

SUPPORTING INFORMATION

Design of an alkaline pyridyl acceptor-based calix[4]arene dye
and synthesis of stable calixarene-TiO₂ porous hybrid materials for
efficient photocatalysis

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Table of Contents

1. Experimental section.....	3
2. Scheme S1. The synthetic route of C4BTP	5
3. Scheme S2. The chemical structure of ReP	5
4. Fig. S1. N ₂ adsorption-desorption isotherms of gel-TiO ₂ and C4BTP-TiO ₂	10
5. Fig. S2. The pore size distributions of gel-TiO ₂ and C4BTP-TiO ₂ (5 wt%).....	10
6. Table S1. BET surface areas, pore volumes, and pore widths of gel-TiO ₂ and C4BTP-TiO ₂	11
7. Fig. S3. The TG-DTG spectrum of C4BTP-TiO ₂	11
8. Fig. S4. The EDX of Pt/C4BTP-TiO ₂	12
9. Table S2. ICP-AES results of ReP loading and calculated TON values of corresponding catalysts.....	12
10. Fig. S5. ATR-IR spectra of C4BTP , C4BTP-TiO ₂ (5.0 wt%), ReP and ReP-C4BTP-TiO ₂ (5.0 wt%).....	13
11. Fig. S6. 2p XPS spectra, N 1s XPS spectra, full XPS spectra of C4BTP and C4BTP-TiO ₂ (5.0 wt%) samples.....	13
12. Fig. S7. Cyclic voltammogram of C4BTP in 0.1 M TBAPF ₆ in THF solution with a scan rate of 40 mV s ⁻¹	14
13. Table S3. H ₂ production data of Pt/C4BTP-TiO ₂ with different dye contents and Pt/gel-TiO ₂ /C4BTP materials.....	14
14. Table S4. Performances of DSP systems based on metal-free sensitizers for photocatalytic H ₂ production studies in recent years.....	15
15. Table S5. H ₂ production and AQY results of Pt/C4BTP/gel-TiO ₂ and Pt/C4BTP-TiO ₂ with different dye contents.....	16
16. Table S6. H ₂ production data and calculated TON values of Pt/C4BTP-TiO ₂ (5.0 wt%) in recycling experiment.....	16
17. Fig. S8. ¹³ C NMR spectra of carbon source A) before and B) after irradiation.....	17
18. Fig. S9. GC-MS spectra of ReP-C4BTP-TiO ₂ in the A) ¹³ CO ₂ -saturated and B) CO ₂ -saturated DMF- <i>d</i> ₇ with BIH under visible light ($\lambda > 420$ nm).....	18
19. Fig. S10. A) Emission spectra and B) photoluminescence decays of C4BTP, sensitized gel-TiO ₂ /C4BTP and C4BTP-TiO ₂ (5.0wt%).....	19
20. References.....	19

Experimental section

Materials

Solvents were purified using an MBRAUN MB SPS-800 system. Anhydrous solvents used in the Suzuki coupling reaction were degassed by bubbling with N₂ for 20 min. All other chemicals and reagents were used as received from commercial sources without further purification. Specifically, butyl titanate (Ti(OBu)₄) 99.0%, tetrahydrofuran (THF) 99.0%, acetic acid 99.5%, ethanol 99.5%, methanol 99.5%, TEOA 98.0%, and H₂PtCl₆•6H₂O 99.95% were used.

Characterizations

The ¹H and ¹³C NMR spectra were tested on a Bruker 400 MHz spectrometer. Mass spectra data were obtained on an ultrafleXtreme MALDI-TOF/TOF mass spectrometer (Bruker Daltonics). The absorption spectra were observed with a Shimadzu UV-3600 spectrometer and fluorescence spectra were measured with an Edinburgh Instruments Ltd FLS980 spectrometer. Powder X-ray diffraction (PXRD) was recorded on a Rigaku Smart Lab diffractometer (Bragg-Brentano geometry, Cu-Kα1 radiation, λ = 1.54056 Å). Transmission electron microscopy (TEM) images, high-resolution transmission electron microscopy (HRTEM), high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) micrographs, selected area electron diffraction (SAED), energy dispersive X-ray spectroscopy (EDX), and elemental mapping were obtained by a JEM-2100F transmission electron microscope at 300 kV. Scanning electron microscopy (SEM) micrographs were recorded on Hitachi Ultra-high Resolution FE-SEM SU8010 microscope. Gas adsorption measurements were performed using ultra-high purity N₂ and CO₂ gas on Quantachrome Auto-sorb-iQ2-MP analyzer. The Mott-Schottky curves were measured using a CHI760E electro-chemical analyzer (China) in a three-electrode cell. Pt plate was used as counter electrode and Ag/AgCl electrode (3 M KCl) was used as reference electrode. The electrolyte was a 0.5 M Na₂SO₄ aqueous solution. The working electrode was prepared on fluorine-doped tin oxide (FTO) glass by

dispersing materials (2 mg) in ethanol (1 mL) with Nafion (10 μ L), and the exposed area of the electrode was 1 cm². The photocatalytic hydrogen production system was Perfect Light Lab Solar-IIIAG and H₂ measurement was performed on Agilent 7820A gas chromatography with a thermal conductivity detector (TCD). The amounts of Pt NPs and ReP loaded on samples were detected by ICP-AES (spectra range: 120-800 nm, holographic grating, 2924 line/mm, SPECTRO CIROS VISION). Attenuated total reflection-infrared intensity (ATR-IR) spectra were monitored by Frontier FT-IR spectrometer (spectra range 4000-450 cm⁻¹, an average of 64 scans). X-ray photoelectron spectroscopy (XPS) measurements were carried out using an XR6 monochromated AlK α X-ray source ($h\nu = 1486.6$ eV) with a 900 mm spot size in an ultrahigh vacuum chamber (ESCALAB 250Xi). The pass energy was 20 eV.

