Supporting Information

Assembly of Thiacalix[4]arene-Supported High-Nuclearity Cd_{24} Cluster with Enhanced Photocatalytic Activity

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Characterizations and additional Figures

PXRD measurements

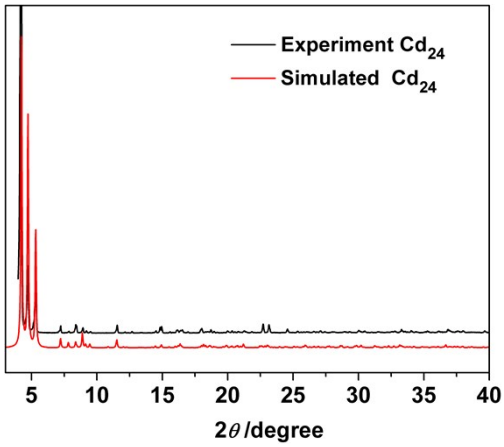

Fig S1. PXRD of compound **Cd_{24}**

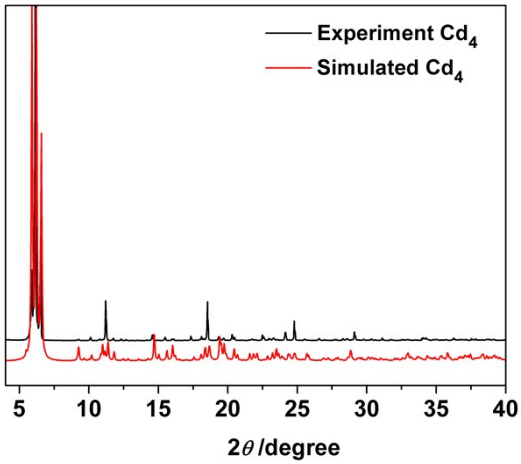

Fig S2. PXRD of compound **Cd_4**

Plot of Cd_4 unit

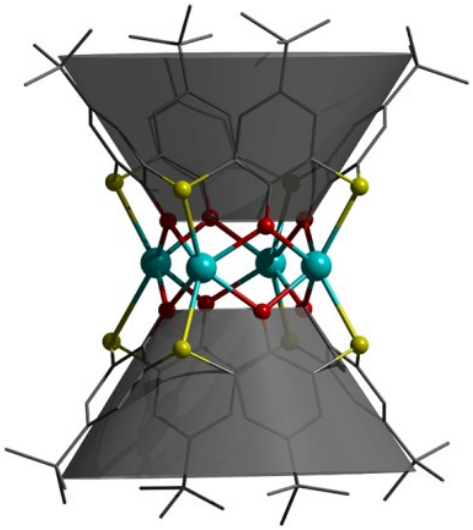

Fig. S3 Molecular structure of $[Cd_4(TC4A)_2]$ (**Cd_4**)

