

Supporting Information

Structural characterization:

The phase structure and crystallinity of the prepared catalysts were observed by Powdered X-ray diffraction (XRD) analysis. The Powdered X-ray diffraction were recorded on a Bruker AXS diffractometer (D8 advance) at a generator voltage of 40kv and 30 mA current using cu-K α . radiation ($\lambda=1.5406\text{ \AA}$). The samples were scanned in the range of (2 $\theta=5-100$) with the scan rate 1s/step. Field emission scanning electron microscopic (FESEM) characterization was done on FEI Nova Nano SEM-450. Transmission electron Microscopy (TEM) image of the representative TNR sample was obtained by using a JEOL 2010EX TEM instrument equipped with the high resolution objective –lens pole piece at an acceleration voltage of 200Kv fitted with a CCD camera. The optical properties were characterized by using UV-vis diffuse reflectance spectroscopy (DRS) Perkin Elmer Lambda 750) equipped with an integral sphere using BaSO₄ as a reference. Fourier transmission infrared spectroscopy were carried by FTIR-6800 is JASCO Europe Italy. Photo electro chemical properties were carried by CH instrument model CHI660C, Shanghai Chenhua Device Company, Time –Resolved Electrochemical instrument using a 450 W xenon arc lamp (Newport, USA). GC analysis was performed by gas chromatograph TCD detector (Perkin Elmer Clarus 590 GC containing molecular Sieve/5 \AA column) using nitrogen (N₂) as carrier gas.

Platinization Calculation:

0.25 mL of H₂PtCl₆ from 8wt % aqueous solution:

$$\text{Density} = \text{mass/volume} \quad (d=m/v)$$

$$V=m/d$$

$$\text{Mass of H}_2\text{PtCl}_6 = 100\text{g(given)}$$

$$\text{Density of 1w\%} = 1.05\text{g/cm}^3$$

$$V=100/1.05$$

1g of TiO₂ (1w%) is taken 10 mg,

1w% of platinum M. Wt is 195.084 g in H₂PtCl₆, M. Wt is 409.81g/mol therefore 10mg platinum = $409.81 \times 10 / 195.084$