Cyclic voltammograms (CVs) were recorded using a CHI760E electrochemical analyzer with platinum plate as working electrode, Ag/AgCl (3 M KCl) as reference electrode, Pt wire as counter electrode, and 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte in THF with a scan rate of 40 mV s⁻¹.

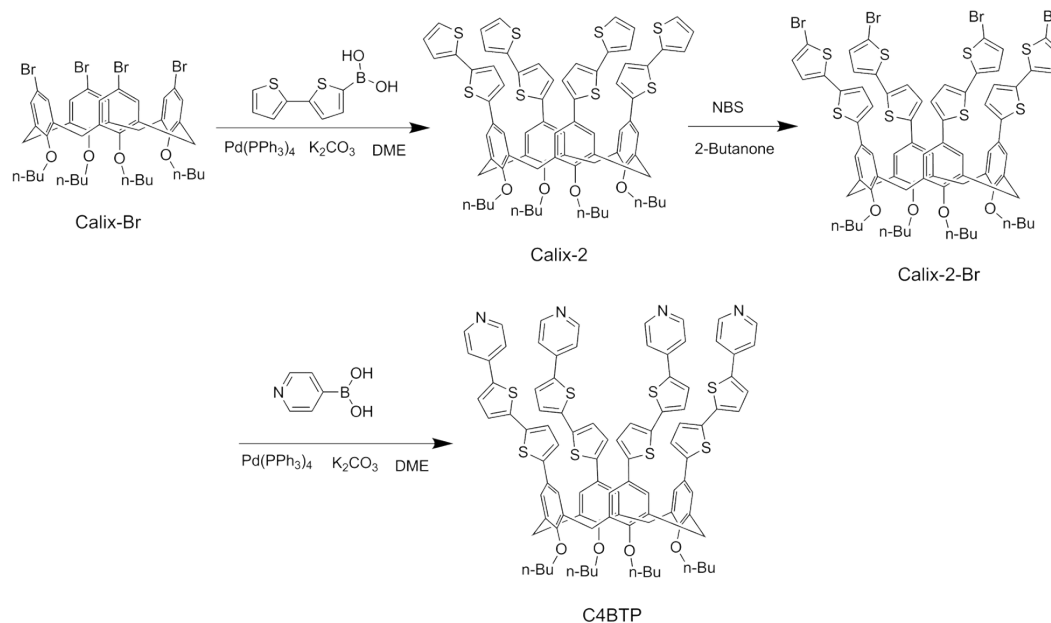
For the CV tests, the determination of oxidation potential was calibrated by ferrocenium/ferrocene (Fc⁺/Fc) redox couple standard. Specifically, the initial oxidation potentials (E_{onset}) of **C4BTP** and ferrocene were obtained from respective CV curves by using the tangent method. Then the corresponding HOMO and LUMO levels were calculated by equations $E_{\text{HOMO}} = -(E_{\text{OX}} \text{ (vs Fc}^+/\text{Fc)} + 4.8)$ and $E_{\text{LUMO}} = E_{\text{HOMO}} - E_{0-0}$, where E_{LUMO} is relevant to the excited state potential of photosensitizer. The above equations rely on the scale: -4.8 eV for 0.0 V versus Fc⁺/Fc, which is based on the calculations obtained by Pommerehne et al,¹ and Bard and Faulkner reported -4.5 eV to be equivalent to 0.0 V vs. NHE.²

Apparent quantum yields (AQYs) were determined using an incident LED light source (Zolix, MLED4-1, M450L, $\lambda = 450$ nm, light intensity 100 mW cm⁻², irradiating area 0.8 cm²) at 20 °C. The number of incident photons was measured by a standard method using a K₃[Fe^{III}(C₂O₄)₃] actinometer and the photon flux was determined to be 1083 μ mol h⁻¹. And AQY (Φ) was calculated according to the

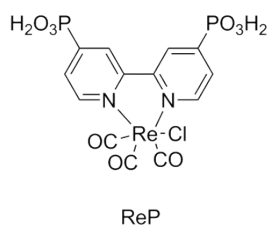
following equation:

$$\phi = \frac{\text{number of transferred electrons}}{\text{number of incident photons}} \times 100\% = \frac{n(\text{H}_2) \times 2}{n(\text{photons})} \times 100\%$$

Synthesis



Scheme S1. The synthetic route of **C4BTP**.



Scheme S2. The chemical structure of **ReP**.

Synthesis of Calix-Br

Calix-Br was prepared according to the method reported in our previous literature.³

Synthesis of Calix-2

Calix-Br (100.00 mg, 0.10 mmol), 2,2'-Bithiophene-5-boronic acid (198.10 mg, 0.83 mmol), and Pd(PPh₃)₄ (60.88 mg, 0.05 mmol) were added to a flask under nitrogen atmosphere, and then K₂CO₃ (239.40 mg, 2.08 mmol, 2 M) aqueous solution and dimethoxyethane (15 mL) was added in the flask by injection syringe after

removing oxygen. The reaction was refluxed to 90 °C for 30 h, following by TLC detection of reaction (PE:DCM = 3:1 v/v). The reaction was quenched by adding deionized water, cooled to room temperature, extracted by ammonium hydroxide and dichloromethane, and then the organic phase was dried over anhydrous Na₂SO₄ subsequently. The crude product was obtained by concentrating and evaporating the organic phase in vacuum. Through pre-absorbed with silicone gel, the crude product was further purified by silica gel column chromatography using a mixture of dichloromethane and petroleum ether (6:1). The pale yellow-green solid was crystallized in methanol and dichloromethane. Yield: 82%. Melting point: 230 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.11 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.05-7.00 (m, 1H), 6.99-6.88 (m, 3H), 6.82 (d, *J* = 3.7 Hz, 1H), 6.72 (d, *J* = 3.6 Hz, 1H), 4.49 (d, *J* = 13.2 Hz, 1H), 4.01-3.89 (m, 2H), 3.23 (d, *J* = 13.4 Hz, 1H), 1.93 (dt, *J* = 15.1, 7.5 Hz, 2H), 1.48 (dt, *J* = 14.3, 7.2 Hz, 2H), 1.02 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃,) δ: 156.5, 143.3, 137.9, 135.3, 135.3, 128.3, 127.6, 125.7, 124.5, 123.7, 123.1, 122.5, 75.1, 32.3, 31.1, 19.4, 14.1; ESI-MS: *m/z* 1327.3092 ([M + Na]⁺), calculated: *m/z* 1304.3196 ([M]⁺).