TGA analysis of Cd_{24} and Cd_4

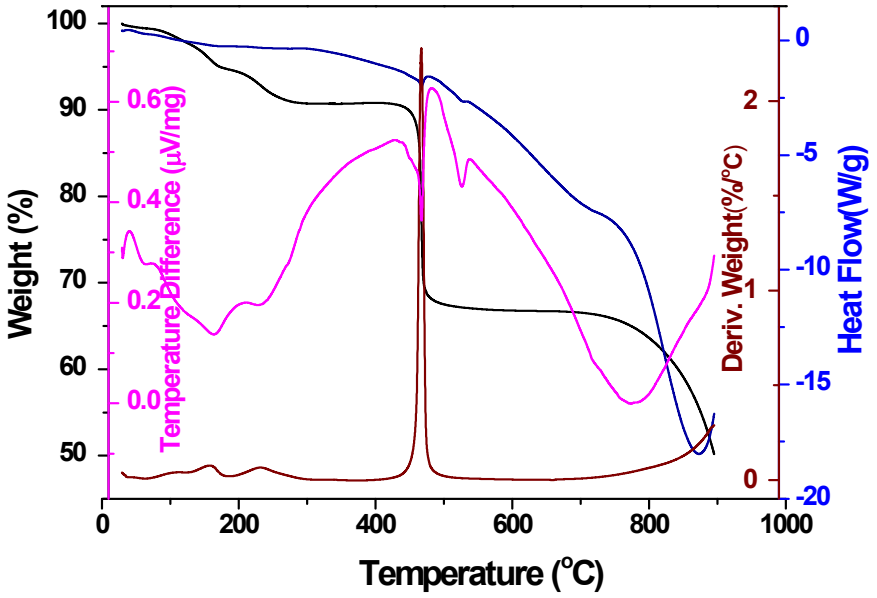

Fig. S4 The TGA curves of Cd_{24}

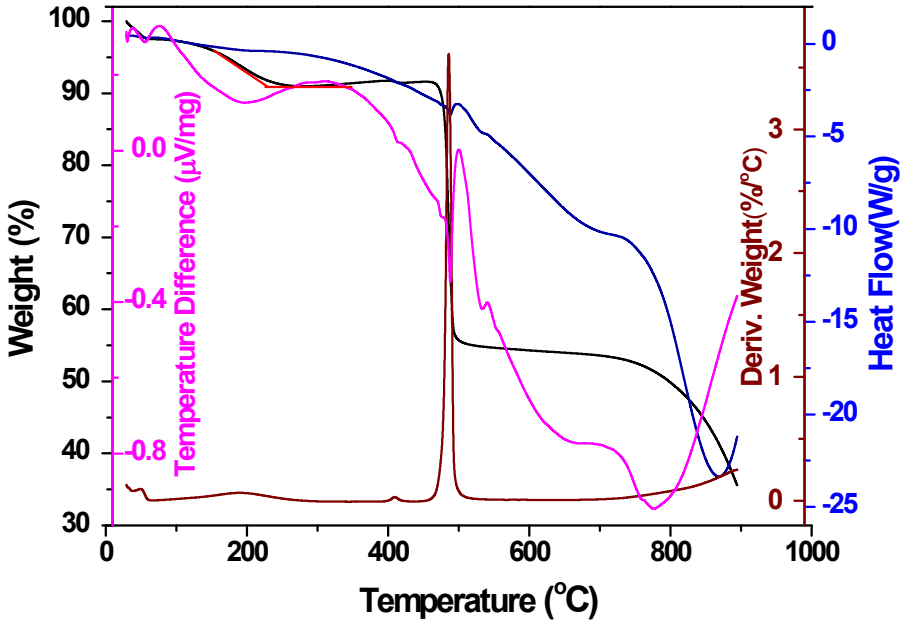

Fig. S5 The TGA curves of compound Cd_4.

Calculating hydrogen evolution rates

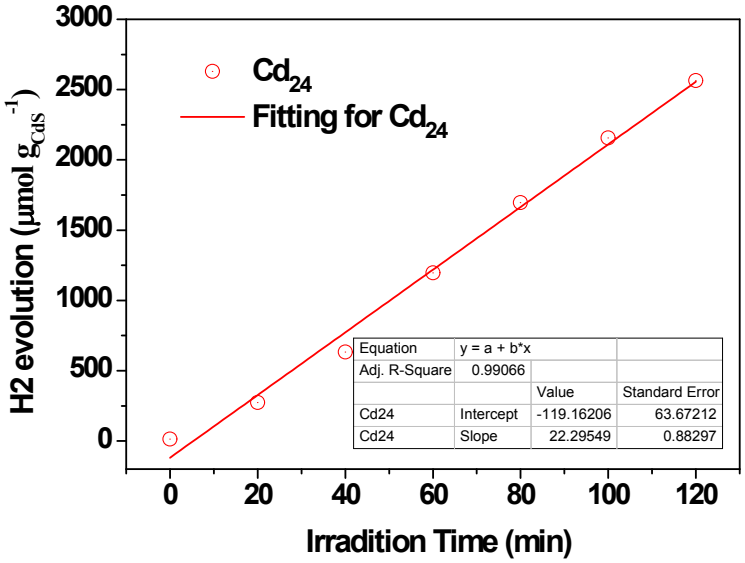

Fig. S6 Calculating hydrogen evolution rates of Cd_{24} considering the molecule CdS proportions (37.24%, 1.36 mmol g_{CdS}^{-1} h^{-1}).

