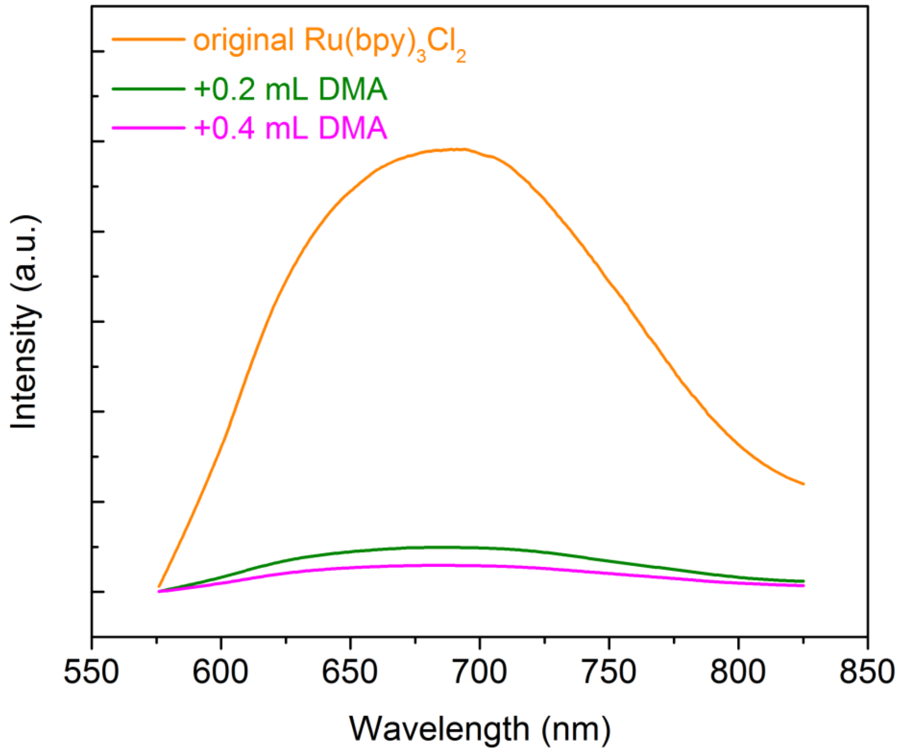

Fig. S9 Photoluminescence spectra of ($Ru(bpy)_3Cl_2$, 4 mg) in a mixed solution of 5mL DMF/H_2O (v/v, 4/1). And changing spectra after 0.2 and 0.4 mL DMA was added into the solution.

