Supplementary Information

Photocatalytic hydrogen evolution from water based on Zn-terpyridine 2D coordination nanosheets

Shuo Xiang, ‡[a] Arshad Khan, ‡[ab] Zeyan Zhou,[a] Bingling He,[a] Xin Wang,*[c] Binju Wang[d] and Qunhong Weng,*[a]

[a] College of Materials Science and Engineering, Hunan Joint International Laboratory of Advanced Materials and Technology for Clean Energy, Hunan University, 2 Lushan S Rd, Changsha, 410082 P.R. China

[b] School of Chemistry and Environmental Engineering, Sichuan University of Science & Engineering, Zigong 643000, Sichuan, P. R. China

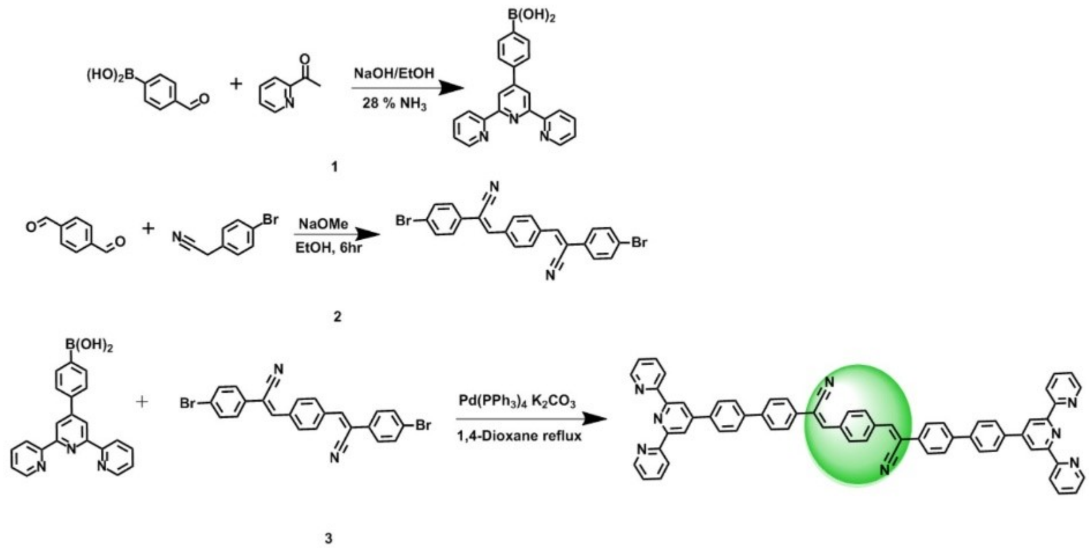
[c] School of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan 030024, P. R. China

[d] State Key Laboratory of Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, P. R. China

‡ Authors contributed equally.

* Corresponding author E-mail: wangxin01@tyut.edu.cn (X. Wang); wengqh@hnu.edu.cn (Q. Weng)

Tpy was synthesized using a three-step method. Firstly, compound 1 and compound 2 were synthesized, and their structures were proved by NMR. Then compound 1 and compound 2 were used as precursors to synthesize Tpy ligand, whose structure was demostrated by NMR, MALDI-TOF-MS and FT-IR spectroscopies.



Scheme S1 Illustrative synthetic route of Tpy.

Compound 1: ^{1}H NMR (400 MHz, MeOD) δ 8.68 (d, J = 3.7 Hz, 2H), 8.65 (s, 2H), 8.61 (d, J = 7.9 Hz, 2H), 7.98 (t, J = 7.6 Hz, 3H), 7.78 (d, J = 6.9 Hz, 2H), 7.74 (d, J = 6.9 Hz, 2H), 7.46 (t, J = 5.6 Hz, 2H).