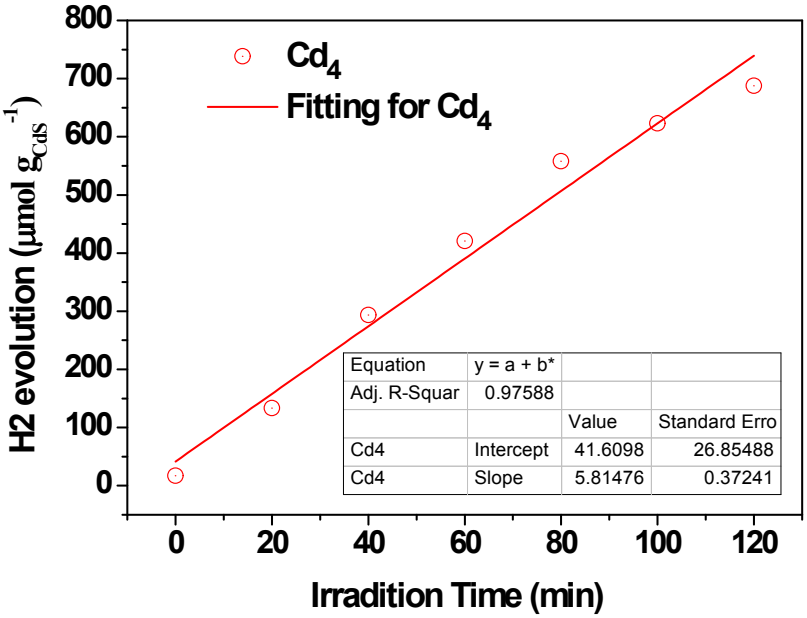

Fig. S7 Calculating hydrogen evolution rates of Cd_4 considering the molecule CdS proportion (27.82%, 0.35 mmol g_{CdS}^{-1} h^{-1}).

Diffuse reflectance spectra

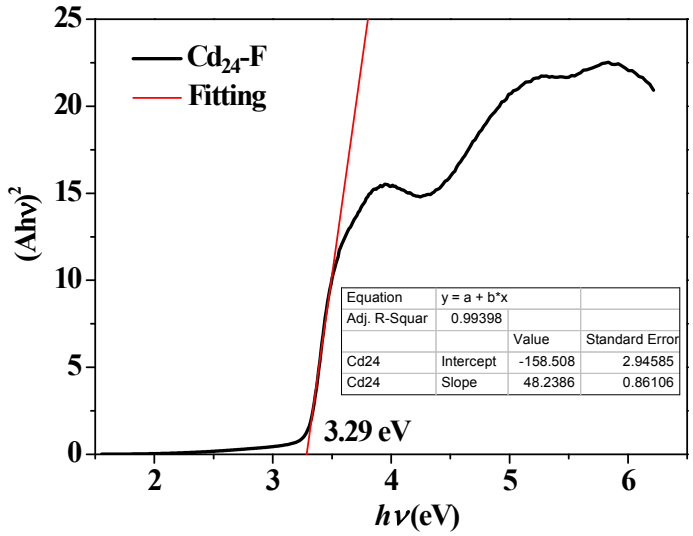

Fig. S8 The diffuse reflectance UV-vis-NIR spectra of K-M function vs. energy (eV) for **Cd_{24}**-F (calculated band gap: 3.26 eV, defined as semiconductor with a direct band gap)

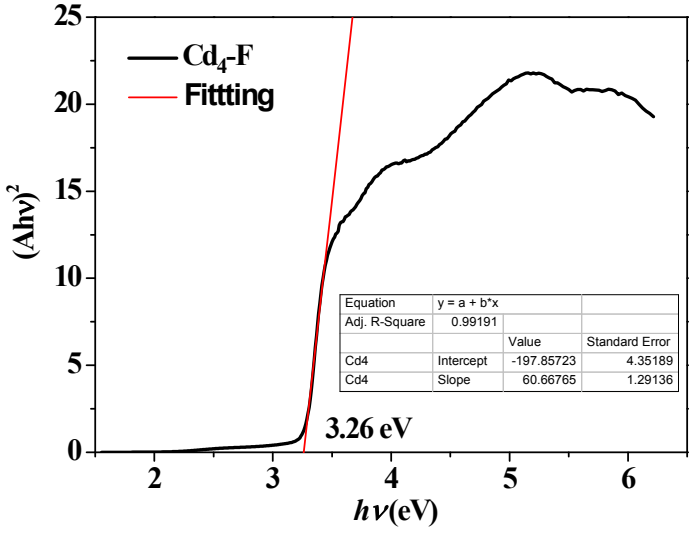

Fig. S9 The diffuse reflectance UV-vis-NIR spectra of K-M function vs. energy (eV) for **Cd_4**-F (calculated band gap: 3.26 eV, defined as semiconductor with a direct band gap).