Synthesis of Calix-2-Br

Calix-2 (134.00 mg, 0.10 mmol) and N-Bromosuccinimide (151.30 mg, 0.85 mmol) was added to 10 mL 2-butanone in a flask, which was stirred out of light at room temperature for overnight. The process of reaction was monitored by TLC and sodium thiosulfate (320.00 mg, 2.20 mmol) aqueous solution was added to reduct the rest of N-bromosuccinimide. The mixture was extracted by dichloromethane and deionized water three times, and then the organic phase was dried over anhydrous Na₂SO₄, concentrated and evaporated in vacuum, subsequently. The yellow-green powder was crystallized in methanol and dichloromethane. Yield: 89.8%. Melting point: 191 °C. ¹H NMR (400 MHz, CDCl₃) δ 6.92 (d, *J* = 10.6 Hz, 2H), 6.89 (d, *J* = 3.8 Hz, 1H), 6.83-6.77 (m, 1H), 6.77 (s, 2H), 4.51 (d, *J* = 13.3 Hz, 1H), 3.97 (t, *J* = 7.4 Hz, 2H), 3.25 (d, *J* = 13.4 Hz, 1H), 1.95 (dt, *J* = 14.8, 7.5 Hz, 2H), 1.49 (dt, *J* = 14.7, 7.5 Hz, 2H), 1.04 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 156.6,

143.9, 139.3, 135.3, 134.4, 130.5, 128.1, 125.7, 124.5, 123.0, 122.5, 110.3, 75.2, 32.3, 31.0, 19.4, 14.1; ESI-MS: m/z 1638.9510 ($[M + Na]^+$, calculated: m/z 1615.9617 ($[M]^+$).

Synthesis of C4BTP

Calix-2-Br (200.00 mg, 0.12 mmol), pyridine-4-boronic acid (121.78 mg, 0.99 mmol), and Pd(PPh₃)₄ (11.44 mg, 0.10 mmol) were added to a flask under nitrogen atmosphere, and then K₂CO₃ (276.00 mg, 2.00 mmol, 2 M) aqueous solution and dimethoxyethane(10 mL) was added in the flask by using injection syringe after bubbling pure nitrogen 20 min to remove oxygen in the solution. The reaction was refluxed at 90 °C for 60 h, following TCL monitoring. The reaction was quenched by adding 0.2 M HCl aqueous solution, cooled to room temperature, extracted with dichloromethane, and then the organic phase was dried over anhydrous Na₂SO₄ subsequently. The crude product was obtained by concentrating and evaporating in vacuum, further purified by silica-gel column chromatography using an eluent consisting of dichloromethane, ethyl acetate, triethylamine and methanol (30 : 10 : 3 : 1). The orange powder was crystallized in methanol. Yield: 54.8%. Melting point: > 300 °C (decomposition). ¹H NMR (400 MHz, CDCl₃) δ 8.50 (d, J = 6.1 Hz, 2H), 7.30 (d, J = 3.9 Hz, 2H), 7.25 (d, J = 3.8 Hz, 1H), 7.07-7.02 (m, 1H), 7.00 (s, 2H), 6.97 (d, J = 3.6 Hz, 1H), 6.84 (d, J = 3.6 Hz, 1H), 4.55 (d, J = 13.4 Hz, 1H), 4.00 (t, J = 7.4 Hz, 2H), 3.29 (d, J = 13.4 Hz, 1H), 1.97 (dt, J = 15.1, 7.6 Hz, 2H), 1.51 (dt, J = 14.6, 7.4 Hz, 2H), 1.06 (t, J = 7.4 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃,) δ : 156.8, 150.1, 144.6, 141.1, 139.9, 138.5, 135.4, 134.7, 128.0, 126.1, 125.8, 125.1, 124.0, 122.7, 119.1, 75.2, 32.3, 31.1, 19.4, 14.1; ESI-MS: m/z 1635.4178 ($[M + Na]^+$), calculated: m/z 1635.4156 ($[M + Na]^+$).

Synthesis of ReP

ReCl(bpy)(CO)₃ (**ReP**) was prepared according to the method reported in literature.⁴

Preparation of C4BTP-TiO₂ materials

C4BTP-TiO₂ materials were prepared through a sol-gel method. Tetrabutyl titanate (1 mL), acetic acid (168 μ L), deionized water (106 μ L) and THF (1 mL) were

added into 20 mL glass bottle and the mixture was stirred at room temperature, and then calculated weight of **C4BTP** dissolved in THF (1 mL) was dropwise added. The transparent gelatum was formed in several minutes and was soxhleted with deionized water for 72 h and then evaporated to dryness at room temperature to obtain orange-red solid. Lastly, the solid was calcined in Muffle furnace at 200 °C for 2 h. The materials of 1.0/2.5/5.0/7.5 wt% C4BTP-TiO₂ were different in the doping amount of **C4BTP**. Similarly, gel-TiO₂ material was prepared though the same procedure but without dye doping.

Preparation of Pt/C4BTP-TiO₂ photocatalysts

Hybrid material (100 mg), distilled water (80 mL), methanol (10 mL) and 10 mM H₂PtCl₆ aqueous solution (334 μL) were added into a quartz reactor. The mixture was degassed by vacuuming and irradiated with 300 W xeon lamp (without filter) for 30 min, and then the Pt nanoparticles were loaded onto C4BTP-TiO₂. Pt loading (0.65 wt%) was testified by the inductively coupled plasma atomic emission spectrometry (ICP-AES).