$$= 21.0068\text{mg is required for 10mg of platinum.}$$

$$= 95.23\text{cm}^3 \text{ this is only 1w\% of H}_2\text{PtCl}_6.$$

$$\frac{95.23 \times 21.0068}{8 \times 1000}$$

=0.25ml platinum from 8w% of H₂PtCl₆

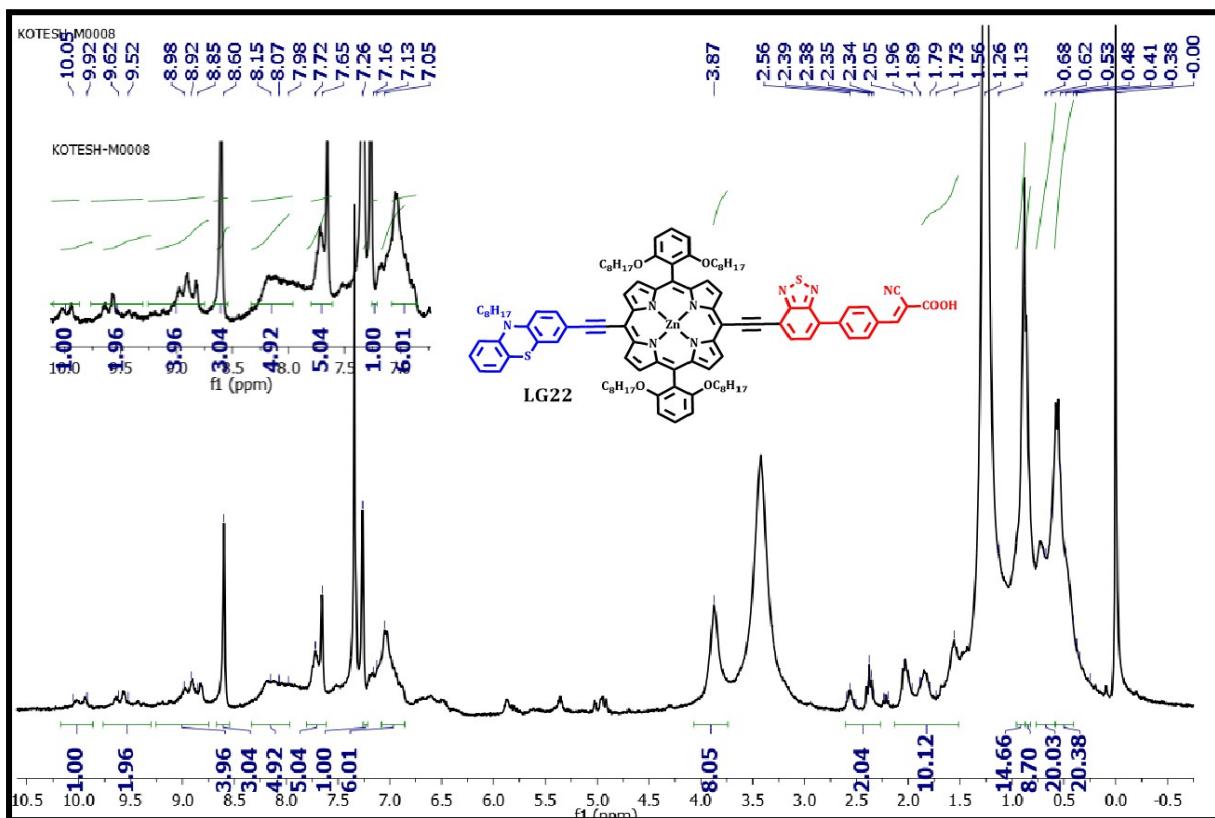


Figure S1. ¹H NMR spectrum (500 MHz, CDCl₃+ C₅D₅N) of LG22.

Data: LGB-24-PH0001.2K1[c] 24 Dec 2018 13:58 Cal: 24-12-2018 24 Dec 2018 13:39
 Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Reflectron_HiRes, Power: 110, Blanked, P.Ext. @ 3000 (bin 113)
 %Int. 28 mV[sum= 1382 mV] Profiles 1-50 Smooth Gauss 5