FT-IR spectra

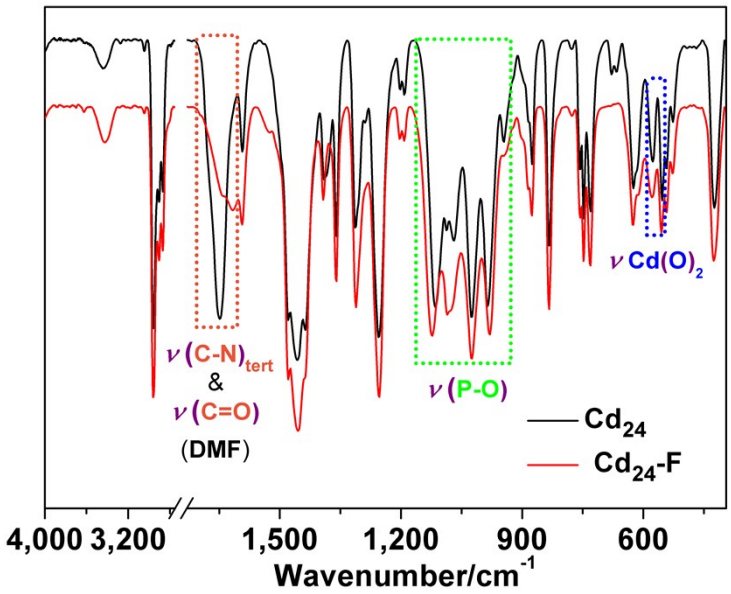

Fig. S10 FT-IR spectra of **Cd_{24}** and **Cd_4-F**, which indicated the release of DMF both coordinated and in the crystal lattice after photocatalytic water splitting experiments.

MALDI-TOF mass spectra

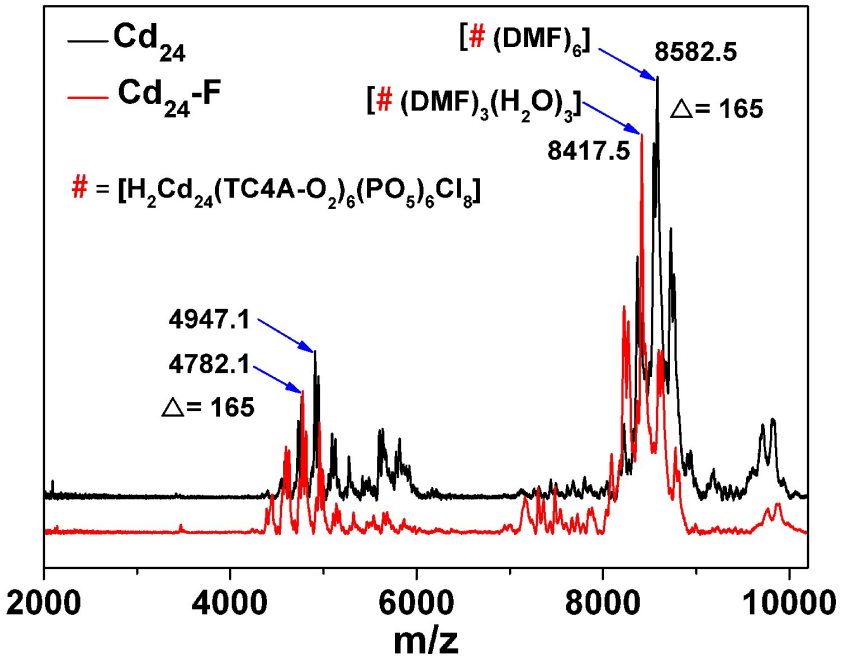

Fig. S11 MALDI-TOF mass spectra of **Cd_{24}** and **Cd_4-F** showing the partially release of coordinated DMF after photocatalytic water splitting experiments.