Preparation of sensitized Pt/gel-TiO₂/C4BTP photocatalysts

Pt nanoparticles were loaded onto gel-TiO₂ by the photo deposition method mentioned above. The as-prepared gel-TiO₂ powder (94 mg) was dispersed in 0.3 mM THF solution of C4BTP (10 mL) and stirred at room temperature for 6 h in the dark, and then centrifuged and washed with THF until the eluent was colourless. The solid was dried in vacuum at room temperature for overnight. The amount of adsorbed C4BTP was determined to be 4.9 wt% by testing the ΔAbs of the THF solution before/after dye sensitization.

Preparation of ReP/C4BTP-TiO₂ (5.0 wt%) photocatalysts

C4BTP-TiO₂ (5.0 wt%) (10 mg) and 0.8 mM ReP aqueous solution (0.375 mL) were added into deionized water and stirred for 4 h. The mixture was centrifuged and the precipitated powder was washed with distilled water for 3 times and then dried in vacuum at room temperature for overnight.

Theoretical calculation of C4BTP

The electronic structures of **C4BTP** were calculated by using density functional theory (DFT) computation at the M06-2X⁵/6-31G(d,p)⁶ level in the Gaussian 09 package.⁷

Photocatalytic H₂ production

The photocatalytic H₂ production experiments were performed in a glass reactor with quartz cover connected to a closed gas circulation, in which the reaction mixture can be degassed by vacuuming. 20 mg photocatalyst was dispersed in 100 mL of 10 vol% TEOA aqueous solution (pH \approx 12). Then the suspension was stirred continuously and irradiated by a 300 W Xe lamp with a cut-off filter ($\lambda > 420$ nm). The amount of produced H₂ was determined at an interval of 1 h with online gas chromatography.

Photocatalytic CO₂ reduction

ReP/C4BTP-TiO₂ (10 mg), dry DMF (10 mL), and 1,3-dimethyl-2-phenyl- 1,3-dihydrobenzimidazole (BIH) (134 mg) were added into a 40 mL quartz bottle. The suspension was degassed by alternately vacuumed and bubbled with N₂ for 3 times, followed by bubbling with pure CO₂ for 30 min. Then the mixture in bottle was sealed with a septum and irradiated using a 300 W Xe lamp with a cut-off filter ($\lambda > 420$ nm). The gaseous products were aspirated with syringe and determined by injection into gas chromatography (Fuli Model GC9790 II equipped with TCD and FID detectors and TDX-01 packed column).

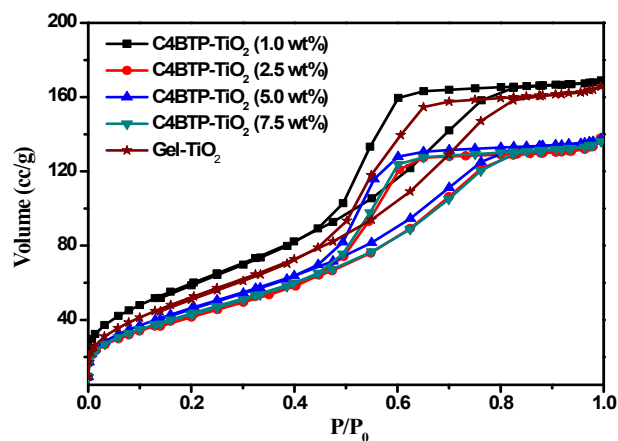


Fig. S1. N₂ adsorption-desorption isotherms of gel-TiO₂ and C4BTP-TiO₂ (1.0/2.5/5.0/7.5 wt%) at 77 K.

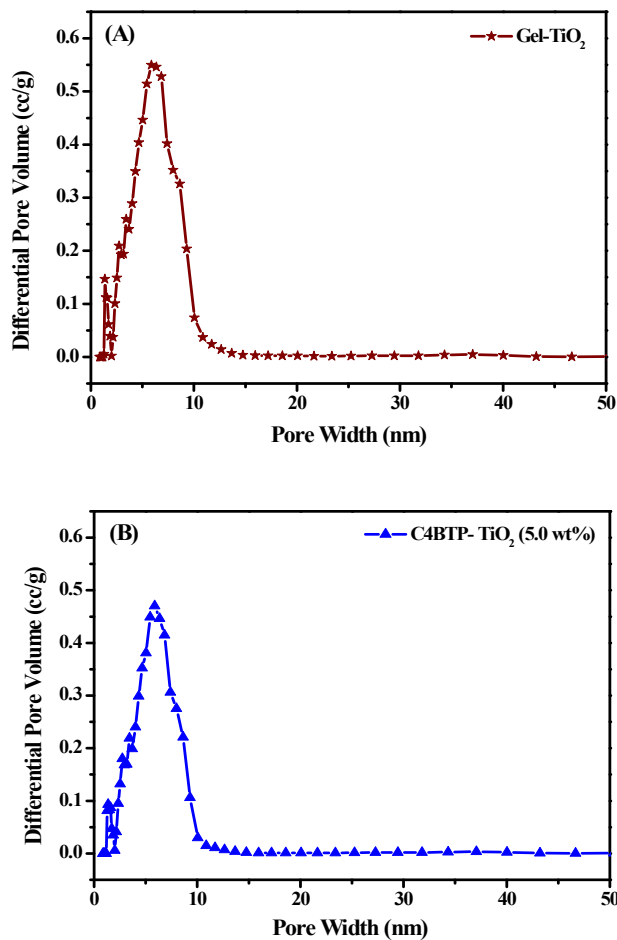


Fig. S2. The pore size distributions of A) gel-TiO₂ and B) C4BTP-TiO₂ (5.0 wt%) .

Table S1. BET surface areas, pore volumes and pore widths of gel-TiO₂ and C4BTP-TiO₂ (1.0 / 2.5 / 5.0 / 7.5 wt%) derived from 77 K N₂ sorption isotherms.