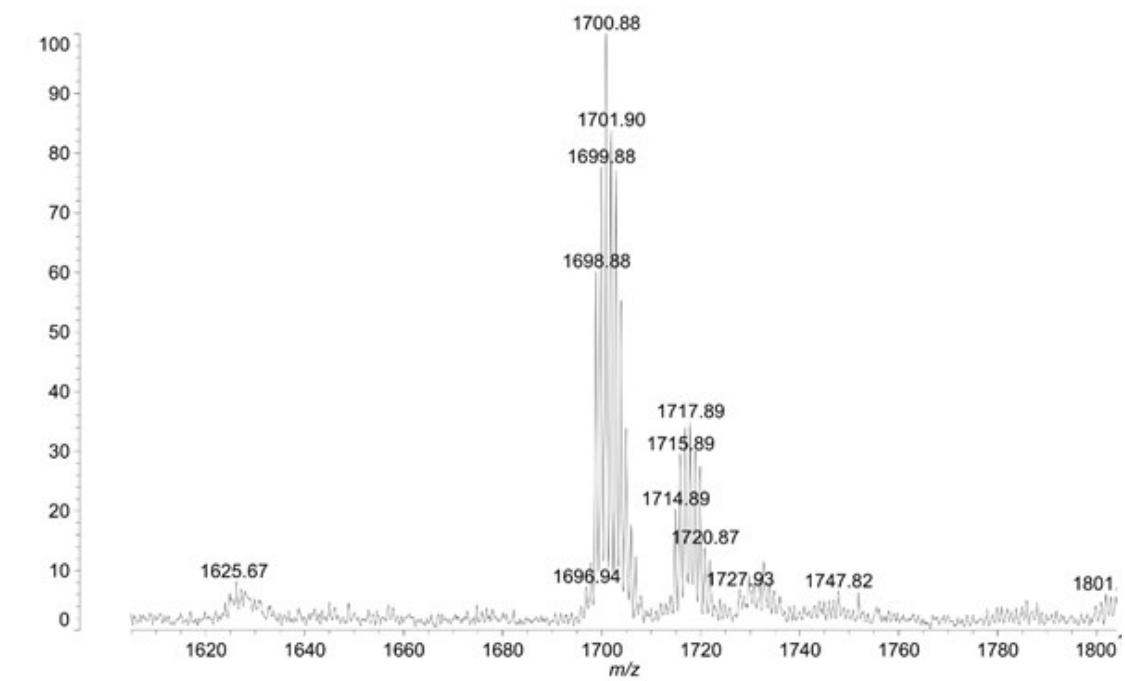


Figure S2. MALDI-TOF of LG22.

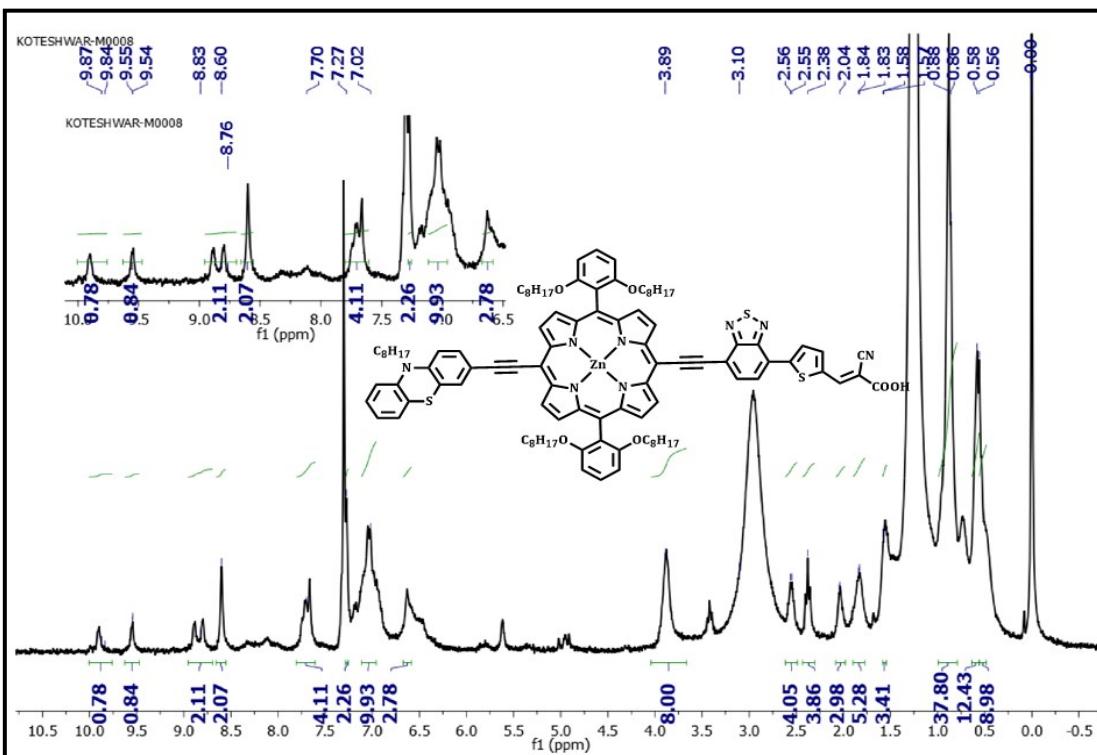


Figure S3. 1H NMR spectrum (500 MHz, $CDCl_3 + C_5D_5N$) of LG23.