Raman spectra

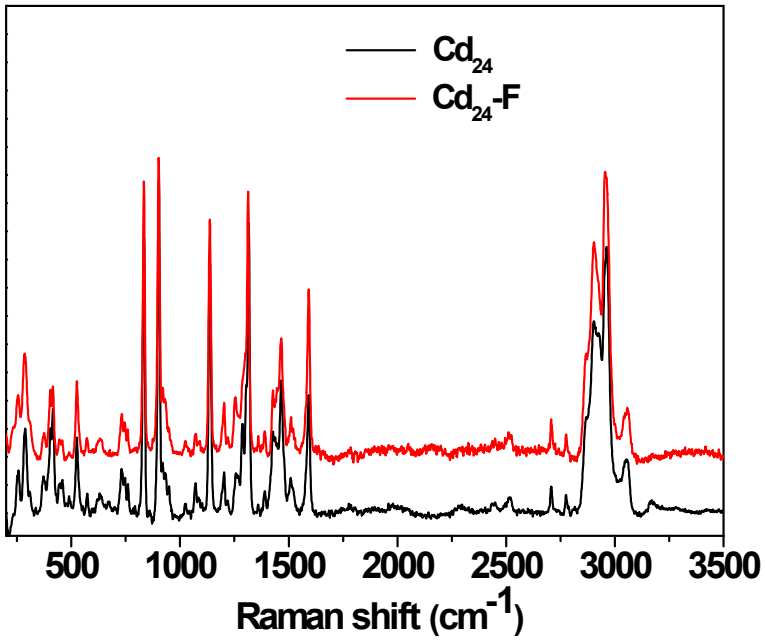

Fig. S12 The Raman spectra of **Cd_{24}** and **Cd_{24}**-F, showing the satiability of photocatalyst of **Cd_{24}**.

Tables

Table S1 Crystallographic data and structure refinement for complexes **Cd_{24}** and **Cd_4**

Complex	Cd_{24}	Cd_4
CCDC number	1582708	1582709
Formula	$C_{288}H_{378}Cd_{24}Cl_8N_{16}O_{82}P_6S_{24}$	$C_{88}H_{108}Cd_4N_2O_{11}S_8$
Mr	9312.50	2075.84
Crystal system	Trigonal	Monoclinic
space group	R-3 (*No.*148)	C_2/c (*No.* 15)
Temperature (K)	120(2) K	298(2) K
a(Å)	22.4712(7)	32.7990(15)
b(Å)	22.4712(7)	19.0653(8)
c (Å)	62.0494(18)	31.1251(13)
α(°)	90	90
β(°)	90	114.228(2)
γ(°)	120	90
Volume (Å^3)	27134.4(19)	17748.9(14)
Z	3	8
D_c(g/cm^3)	1.710	1.554
μ(mm^{-1})	1.675	1.192
Reflections collected	45339	113983
Unique data	10623	15696
R_{int}	0.022	0.040
GOF on F^2	1.047	1.024
R_1 [I>2sigma(I)]	0.0491	0.0478
wR_2	0.1435	0.1423

$^aR_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$; $^bwR_2 = \{\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$

Table 2 Selected bonds lengths (Å) and angles (°) for compound **Cd_{24}** and **Cd_4**.

Cd_{24}		**Cd_4**	
Cd1–O9	1.974 (6)	Cd1–O4^{i}	2.268 (3)
Cd1–O1	2.193 (4)	Cd1–O4	2.268 (3)
Cd1–O10	2.217 (6)	Cd1–O1^{i}	2.283 (3)
Cd1–O4	2.239 (4)	Cd1–O1	2.283 (3)
Cd1–O6	2.278 (4)	Cd1–S1	2.6779 (11)
Cd1–O8^{i}	2.286 (4)	Cd1–S1^{i}	2.6779 (11)
Cd1–O5	2.436 (5)	Cd2–O4^{i}	2.231 (3)
Cd1–S1	2.7604 (17)	Cd2–O2	2.243 (3)
Cd2–O11	1.948 (5)	Cd2–O1	2.301 (3)
Cd2–O5^{ii}	2.169 (4)	Cd2–O3^{i}	2.303 (3)
Cd2–O1	2.237 (4)	Cd2–S2	2.6849 (12)
Cd2–O8^{i}	2.281 (4)	Cd2–S4^{i}	2.7188 (12)
Cd2–O2	2.309 (4)	Cd3–O2i	2.218 (3)
Cd2–O9^{ii}	2.516 (6)	Cd3–O2	2.218 (3)
Cd2–O9	2.581 (5)	Cd3–O3	2.312 (3)
Cd2–Cl2	2.6087 (8)	Cd3–O3i	2.313 (3)
Cd2–S2	2.6980 (17)	Cd3–S3i	2.6690 (11)
Cd3–O6^{i}	2.206 (4)	Cd3–S3	2.6690 (11)
Cd3–O11	2.229 (6)	Cd4–O8	2.232 (3)
Cd3–O2	2.290 (4)	Cd4–O6^{i}	2.247 (3)
Cd3–O3	2.309 (4)	Cd4–O5	2.259 (4)
Cd3–O7^{ii}	2.346 (5)	Cd4–O5	2.290 (4)
Cd3–O10^{i}	2.553 (6)	Cd4–S5	2.6932 (12)
Cd3–Cl1	2.6248 (18)	Cd4–S6^{i}	2.7216 (12)
Cd3–S3	2.6233 (17)	Cd5–O6	2.238 (3)
Cd4–O7	2.202 (4)	Cd5–O8^{i}	2.248 (3)