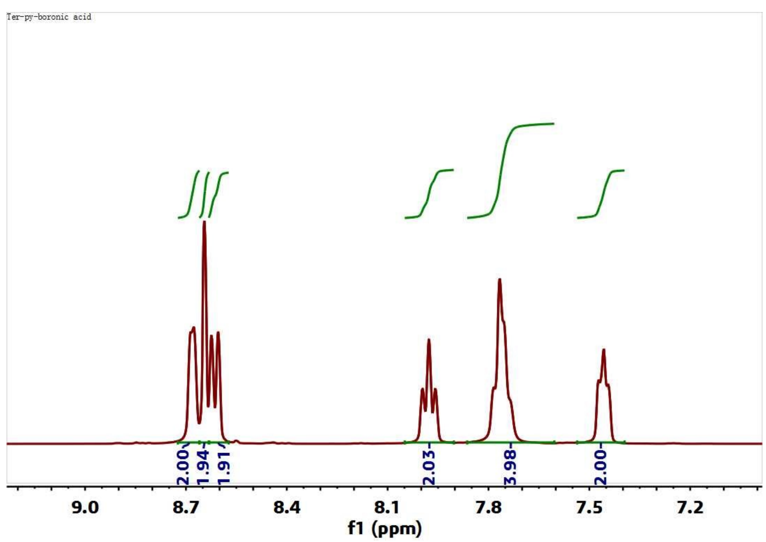


Fig. S1 ^{1}H NMR of compound 1

Compound 2: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 4H), 7.61 (d, J = 8.3 Hz, 4H), 7.58 (d, J = 8.3 Hz, 4H), 7.54 (s, 2H).

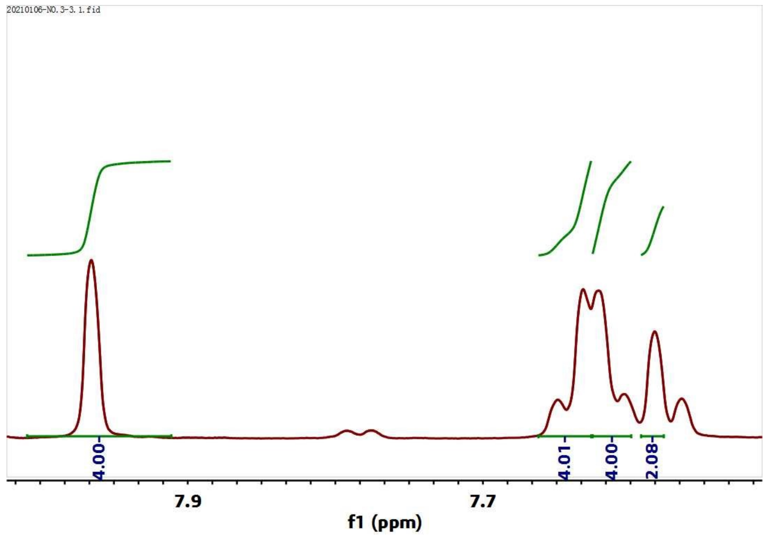


Fig. S2 ^{1}H NMR of compound 2.

Tpy: ^{1}H NMR (400 MHz, TFA) δ 9.29 (d, J = 5.1 Hz, 4H), 9.10 (d, J = 8.0 Hz, 4H), 9.05 – 8.95 (m, 8H), 8.39 (t, J = 6.1 Hz, 4H), 8.15 (d, J = 9.3 Hz, 8H), 8.08 (d, J = 7.5 Hz, 4H), 7.97(s, 2H), 7.96 (s, 8H).

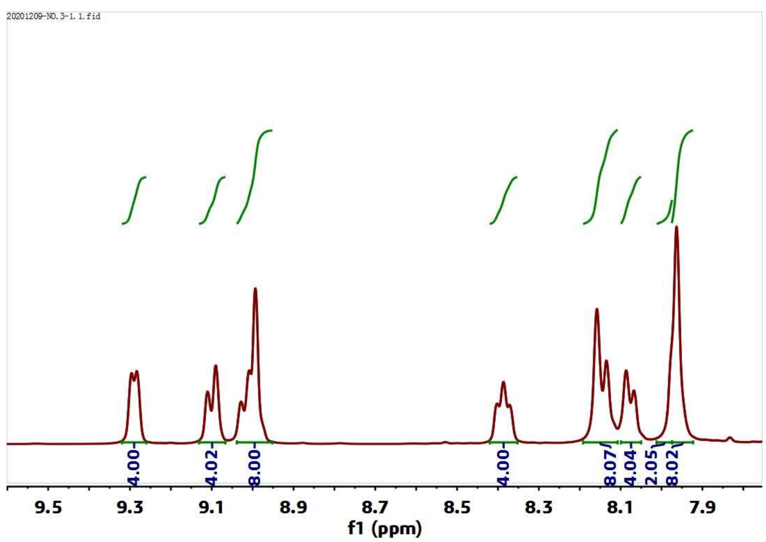


Fig. S3 ^{1}H NMR of Tpy.