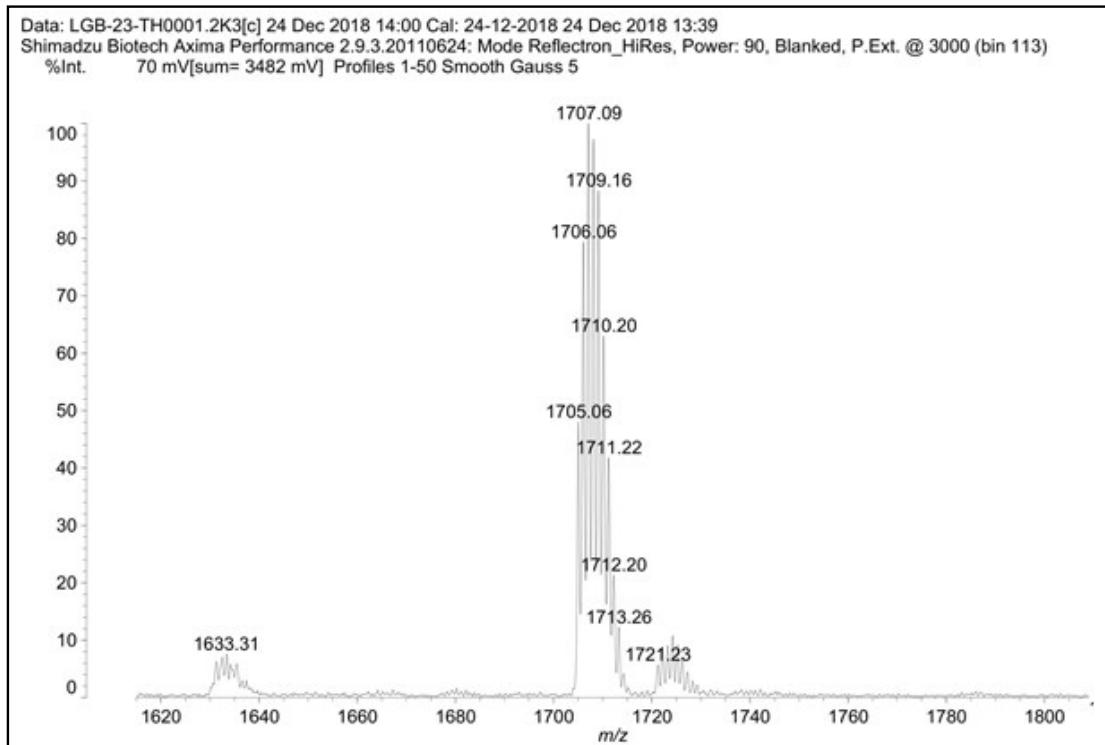


Figure S4. *MALDI-TOF of LG23*

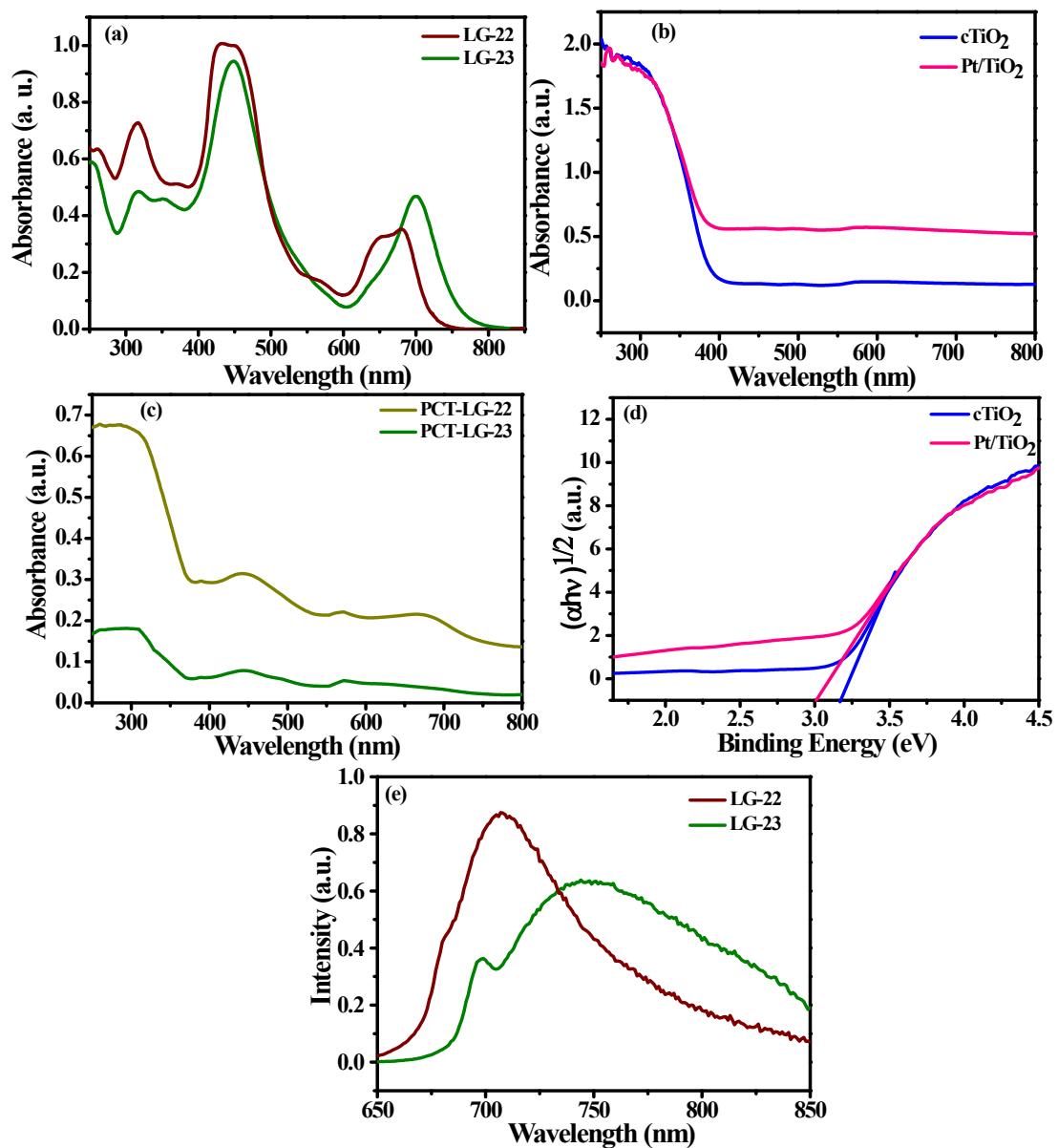


Figure S5: (a) UV-vis absorption spectra of LG-22, LG-23, UV-vis DRS of (b) cTiO₂ and Pt/TiO₂ (c) PCT-LG-22, PCT-LG-23, Tauc