Cd4–O12	2.260 (5)	Cd5–O7	2.253 (4)
Cd4–O4^{iii}	2.294 (4)	Cd5–O7^{i}	2.302 (4)
Cd4–O3^{iii}	2.343 (5)	Cd5–S7	2.7165 (12)
Cd4–Cl1^{iv}	2.7202 (19)	Cd5–S8^{i}	2.6746 (13)
Cd4–S4^{iii}	2.5976 (16)		
Cd3–Cl1–Cd4^{ii}	87.70 (5)	Cd1–O1–Cd2	101.58 (11)
Cd2^{iv}–Cl2–Cd2	116.47 (4)	Cd3–O2–Cd2	105.51 (12)
Cd2^{iv}–Cl2–Cd2^{ii}	116.47 (4)	Cd2^{i}–O3–Cd3	100.61 (11)
Cd2–Cl2–Cd2^{ii}	116.47 (4)	Cd2^{i}–O4–Cd1	104.31 (12)
Cd1–O1–Cd2	104.19 (17)	Cd4^{i}–O5–Cd4	106.87 (15)
Cd3–O2–Cd2	110.87 (17)	Cd5–O6–Cd4^{i}	106.44 (14)
Cd3–O3–Cd4^{i}	119.12 (19)	Cd5–O7–Cd5^{i}	107.05 (16)
Cd1–O4–Cd4^{i}	107.91 (18)	Cd4–O8–Cd5^{i}	106.62 (14)
Cd2^{iv}–O5–Cd1	131.6 (2)		
Cd3^{iii}–O6–Cd1	116.11 (19)		
Cd4–O7–Cd3^{iv}	108.99 (18)		
Cd2^{ii}–O8–Cd1^{iii}	99.87 (16)		
Cd1–O9–Cd2^{iv}	138.5 (3)		
Cd1–O9–Cd2	99.4 (2)		
Cd2^{iv}–O9–Cd2	121.0 (2)		
Cd1–O10–Cd3^{iii}	105.6 (2)		
Cd2–O11–Cd3	130.1 (3)		

Symmetry codes: (i) *x*–*y*+1/3, *x*–1/3, –*z*+2/3; (ii) –*y*+1, *x*–*y*, *z*; (iii) *y*+1/3, –*x*+*y*+2/3, –*z*+2/3; (iv) –*x*+*y*+1, –*x*+1, *z* for Cd_{24}; Symmetry code: (i) –*x*+1, *y*, –*z*+1/2 for Cd_4.

Table S3. Comparison on the photocatalytic performance of some coordination compound based catalysts for photocatalytic H_2 production.*

