Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

1,3,5-Triazine and Dibenzo[b,d]thiophene Sulfone Based Conjugated Porous Polymers for Highly Efficient Photocatalytic Hydrogen Evolution

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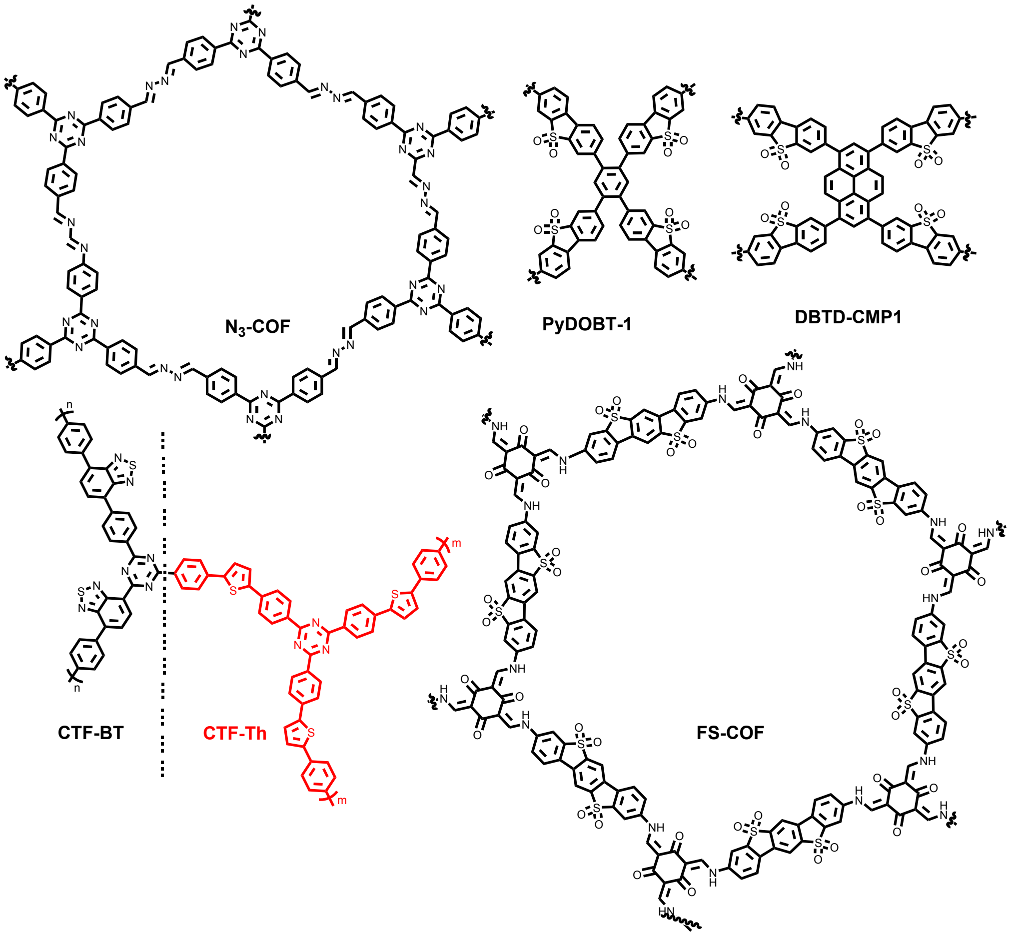


Scheme S1. Some examples of highly efficient photocatalysts for hydrogen evolution.

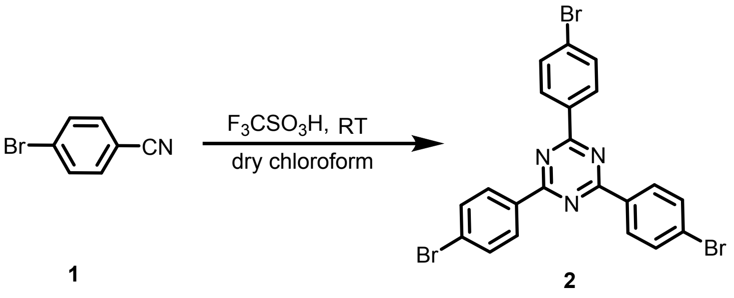
General:

All the chemicals and solvents were commercially available and used without further purification. 2,4,6-tris(4-bromophenyl)-1,3,5-triazine, 3,7-dibromo-dibenzo[b,d]thiophene sulfone, 3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[b,d] thiophene 5,5-dioxide, 2,4,6-Tris(5-bromothiophene-2-yl)-1,3,5-triazine were synthesized according to previous reports (*J. Mater. Chem., 2002, 12, 206–212; Chem. Asian J. 2016, 11, 2555 – 2563; ACS Catal. 2018, 8, 8590−8596; |J. Am. Chem. Soc. 2011, 133, 13437–13444*).