Plot of (d) cTiO₂, Pt/TiO₂, (e) Photoluminescence of PCT-LG-22, PCT-LG-23.

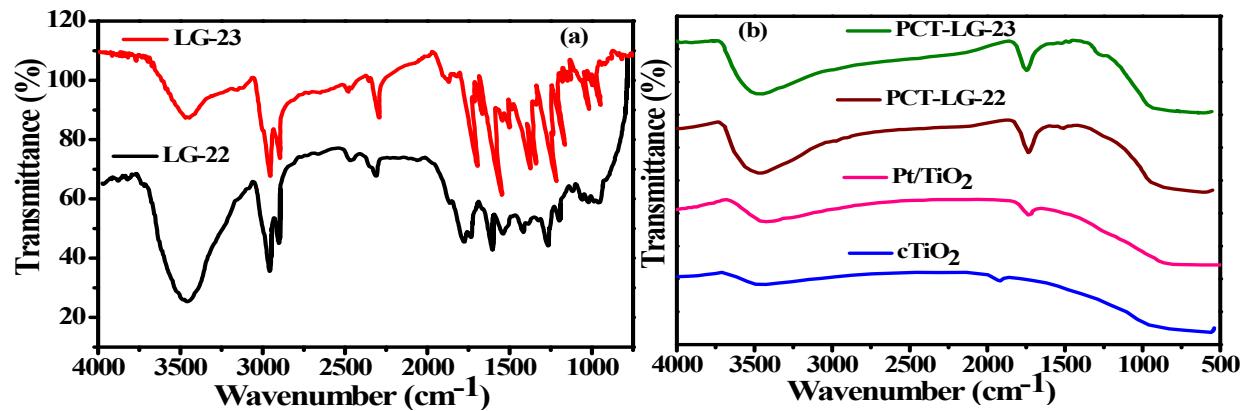


Figure. S6: FTIR analysis of (a) LG-22 and LG-23 dyes, and (b) cTiO₂, Pt/TiO₂, PCT-LG-22 and PCT-LG-23.