MALDI-TOF-MS of Tpy: $[M + H]^+$ calcd for $C_{66}H_{42}N_8$, 947.36; found, 947.35.

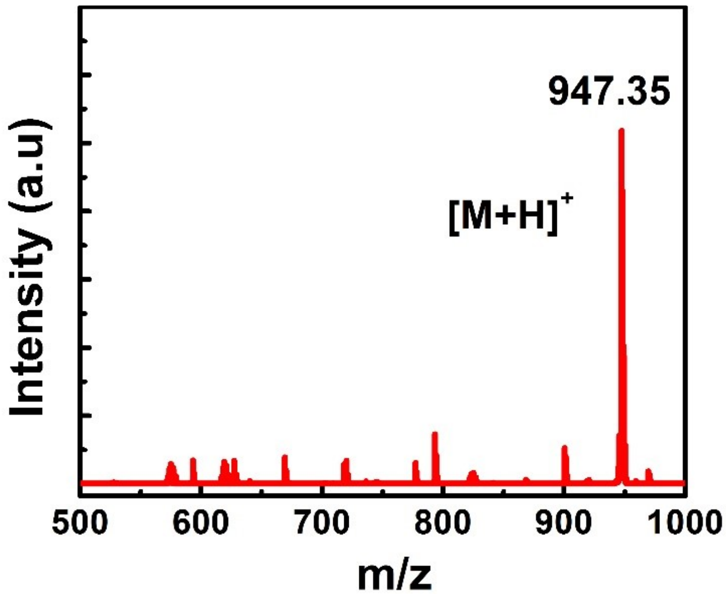


Fig. S4 MALDI-TOF-MS of Tpy

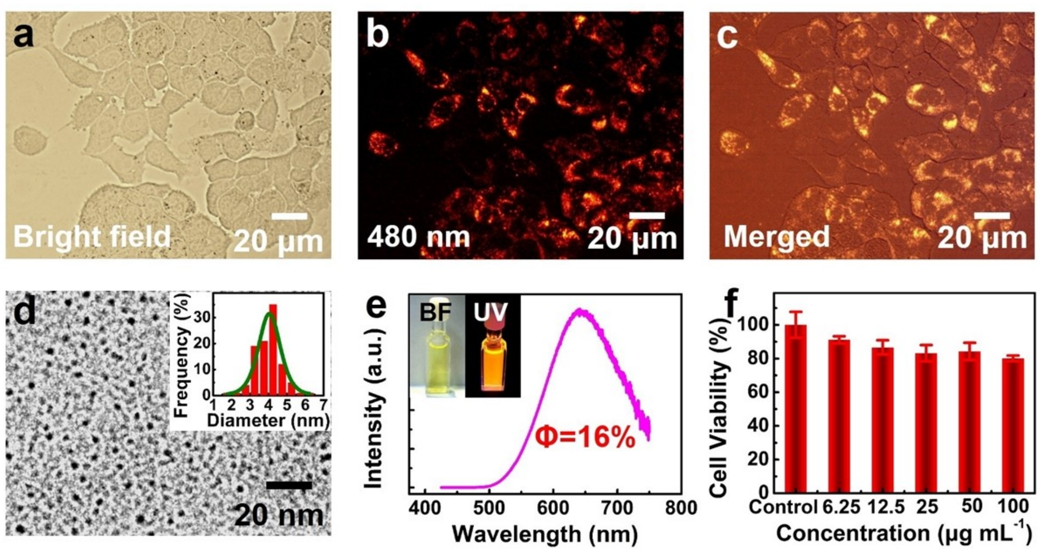


Fig. S5 Live cell imaging of Zn-Tpy CONASH NPs and cytotoxicity assay. (a) Bright-field microscopic, (b) corresponding fluorescence images under light irradiation (λ_{Ex} = 480 nm) and (c) the merged images of the 4T1 cells labelled with the CONASH NPs. (d) TEM image of Zn-Tpy CONASH NPs. The inset is the particle size distribution of Zn-Tpy NPs. (e) Photoluminescence spectra of Zn-Tpy NPs in water. Inset: the fluorescence image of Zn-Tpy NPs dispersed in water. (f) CCK-8 assay of 4T1 cells incubated with the sample for 24 h.