The FT-IR was measured on a Nicolet iS5 FT-IR spectrometer (Thermo Fisher Scientific) at room temperature. TGA was performed on a Q500 TGA by heating polymers at 10 °C min^{-1} under a nitrogen atmosphere. Element analysis was obtained by a Vario EL analyzer. Solid-state ^{13}C-NMR spectra were recorded on an Agilent 600 MHz NMR spectrometer. UV-visible absorption spectra were measured on a Hitachi UH4150 UV-vis spectrometer by measuring the reflectance of powders in the solid state. The photoluminescent spectra were measured with a Hitachi F2700 fluorescence spectrometer. Time-correlated single photon counting was performed on Edinburgh Instruments FLS 980 fluorescence spectrometer. Fluorescence life-times for two polymers in powder state was obtained from fitting time-correlated single photo counting decays to a sum of multiple exponentials, which yield τ_1, τ_2 and τ_3 according to $\sum_{i=1}^{n} B_i exp(-t/\tau_i)$. Powder X-ray diffractions were conducted on X-ray Diffractometer (PANalytical X' Pert Pro). The polymer morphologies were imaged using a field emission SEM (JEOL 6390 LV) and TEM (Tecani G2 Sphere). Surface areas were measured by nitrogen adsorption and desorption at 77.3 K using a micromeritics ASAP2020 HD88 Surface Area and Porosity Analyzer. The surface areas were calculated in the relative pressure (P/P_0) range from 0.05 to 0.30. The samples were degassed at 120 °C for 6 h under vacuum (10^{-5} bar) before analysis. Pore size distributions were derived from the N_2 adsorption branch of the isotherms using non-local density functional theory (NL-DFT). The residual Pd content was determined by inductively coupled plasma mass spectrometry (ICP-MS). The photocurrent was measured on CHI660E electrochemical workstation without bias voltage under UV-Vis light irradiation with 20 s light on-off cycles. The electrode prepared from catalyst was immersed in 0.5 M Na_2SO_4 aqueous solution. Density functional theory calculations were performed using Gaussian 09 program package at the B3LYP 6-31G(d,p) level.

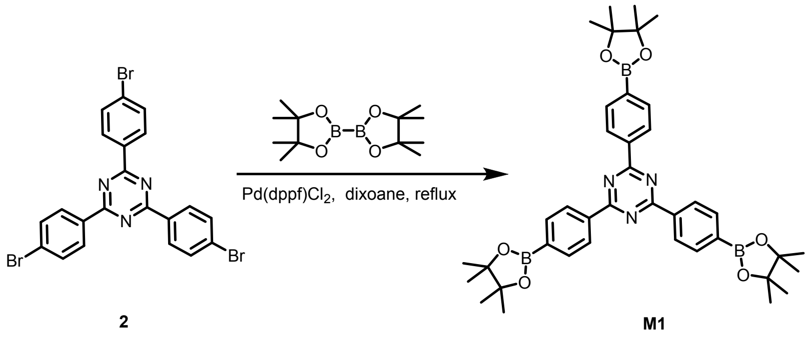
Experimental Section

Synthesis of compound 2



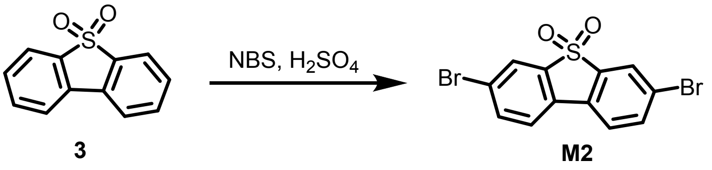
Trifluoromethanesulfonic acid (2.22 g, 14.8 mmol) was dropped into the dry chloroform (40 mL) solution of 4-bromobenzonitrile (0.67g, 3.7 mmol) at 0 °C, Stirring was continued for 2 hours at 0 °C. The mixture was further stirred at room temperature for 24 h. The mixture was poured into water, and the solid was collected and washed with water. The solid was purified with recrystallization in toluene, affording product as white needle. Yield, 1.41 g (70%). ^1H NMR (400 MHz, $CDCl_3$): 8.60-8.62 (d, *J*=8.63Hz, 6H), 7.70-7.72 (d, *J*=8.63Hz, 6H).