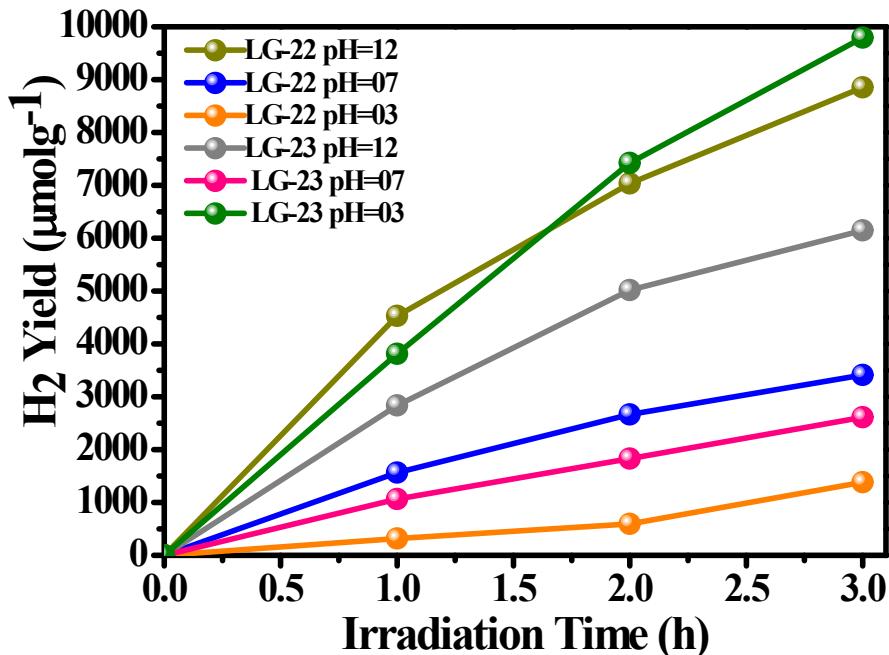


Figure. S7: Time Course for the photocatalytic hydrogen generation.

Photocatalytic Water Splitting Reaction: Hydrogen production calculation

Therefore, the TON can be calculated according to equation (1).

$$TON = \frac{\text{Number of dye molecules adsorbed}}{2 * \text{number of evolved H}_2 \text{ molecules}} \quad (1)$$

The apparent quantum yields (AQY) are calculated according to the following equation (2).

$$AQY(\%) = \frac{H_2 \text{ molecules of evolved} * 2}{\text{incident photons}} (\text{or}) \frac{2X \text{ Rate}}{N} \times 100 \quad (2)$$

Standard area of pure hydrogen gas (H_2) = $3039348.66 \times mL$

In atmospheric condition at normal temperature pressure (NTP)= 22.4 mL

$$1 \text{ m.mol} = 22.4 \text{ mL}$$

0.1 mL (or) 1 m.ml Standard area of pure hydrogen gas (H_2) = 3039348.66 mL

$$? = x \text{ mL}$$

$$= \frac{0.1ml \times X}{3039348.60 * 22.4} = 1.4688 \times 10^{-9} \text{ m.ml} \times X$$