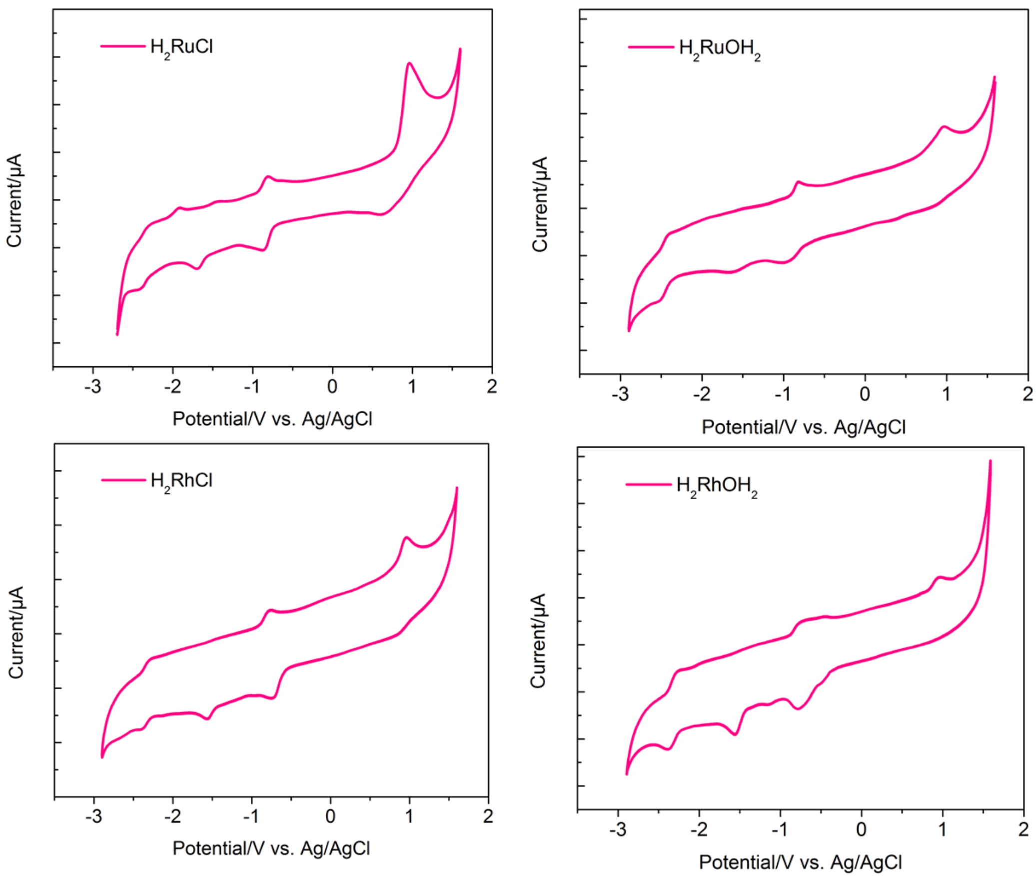

Fig. S10 The cyclic voltammograms (CVs) of 1mM H_2RuCl, H_2RuOH_2, H_2RhCl and H_2RhOH_2 in DMF solvent.

Table S1 Crystal data for H_2RuCl and H_2RhOH_2 complex.

Complex	H_2RuCl	H_2RhOH_2
Temperature	150 K	150 K
Chemical formula	$C_{22}H_{24}Cl_2N_2O_5Ru$	$C_{44}H_{56}N_8O_{25}Rh_2$
CCDC number	1831370	1831371
Formula weight	568.40	1302.78
crystal system	Triclinic	Monoclinic
space group	P-1	$P2_1$
a (Å)	8.4046(3)	8.1896(1)
b (Å)	10.7488(3)	20.1788(2)
c (Å)	12.1725(4)	15.8594(2)
α (deg)	91.608(3)	90
β (deg)	95.600(3)	90.440(1)
γ (deg)	90.126(3)	90
V (Å^3)	1094.21(6)	2620.79(5)
Z	2	2
D_{Calcd} (g cm^{-3})	1.725	1.651
μ (mm^{-1})	8.379	5.920
Ref. collected	5573	26877
Independent ref.	3558	8559
R_{int}	0.0263	0.0521
Goodness of fit	1.022	1.034
$R1$[a] [I > =2σ(I)]	0.0418	0.0308
wR_2[b] [I > =2σ(I)]	0.1211	0.0770

[a] $R_1=\sum(||F_0|-|F_c||)/\sum|F_0|$; [b] $wR_2=[\sum w(F_0^2-F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$

Table S2 Hydrogen evolution performance of some similar molecule catalyst systems by incorporating catalyst into MOF frameworks.[a]

MOFs	Photosensitizer	Catalyst	TON	Amount
$RhOH_2$@UiO (This work)	$Ru(bpy)_3Cl_2$	$[Rh(Cp^*)(bpydc)(OH_2)](NO_3)_2$	470 (174 h)	122.2 μmol (174 h)
$Pt_{0.1}$_Ir_BuiO[S[1]]	$[Ir(ppy)_2(bpydc)]^-Na^+$	Pt/ $H_2Pt(bpydc)Cl_2$	343 (156 h)	11.9μmol (156 h)
Ru-Pt@UiO-67[S[2]]	$H_2Ru(bpydc)(bpy)_2$	$H_2Pt(bpydc)Cl_2$		>0.5 μmol (5 h)
UiO-66-[FeFe]-(dcbdt)$(CO)_6$[S[3]]	$Ru(bpy)_3Cl_2$	$H_2[FeFe](dcbdt)(CO)_6$		~3.5μmol (2.5 h)

[a]dcbdt= 1,4-dicarboxylbenzene-2,3-dithiolate.