	C4BTP-TiO ₂ (1.0 wt%)	C4BTP-TiO ₂ (2.5 wt%)	C4BTP-TiO ₂ (5.0 wt%)	C4BTP-TiO ₂ (7.5 wt%)	Gel-TiO ₂
Surface Area (m ³ /g)	223.3	160.2	174.8	162.8	197.7
Volume (ml/g)	0.261	0.213	0.213	0.211	0.256
Pore Width (nm)	1.48/5.86	1.28/5.96	1.36/5.88	1.27/6.20	1.36/6.12
Micropore					
Surface Area (m ³ /g)	161.4	182.3	136.8	236.1	215.9
Mesoporous					
Surface Area (m ³ /g)	205.2	164.8	164.6	150.0	189.4

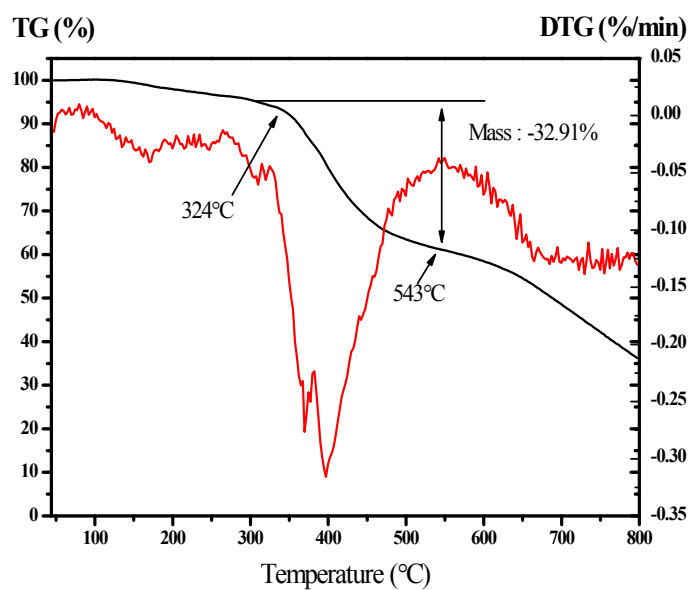


Fig. S3. The TG-DTG spectrum of C4BTP.

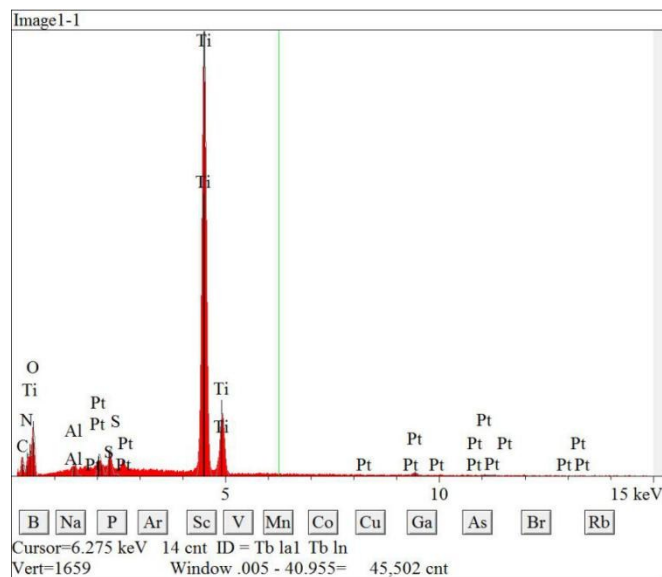


Fig. S4. The EDX result of Pt/C4BTP-TiO₂ (5.0 wt%).

Table S2. ICP-AES results of ReP loading and calculated TON values of corresponding catalysts.

Sample	ReP adding amount (μmol)	Measured ReP loading amount (μmol)	TON _{ReP}
ReP/C4BTP-TiO ₂ (5 wt%)	0.1	0.0628	44.6
		0.0636	44.0
ReP/C4BTP-TiO ₂ (5 wt%)	0.3	0.165	49.1
		0.161	50.3
ReP/C4BTP-TiO ₂ (5 wt%)	0.6	0.253	40.1
		0.261	38.9
ReP/C4BTP/gel-TiO ₂ (5 wt%)	0.3	0.28	12.5
		0.27	12.9
ReP/gel-TiO ₂	0.3	0.25	5.1
		0.27	4.7

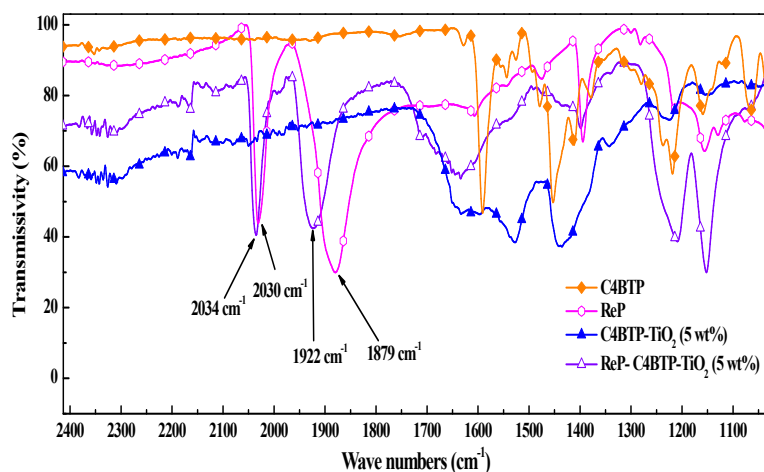


Fig. S5. ATR-IR spectra of **C4BTP**, **C4BTP-TiO₂** (5.0 wt%), **ReP** and **ReP/C4BTP-TiO₂** (5.0 wt%).