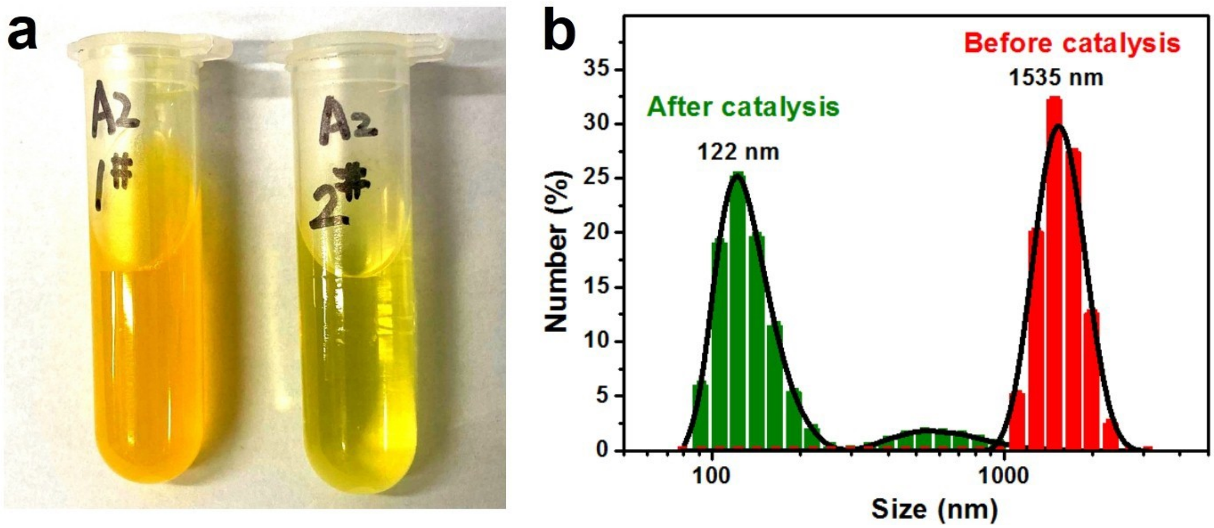


Fig. S6 (a) Photograph of the Zn-Tpy solution before (left) and after (right) cyclic photocatalysis test. (b) DLS analysis of Zn-Tpy samples before and after cyclic photocatalysis test.

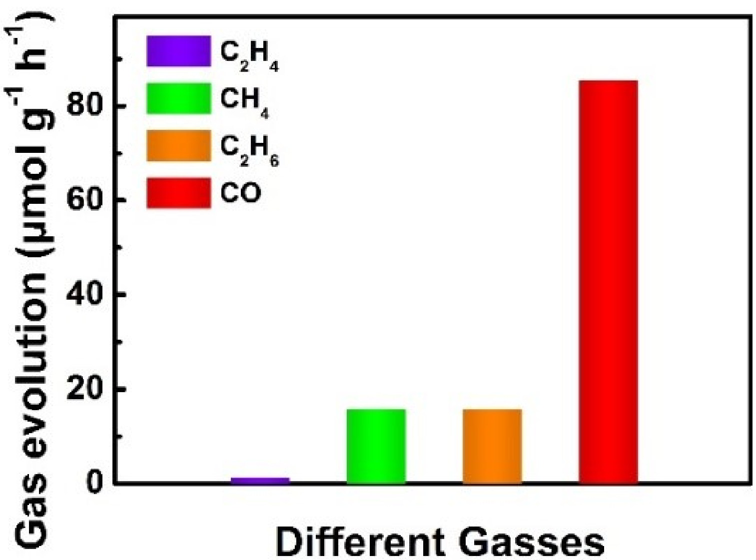


Fig. S7 Photocatalytic evolution activities of different fuels with the saturation of CO_2. The evolution activities of C_2H_4, CH_4, C_2H_6, and CO were 1.21, 15.73, 15.71 and 85.39 μmol g^{-1} h^{-1}, respectively.