Photocatalysts	Sacrificial agent	Co-catalyst	H_2 evolution (reference)	Catalyst weight (mg)	H_2 evolution ($\mu mol/g_{cat}/h$)	Stability evidence	Ref.
Cd_4	TEOA	-	-	50	**95.7**	Reuse, UV-vis, IR, Multi-TOF, Raman	This work
Cd_{24}	TEOA	-	-	50	**477.5**		
Uio-66(Zr)	CH_3OH	-	~1.0 mL(3h)	45	~281	Laser flash photolysis	S1
Uio-66-(NH_2) (Zr)	CH_3OH	-	~0.85 mL(3h)	45	~331		
Uio-66(Zr)	TEOA	-	none	50	none	Reuse, PXRD	S2
	TEOA	1%Pt	3.9 μmmol/g/h	50	3.9		
	TEOA	RhB:1.63 mg/g	2.7 μmmol/g/h	50	2.7		
	TEOA	RhB:7.43 mg/g	33.9 μmmol/g/h	50	33.9		
	TEOA	RhB:2.54 mg/g+1%Pt	5.6μmmol/g/h	50	5.6		
	TEOA	RhB:7.43 mg/g+ 1%Pt	116.0μmmol/g/h	50	116.1		
MIL-125(Ti)	TEOA	Pt	none	10	none	Reuse	S3
MIL-125(Ti)-NH_2	TEOA	-	5 μmol (3h)	10	166.7		
	TEOA	Pt	33μmmol (9h)	10	367		
MIL-125(Ti)-NH_2	TEOA	-	2.3 μmol/h	10	230	Reuse, PXRD, FT-IR	S4
	TEOA	0.5%Pt	3.3 μmol/h	10	333		
	TEOA	1%Pt	14μmmol (3h)	10	467		
	TEOA	1.5%Pt	15.5μmmol (3h)	10	517		
	TEOA	2%Pt	13μmmol(3h)	10	433		
MIL-125(Ti)-NH_2	TEOA	-	7μmmol/g/h	30	7	Reuse, FT-IR	S5
	TEOA	2 % rGO	35μmmol//h/g_{cat}	30	35		
	TEOA	4 % rGO	50μmmol//h/g_{cat}	30	50		
	TEOA	6 % rGO	91μmmol//h/g_{cat}	30	91		
	TEOA	8 % rGO	67μmmol//h/g_{cat}	30	67		
	TEOA	10 % rGO	66μmmol//h/g_{cat}	30	66		
MIL-101(Cr)	TEOA	Ni	0.22μmmol(2h)	50	2.2	-	S6

	TEOA	Mo	0.15μmmol(2h)	50	1.5		
	TEOA	Ni,Mo	0.84μmmol(2h)	50	8.4		
NH_2-Uio-66(Zr/Ti)-	TEOA	Pt	2.4μmmol/mol	50	0.094	-	S7
NH_2-Uio-66(Zr/Ti)-120-16	TEOA	Pt	3.5μmmol/mol	50	0.14		
NH_2-MIL-101(Cr)	TEOA	-	~3 μmmol(6h)	10	~50	Reuse	S8
	TEOA	RhB +0.5%Pt	28μmmol(6h)	10	467		
	TEOA	RhB +1%Pt	31.5μmmol(6h)	10	525		
	TEOA	RhB +1.5%Pt	35μmmol(6h)	10	583		
	TEOA	RhB +2%Pt	30.5μmmol(6h)	10	508		
	TEOA	RhB +3%Pt	25μmmol(6h)	10	417		
Ti-MOF-Ru$(tpy)_2$	TEOA	-	2.1 μmmol (6h)	10	35	Reuse, PXRD	S9
	TEOA	Pt	10.9μmmol (6h)	10	181.7		
Al-PMOF	EDTA	Pt	200μmmol/g/h	3.5	200	PXRD, SEM	S10
$Zn_{0.986(12)}$TCPP[$Al(OH)_2$]	EDTA	Pt	100μmmol/g/h	3.5	100		
MIL-125-NH_2	TEOA	-	17μmmol/g/h	6	17	PXRD, SEM	S11
	TEOA	0.97%Co1	267μmmol/g/h	6	267		
	TEOA	1.7% Co2	381μmmol/g/h	6	381		
	TEOA	1.93% Co3	553μmmol/g/h	6	553		
Gd-MOF	TEOA	-	7.71μmmol/h	50	154.2	PXRD	S12
	TEOA	1.5 wt% A	10.6μmmol/h	50	212		
Uio-66-[FeFe]	Ascorbic acid	$[Ru(bpy)_3]^{2+}$	3.5 μmmol	5	280	-	S13
(FeFe)@ZrPF	Ascorbic acid	-	3.5 μmmol (2 h)	~5	350	-	S14
NH_2-MIL-125(Ti)	TEA	-	2.5 μmmol (25 h)	5	20	Reuse	S15
Co-NH_2-MIL-125(Ti)	TEA	-	37.5 μmmol (20 h)	5	375		
Uio-66(Zr)	L-ascorbic acid	0.16 %Pt	none	10	none	Reuse	S16
	L-ascorbic acid	0.16 %Pt +ErB(30mg)	4.6μmmol/h	10	460		
Uio-67(Zr)	EDTA-2Na	Pt	0.35μmmol (4h)	5	17.5	-	S17
	EDTA-2Na	Pt-Ru	0.5μmmol (4h)	5	25		