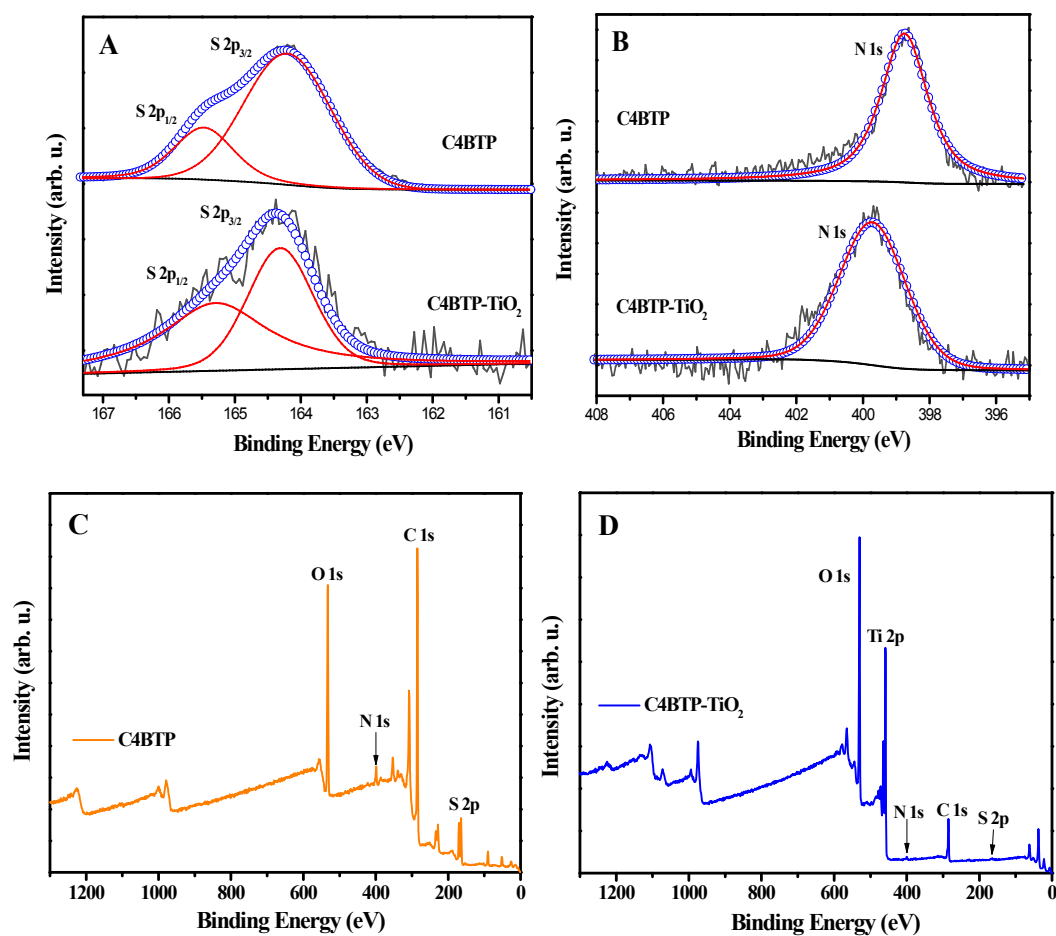


Fig. S6. A) S 2p and B) N 1s XPS spectra for **C4BTP** and **C4BTP-TiO₂** (5.0 wt%), and full XPS spectra of C) **C4BTP** and D) **C4BTP-TiO₂** (5.0 wt%) samples.

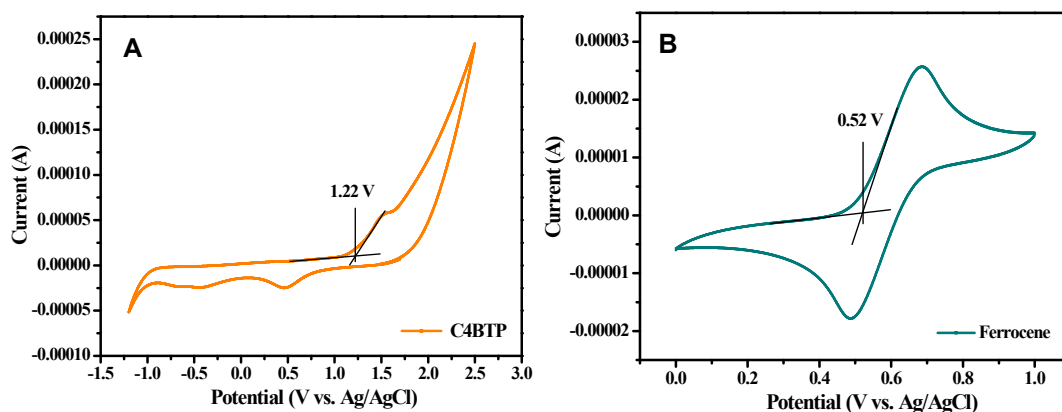


Fig. S7. Cyclic voltammogram of A) C4BTP and B) ferrocene in 0.1 M TBAPF₆ in THF solution with a scan rate of 40 mV s⁻¹.

Table S3. H₂ production data of Pt/C4BTP-TiO₂ with different dye contents and Pt/gel-TiO₂/C4BTP materials.

Photocatalysts	Activity/	Activity/	TON _[Pt] (5 h) ^[c] TON _[dye] (5 h) ^[d]	
	mmol g ⁻¹ h ⁻¹ [a]	mmol g ⁻¹ _[Pt] h ⁻¹ [b]		
Pt/C4BTP-TiO ₂ (1.0 wt%)	5.38	827.93	807	4337
Pt/C4BTP-TiO ₂ (2.5 wt%)	7.81	1201.64	1172	2518
Pt/C4BTP-TiO ₂ (5.0 wt%)	11.99	1844.85	1799	1933
Pt/C4BTP-TiO ₂ (7.5 wt%)	8.59	1320.84	1288	923
Pt/gel-TiO ₂ /C4BTP	0.53	81.93	80	86

[a] = (H₂ amount in 5 h/ total mass of catalysts) / 5 h

[b] = H₂ amount vs. Pt loading mass = [a] / Pt loading mass fraction = [a] / 0.0065

[c] = H₂ amount vs. Pt loading amount = [b] × 5 × 195.05 / 1000

[d] = H₂ amount vs. dye loading amount = [a] × 5 × 0.001 × 1612^[e] / corresponding dye loading mass fraction

Table S4. Performances of DSP systems based on metal-free sensitizers for photocatalytic H₂ production studies in recent years^a.