75 mL pyrex glass containing empty space= 55 mL due to 20 mL catalytic solution

$$1.4688 \times 10^{-9} \text{ m.ml} \times X = 1 \text{ mL}$$

$$?=0.1mL$$

$$1.4688 \times 10^{-9} \text{ m.ml} / 0.1 \text{ mL} / 1 \text{ mL}$$

$$= 1.4688 \times 10^{-8} \times X$$

$$= 1.4688 \times 10^{-5} \text{ X m.ml}$$

$$= 0.014688 \times 10^{-3} \times X \mu.\text{ml}$$

$$10 \text{ mg of catalyst} = 0.014688 \times 10^{-3} \times X \mu.\text{ml}$$

$$55 \text{ ml empty space}=?$$

$$H_2 = \frac{0.014688 \times 10^{-3} \times 55 \mu.\text{ml}}{10 \text{ mg}}$$

$$= \frac{0.014688 \times 10^{-3} \times 55 \mu.\text{ml} \times 1000}{10 \text{ mg}}$$

$$= 0.08078 \mu.\text{ml} / g \times X$$

Calculation of Number of incident proton 'N'

$$N = \frac{E\lambda}{hc}$$

$$E = Nhv \text{ (according to plank equation)}$$

$$\nu = \frac{c}{\lambda}$$

$$E = Nh\frac{c}{\lambda}$$

E=Incident light of radiation

E= 2.75×10^{-3} joule

λ =wave length of light(420nm)

$h =$ plank constant (6.626×10^{-34} Js) or 6.626×10^{-27} erg-s

c=speed of light(3×10^8 m/s) or 3×10^{10} cm/s

Surface area of reactor= 6.5cm^2

Irradiation time=4hours

$$\frac{2.75 \times 10^{-3} j \times 420 \times 10^{-9} m}{6.626 \times 10^{-34} Js} \times 3 \times 10^8$$

N=

m/s

$$N = 2.75 \times 10^{-3} j \times 420 \times 10^{-9} m \times 6.5 \text{cm}^2 \times 4 \times 3600 \text{s}$$

$$6.626 \times 10^{-34} \text{ J-s} \times 3 \times 10^{10} \text{cm/s}$$

$$N = 5.43 \times 10^{13}$$

Table S1: Comparison of photocatalytic hydrogen generation efficiency of different reported photosensitizers

Sl. No	Photocatalyst	Light Source	pH	SED	H ₂ Yield	TON	AQY (%)	Reference
1	Zn-CoDETPP	300W Xe lamp	-	TEOA	$43 \mu\text{mol h}^{-1}$	-	7.36	1
2	$[\text{ZnTMPyP}]^4$ + MoS_2/RGO	300W Xe lamp	7		$2560 \mu\text{mol h}^{-1} \text{g}^{-1}$	-	15.2	2
3	ZnTCPP-MoS ₂ /TiO ₂	300W Xeon-lamp equipped with a cut-off filter ($\lambda > 420$ nm).	8	TEOA	10.2	261	-	3
4	YD2-o-C8	LED	4	Ascorbic Acid	$47700 \mu\text{mol g}^{-1} \text{h}^{-1}$	2370	1.22	4
5	PdTAPP-TFPT	300 W Xe lamp		sodium ascorbate	$30880 \mu\text{mol g}^{-1}$	-	0.75	5
6	Pt/THPP-Zn-TiO ₂	300W Xe Lamp	-	TEOA	1239.8 μmol	-	-	6

					$\text{g}^{-1} \text{ h}^{-1}$			
7	ZnCoDETPP	300W Xe Lamp	-	TEOA	43 $\mu\text{mol h}^{-1}$	-	7.36	7
8	2%NP/g - C ₃ N ₄	300W Xe Lamp	-	TEOA	2297 $\mu\text{mol g}^{-1} \text{ h}^{-1}$	15	-	8
8	PHPT-LG5	450W Xe -lamp	7	TEOA	4196 $\mu\text{mol g}^{-1} \text{ h}^{-1}$	8392	7.43	9
9	PCT-LG-DtT	450W Xe -lamp	7	TEOA	6641 $\mu\text{mol g}^{-1} \text{ h}^{-1}$	13282	61.13	10
10	PCT-LG-tT	450W Xe -lamp	7	TEOA	7396 $\mu\text{mol g}^{-1} \text{ h}^{-1}$	14792	54.89	10
11	PCT-LG-22	Xenon-300W Lamp	12	TEOA	8,850.9	11,801.2	15.67	This work
12	PCT-LG-23	Xenon-300W Lamp	3	TEOA	9,793.5	13,058	17.34	This work

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