Al-TCPP	TEOA	-	1.5μmmol/g/h	5	1.5	Reuse, PXRD, TEM, HAADF-STEM	S18
	TEOA	Pt coordination	129μmmol/g/h	5	129		
MIL-100(Fe)	CH_3OH	-	5.9μmmol/g/h	45	5.9	Reuse	S19
	CH_3OH	0.5% Pt	53μmmol/g/h	45	53		
	CH_3OH	0.8% Pt	109μmmol/g/h	45	109		
	CH_3OH	1% Pt	98μmmol/g/h	45	98		
	CH_3OH	4% Pt	74μmmol/g/h	45	74		
Cd-MOF	TEOA	-	3.13μmmol/h	10	313	Reuse, PXRD	S20
CdS@Cd-MOF	Na_2SO_3-Na_2S	gel-to-crystal	729μmmol/g/h	20	729	-	S21
Cd-MOF@TiO_2	Na_2SO_3-Na_2S	gel-to-crystal	217μmmol/g/h	20	217		
ZAVCl MOF	ethanol	-	20 μmmol/g/h	30	20	Reuse	S22
CdS@ ZAVCl MOF	ethanol	-	16 μmmol/g/h	30	16		
CdS@ ZAVCl MOF	ethanol	Pt	398-418μmmol/g/h	30	398-418		
MIL-101(Cr)	Lactic acid	0.5%Pt	none	20	none	Reuse, PXRD	S23
CdS@MIL-101(Cr) (5)	Lactic acid	0.5%Pt	22 μmmol/g	20	1100		
CdS@MIL-101(Cr) (10)	Lactic acid	0.5%Pt	75.5 mol/g_{CdS}/h	20	7550		
Ui66(Zr)	Na_2SO_3-Na_2S	Pt	none	50	none	Reuse, PXRD, BET	S24
CdS@ Ui66(Zr)	Na_2SO_3-Na_2S	Pt	11.2mol/g_{CdS}/h	50	1702		
CdS@Ti-MCM-41	Na_2SO_3	-	250 umol/g_{CdS}/h	200	21.8	Reuse, UV-vis	S25
	Na_2SO_3	2%Pt	875 umol/g_{CdS}/h	200	76.1		
CdS@MCM-48	ethanol	-	0.22mmol/g/h	40	220	-	S26
CdS/Ti(0.02)-MCM-41	TEA	-	47.11μmmol (5h)	200	47.1	-	S27
Cu-en-[$PNb_{12}O_{40}(VO)_6$]	CH_3OH	0.75% Pt	44.35μmmol/g/h	100	44.35	Reuse, PXRD	S28
Cu-enMe-[$PNb_{12}O_{40}(VO)_6$]	CH_3OH	0.75% Pt	43.86μmmol/g/h	100	43.86		
Cu^{I}_{12}-[α-$PW_{12}O_{40}$] MOF	ethanol	1% Pt	192μmmol/g/h	100	192	Reuse, PXRD	S29
Co-pn-[$PNb_{12}V_2O_{40}(VO)_4$]	CH_3OH	1% H_4PtCl_6	19.25 μmmol/g/h	50	19.25	Reuse, PXRD, IR	S30
Co-pn-[$PNb_{12}O_{40}(VO)_6$]	CH_3OH	1% H_4PtCl_6	29.25 μmmol/g/h	50	29.25		
$Cr_3[Ta_3P_2W_{15}O_{62}]$	CH_3OH	-/ 1.2 mg H_4PtCl_6	30.9/198.3μmmol/g/h	27	198.3	UV-vis, IR	S31
$Cr_4[Ta_3P_2W_{15}O_{62}]$	CH_3OH	-/ 1.2 mg H_4PtCl_6	17.8/89.2μmmol/g/h	27	89.2		

*Note: The photocatalytic water splitting performance of the coordination compounds without co-catalyst are highlighted in red.

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