Table S3 CO_2 photo-reduction performance of some similar molecule catalyst systems by incorporating catalyst into MOF frameworks.[a]

MOFs	Photosensitizer	Catalyst	TON (CO)	TON (H_2)	TON ($HCOO^-$)	TON($HCOO^-$) /TON(CO)
RhCl@UiO (This work)	$Ru(bpy)_3Cl_2$	$[Rh(Cp^*)(bpydc)(Cl)]Cl\bullet H_2O$	2.7	76.0	38.9	14.4
$\{Zr_6(O)_4(OH)_4$-$[Re(CO)_3Cl(bpydb)]_6\}$ [S[4]]	$Re(CO)_3Cl$(bpydb)	$Re(CO)_3Cl$(bpydb)	6.44	0.4	-	-
$\{Zr_6(O)_4(OH)_4$-$[Re(CO)_3Cl(bpydc)]_6\}$[S[5]]	$Re(bpydc)(CO)_3Cl$	$Re(bpydc)(CO)_3Cl$	10.9	2.5	-	-
$Zr_6O_4(OH)_4(Mn(bpydc)(CO)_3Br)_{2.3}(bpydc)_{0.7}(bpdc)_3$[S[6]]	$Ru(dmb)_3](PF_6)_2$	$Mn(bpy)(CO)_3Br$	4.5	1.0	110	24.4
MOF-253-$Ru(CO)_2Cl_2$[S[7]]	$Ru(CO)_2Cl_2$	$Ru(bpydc)(CO)_2Cl_2$	7.3	11.9	35.8	4.9
Cp*Rh@UiO-67[S[8]]	$Ru(bpy)_3Cl_2$	$Cp^*Rh(bpydc)Cl_2$	-	54	85	∞
Zr-bpdc/RuCO[S[9]]	$[Ru(bpy)_3](PF_6)_2$	$[Ru(H_2bpydc)(terpy)(CO)](PF_6)_2$	18.1	33.8	73.2	4.0

[a]Bpydb= 4,4'-(2,2'-bipyridine-5,5'-diyl)dibenzoate, dmb= 4,4'-dimethyl-2,2'-bipyridine, terpy= 2,2': 6',2''-terpyridine.

Table S4 Photocatalytic CO_2 reduction results for RuCl@UiO, $RuOH_2$@UiO, RhCl@UiO and $RhOH_2$@UiO under CO_2 atmosphere by a LED lamp.[a]

Entry	Catalyst	Sacrificial agent	TON (CO)	TON (H_2)	TON ($HCOO^-$)	TON($HCOO^-$) /TON (CO)
S22	RuCl@UiO	TEOA 0.1 mL	0.5	0.5	5.1	10.2
S23	$RuOH_2$@UiO	TEOA 0.1 mL	2.5	3.9	26.0	10.4
S24	RhCl@UiO	TEOA 0.1 mL	1.0	10.0	9.9	9.9
S25	$RhOH_2$@UiO	TEOA 0.1 mL	0.9	9.5	5.7	6.3
S26	RuCl@UiO	DMA 1 mL	<0.1	0.42	1.3	1.3
S27	$RuOH_2$@UiO	DMA 1 mL	<0.1	0.32	1.1	1.1
S28	RhCl@UiO	DMA 1 mL	0.15	0.1	1.4	9.3
S29	$RhOH_2$@UiO	DMA 1 mL	0.13	0.35	1.5	11.5

[a]Conditions: Photosensitizer ($Ru(bpy)_3Cl_2$, 4 mg), Photocatalyst (4 mg), sacrificial agent, solvents (MeCN 5 mL), CO_2 bubbling for 20 min, and irradiation with a 100 W LED lamp for 6 h.

Table S5 Electrochemical potentials ($E_{1/2}$ *vs.*Ag/AgCl) of 1mM H_2RuCl, H_2RuOH_2, H_2RhCl and H_2RhOH_2 in DMF solvent.

Complex[a]	$E_{1/2}$(ox) / V *vs.* Ag/AgCl	$E_{1/2}$(red) / V *vs.* Ag/AgCl[b]
H_2RuCl	0.962[ir]	-0.838, -1.697[ir], -2.417[ir]
H_2RuOH_2	0.967[ir]	-0.862, -1.642[ir], -2.512[ir]
H_2RhCl	0.962[ir]	-0.748, -1.552[ir], -2.348
H_2RhOH_2	0.967[ir]	-0.745, -1.567[ir], -2.342

[a]Measured conditions: Ag/AgCl was as reference electrode, glassy carbon was as working electrode, and platinum plate was as counter electrode. Solvent: DMF, electrolyte: Bu_4NPF_6 (0.1 M), scan rate: 0.1 V/s. ir = irreversible.
[b]Translation to values *vs.* NHE: +0.2.

Supplementary References

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