No.	reference	PS	H ₂ production	TON _[dye]	time
1	<i>ChemSusChem</i> , 2018, 11 , 793.	AD418	4,359 μmol/g	872 ^b	20 h
2	<i>Appl. Energy Mater.</i> , 2018, 1 , 2813.	Dyad	4,176 μmol/g	1044 ^b	6 h
3	<i>Org. Lett.</i> , 2017, 19 , 1048.	S1	63,112 μmol/g	10200	48 h
4	<i>Susta. Energy Fuels</i> , 2017, 1 , 694.	CBZ-Th	10,083 μmol/g	2017	20 h
5	<i>Int. J. Hydro. Energy</i> , 2017, 42 , 15731.	ChI-2	1,580 μmol/g	—	6 h
6	<i>Dyes Pigm.</i> , 2017, 139 , 7.	YFT-2	10,438 μmol/g	712 ^b	10 h
7	<i>Dyes Pigm.</i> , 2016, 134 , 498.	D2	106,667 μmol/g	1640 ^b	16 h
8	<i>J. Mater. Chem. A</i> , 2015, 3 , 21713.	C16	42,576 μmol/g	2930 ^b	20 h
9	<i>Int. J. Hydro. Energy</i> , 2015, 40 , 9069.	DN5	93,200 μmol/g	1864 ^b	6 h
10	<i>New J. Chem.</i> , 2015, 39 , 713.	D2	566.9 μmol/g	10901	6 h
11	<i>Phys. Chem. Chem. Phys.</i> , 2015, 17 , 13710.	DNPT	1,208 μmol/g	9664	10 h
12	<i>J. Phys. Chem. C</i> , 2019, 123 , 70.	G3	122,998 μmol/g	2460 ^b	5 h
13	<i>Appl. Energy Mater.</i> , 2018, 1 , 6072.	Dimer 2	81,840 μmol/g	2860 ^b	83 h
14	<i>Appl. Energy Mater.</i> , 2019, 2 , 448.	Dye 1	99,500 μmol/g	11000 ^b	10 h
15	<i>J. Mater. Chem. A</i> , 2019, 7 , 19852.	HO-TPA	278,235 μmol/g	8120	75 h
16	<i>This work</i>	C4BTP	402,400 μmol/g	12981	50 h

^aOnly the best performance in each study is listed.

^bIn these references, TON values were calculated by the equal: $TON = (2 \times \text{amount of H}_2) / \text{dye loading amount}$.

Table S5. AQY results for H₂ production of Pt/C4BTP/gel-TiO₂ and Pt/C4BTP-TiO₂ with different dye contents after 0.5 h irradiation under 450 nm LED light source.

photocatalyst	n(H ₂) / μ mol	AQY / %
Pt/C4BTP/gel-TiO ₂	0.42	0.16
Pt/C4BTP-TiO ₂ (1.0 wt%)	4.23	1.56
Pt/C4BTP-TiO ₂ (2.5 wt%)	5.94	2.19
Pt/C4BTP-TiO ₂ (5.0 wt%)	9.45	3.49
Pt/C4BTP-TiO ₂ (7.5 wt%)	6.75	2.50

Table S6. H₂ production data and calculated TON values of Pt/C4BTP-TiO₂ (5.0 wt%) in recycling experiment.

Round No.	H ₂ amount / mmol g ⁻¹	TON _{dye} ^a	TON _{Pt} ^b
1	38.76	1250	1164
2	37.57	1212	1128
3	31.60	1019	949
4	40.00	1290	1201
5	43.09	1390	1294
6	38.39	1238	1153
7	39.29	1267	1180
8	45.34	1463	1362
9	45.11	1455	1355
10	43.25	1395	1299
Total	402.40	12981	12084

^aTON_{dye} values were calculated by the equal: TON = H₂ amount / dye loading amount, the loading amount of C4BTP was cauculated to be 0.031 mmol per gram catalyst;

^bTON_{Pt} values were calculated by the equal: TON = H₂ amount / Pt loading amount, the loading amount of Pt was cauculated to be 0.033 mmol per gram catalyst.