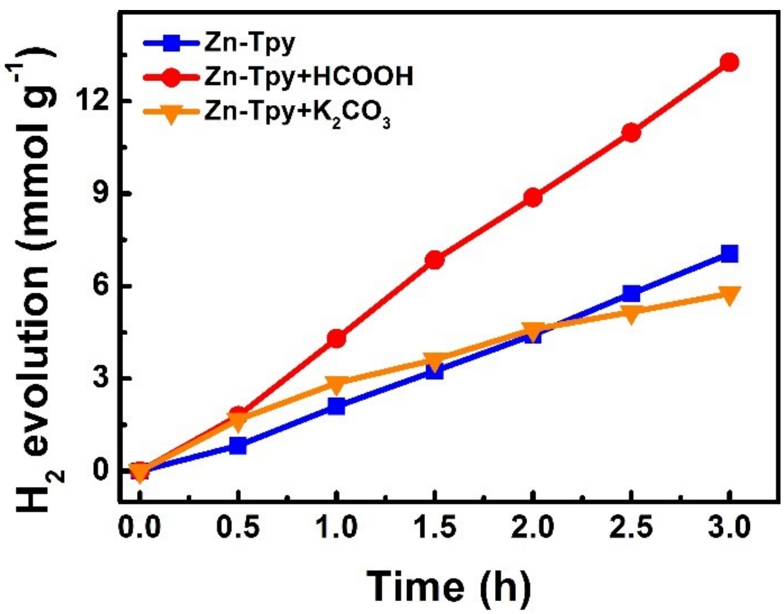


Fig. S8 Comparison of photocatalytic H_2 evolution under different conditions.

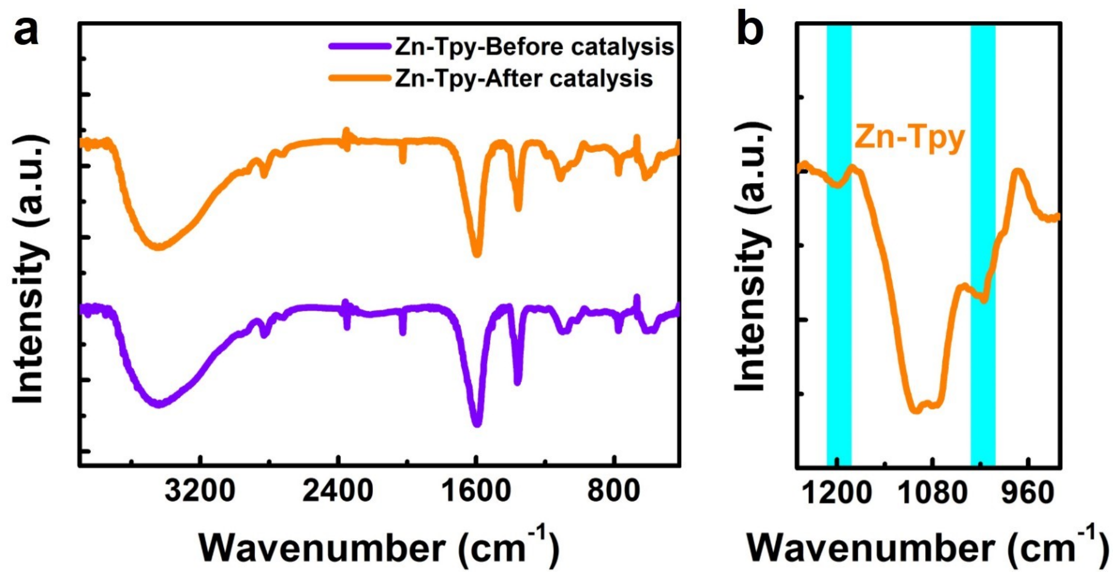


Fig. S9 (a) FT-IR spectra of Zn-Tpy before and after catalysis. (b) The peak of $SO4^{2-}$ in the FT-IR spectra. The changes of FTIR spectra of Zn-Tpy before and after catalysis are almost neglectable, indicating that Zn-Tpy has excellent stability as a photocatalyst. FTIR (KBr, $1/\upsilon_{max}$): 3441, 2923, 2831, 2716, 2349, 2282, 2025, 1595, 1355, 1195, 1114, 1014, 775, 667, 614 cm^{-1}.