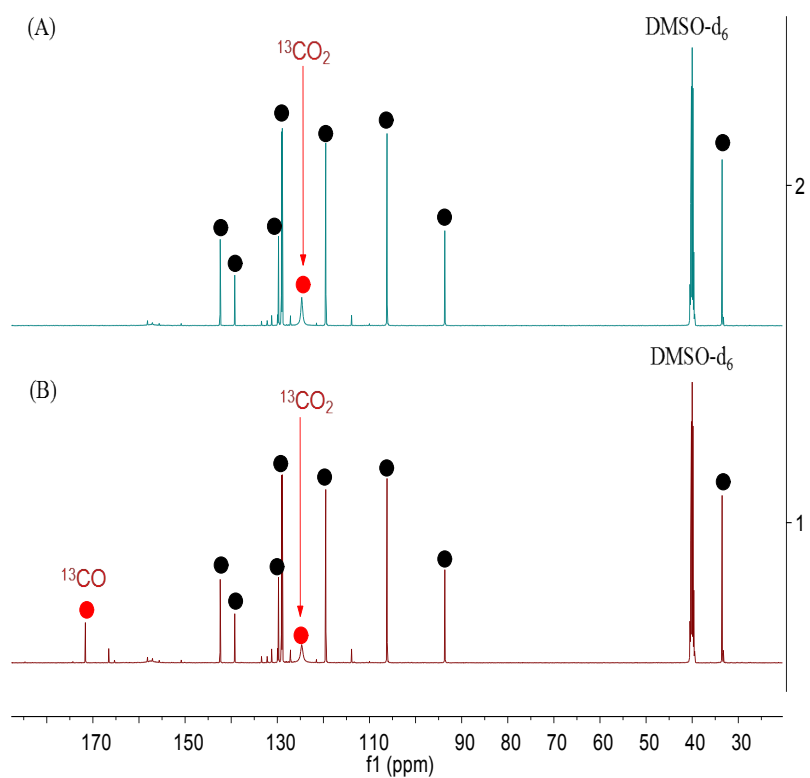


Fig. S8. ^{13}C NMR spectra of carbon source A) before and B) after irradiation. $^{13}\text{CO}_2$ -saturated DMSO- d_6 containing 5 mg of ReP/C4BTP-TiO $_2$ with BIH (67 mg) under visible light ($\lambda > 420$ nm) irradiation for 24 h, the symbols \bullet and \bullet are on behalf of the peaks of BIH and $^{13}\text{CO}_2/^{13}\text{CO}$, respectively.

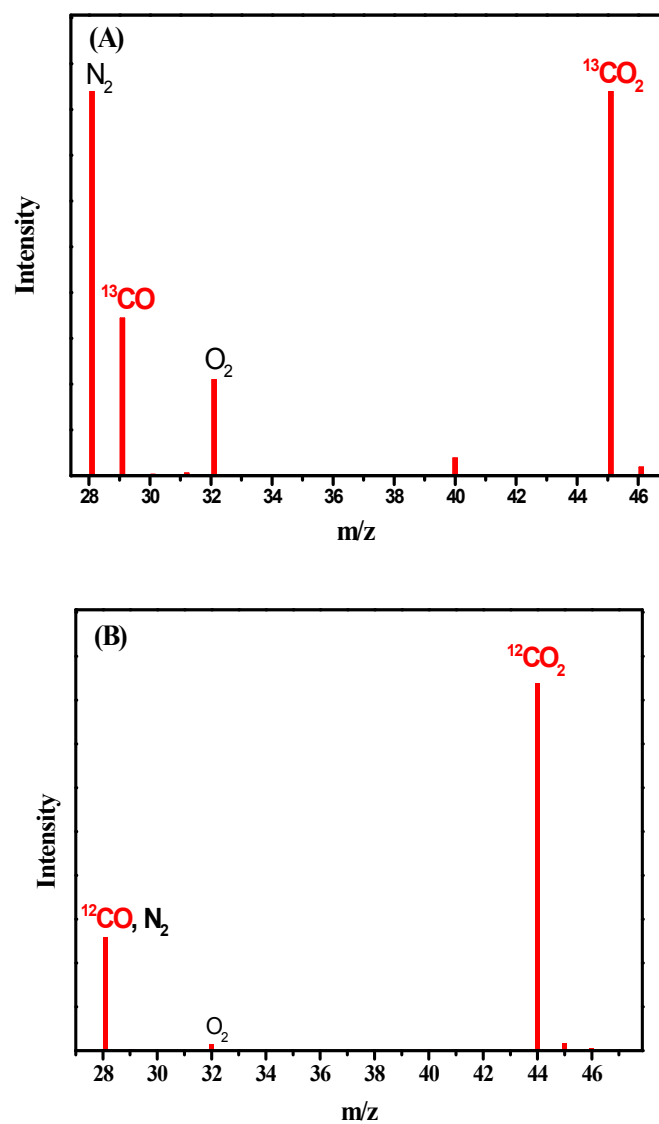


Fig. S9. GC-MS spectra of ReP-C4BTP-TiO₂ in the A) $^{13}\text{CO}_2$ -saturated and B) CO_2 -saturated DMF-*d*₇ with BIH under visible light ($\lambda > 420$ nm) irradiation for 5 h.

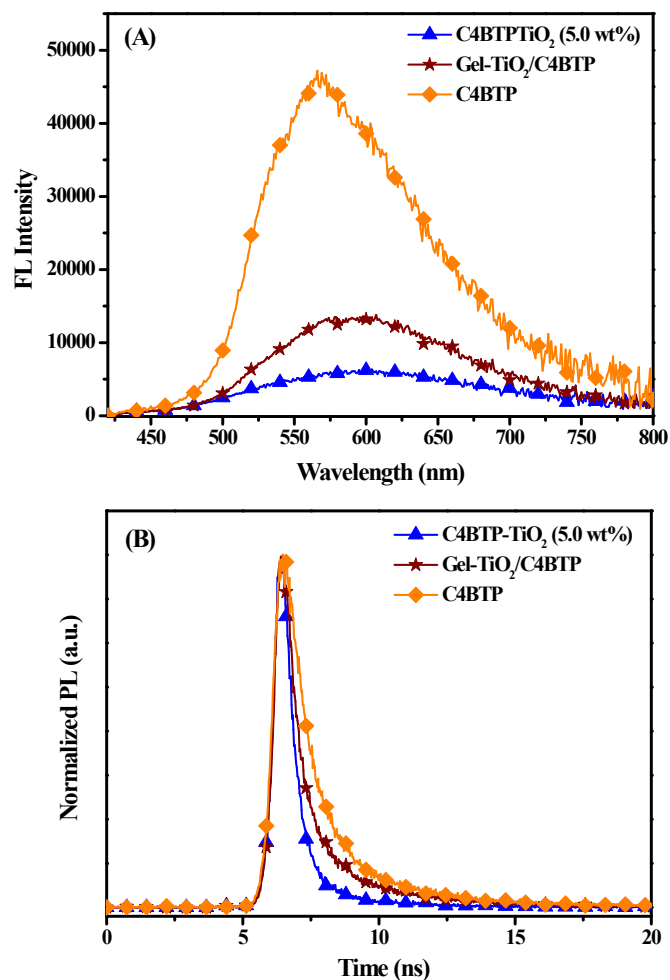


Fig. S10. A) Emission spectra and B) photoluminescence decays of **C4BTP**, sensitized gel-TiO₂/C4BTP and C4BTP-TiO₂ (5.0 wt%).

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