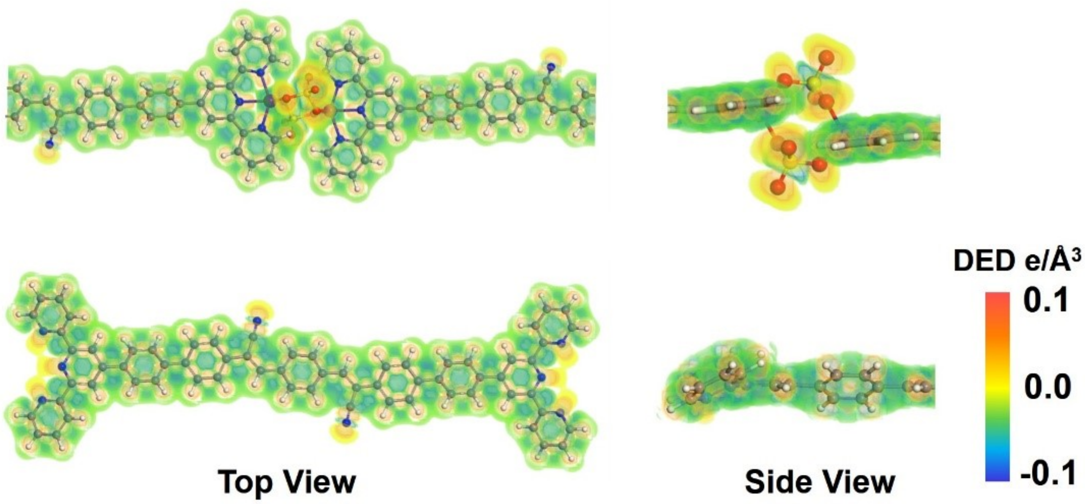


Fig. S10 Deformation electron density maps of the Zn-Tpy and Tpy.

Table S1 Comparison of the photocatalytic hydrogen production activities of non-noble metal-organic compounds.

No.	Catalyst	H_2 production ($\mu mol\ g^{-1}\ h^{-1}$)	Light source	References
1	Zn-Tpy CONASH	3100	300 W Xe lamp: visible range	**This work**
2	Zn-Tpy CONASH-CO_2	11800	300 W Xe lamp: visible range	**This work**
3	Thiazolo thiazole-COF (TpDTz)$^+$ Ni-cluster co-catalyst	941	300 W Xe lamp: AM1.5	1
4	Zn-TPY-TTF CPG	530	300 W Xe lamp: visible range	2
5	CdS/Ni-MOF	2508	300 W Xe lamp (λ >420 nm)	3
6	Small-sized Ni NPs anchored in MOF	3022	300 W Xe lamp visible range	4
7	ZIF-8/g-C_3N_4	309.5	300 W Xe lamp (λ >420 nm)	5
8	Ti-MOF-NH_2	170	300 W Xe lamp: visible range	6
9	ZnO/ZnS-30 in MOF-5	435	300 W Xe lamp (λ >420 nm)	7
10	N_2-COF/chloro(pyridine) cobaloxime co-catalyst	782	300 W Xe lamp: AM1.5	8
11	TPA-Zn	3011.1	290 MW Xenon lamp (420–750 nm)	9
12	Ir-complex (P1)/Co(bpy)$_3$Cl$_2$	598	300 W Xe lamp visible range	10
13	Bp-COP and BpZn-COP	1333	300 W Xe-lamp (λ >420 nm)	11
14	Coordination polymers Co-CP	1778	white LED lamp (λ = 420–780 nm, 100mW cm^{-2})	12
15	Co(II)@MIL-125-NH_2	553	300 W Xe lamp (λ >380 nm)	13
16	Cd-TBAPy	86	300 W Xe lamp (λ >420 nm)	14
17	40-P-CdS/Ni-MOLs	29810	300 W Xe lamp (λ >420 nm)	15

Table S2 Photocatalytic hydrogen production activity of noble metal-doped metal-organic materials

No.	Catalyst	H_2 production (μmol g^{-1} h^{-1})	Light source	References
1	Pt@UiO-66-NH_2	257.4	300 W Xe lamp: visible range	16
2	1.5 wt.% Pt/Ti-MOF-NH_2	500	300 W Xe lamp: visible range	6
3	Pt@CdS@Cd(II)-MOF@TiO2 in Cd-MOF	1416	300 W Xe lamp: visible range	17
4	Calix arene based dye-sensitized Pt@UiO-66-NH_2	1528	300 W Xe lamp (λ >420 nm)	18
5	Pt(4.38 wt%)/CuII-MOF	2510	300 W Xe lamp (350-780 nm)	19
6	PtSA-MNS	11320	300 W Xe lamp (λ >420 nm)	20
7	Pt@Zn-TPY-TTF CPG	14765	300 W Xe lamp: visible range	2
8	Au@CdS/MIL-101	25000	300 W Xe lamp (λ >420 nm)	21
9	Au nanodots@thiol-UiO-66@ZnIn2S4 nanosheets	39100.6	300 W Xe lamp: visible range	22
10	Pt complex immobilized MOF-253	58000	300 W Xe lamp (λ >420 nm)	23

Reference

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