Synthesis of M1.



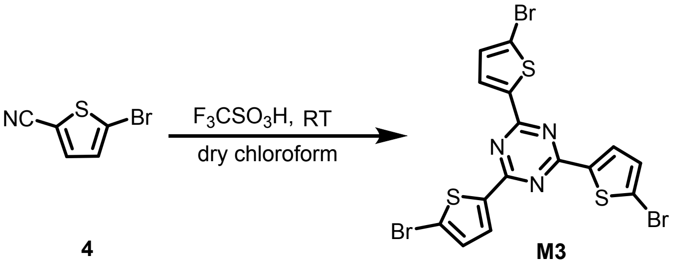
A mixture of 2 (2.40 g, 4.40 mmol), bis(pinacolato)diboron (3.80 g, 14.60 mmol), CH_3COOK (1.20 g, 13.20 mmol), and Pd(dppf)Cl_2 204 mg) in dry 70ml 1,4-dioxane was heated at reflux for 24 h under N_2 atmosphere. After cooling to room temperature, the mixture was poured into water and extracted with CH_2Cl_2. The organic phase was dried with anhydrous Na_2SO_4. The solvent was removed under vacuum, and then the residue was purified by column chromatography (petroleum ether/CH_2Cl_2 1:1) to give M1 (1.55 g, 50%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$): 8.75-8.77 (d, J=8.0 Hz, 6H), 8.01-8.03 ppm (d, J=8.4 Hz, 6H)

Synthesis of M2



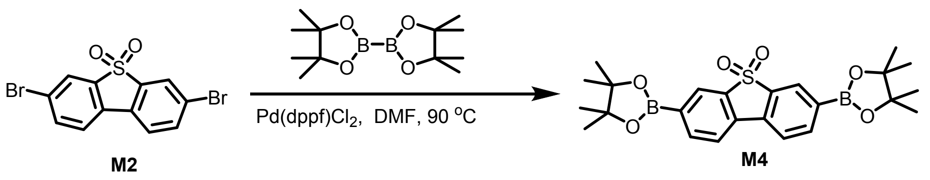
NBS (10.37 g, 58.26 mmol) was added into the solution of 3 (6.00 g, 27.70 mmol) in conc. H_2SO_4 (100 mL) gradually, the mixture was stirred at room temperature for 24h. The mixture was poured into ice water then the solid was filtrated and washed with water and methanol. The product was purified by recrystallization from chloroform to gain 4.50 g white solid in 40 % yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.93 (s, 2H), 7.76-7.78 (d, J=8.0 Hz, 2H), 7.62-7.64 (d, J=8.0 Hz, 2H).

Synthesis of M3



M3 was synthesized and purified according to the similar procedure of compound 2. Yield, 60%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.93 (s, 2H), 7.97-7.98 (d, J=4.0 Hz, 2H), 7.17-7.18 (d, J=4.0 Hz, 2H).

Synthesis of M4



M2 (2.40 g, 4.40 mmol), bis(pinacolato)diboron (3.80 g, 14.60 mmol), CH_3COOK (1.20 g, 13.20 mmol), Pd(dppf)Cl_2 204 mg) and 70ml dry DMF were heated at 90 ^oC for 24 h under N_2 atmosphere. After cooling to room temperature, the mixture was poured into water and extracted with CH_2Cl_2. The organic phase was washed with water three times then the organic phase was collected and dried with anhydrous Na_2SO_4. The solvent was removed under vacuum, and then the residue was purified by column chromatography (petroleum ether/CH_2Cl_2 1:1) to give M4 (1.55 g, 50%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 2H), 8.04-8.06 (d, J=8.0 Hz, 2H), 7.79-7.81 (d, J=8.0 Hz, 2H).

Synthesis of Triazine-Ph-CPP.

A mixture of compound M1 (0.352 g, 0.51 mmol), compound M2 (0.287 g, 0.76 mmol) and $Pd(PPh_3)_4$ (0.029 g, 0.025 mmol) was dissolved in 20 mL DMF. After K_2CO_3 aqueous solution (2.0 M, 1.1 mL) was added, the mixture was degassed by freeze-pump-thaw cycles and filled back with Ar. Then the reaction mixture was stirred for 3 days at 150 °C. After cooling to room temperature, the reaction mixture was poured into deionized water (50 mL). The solid product was collected, and sequentially washed with water, acetone, dichloromethane, tetrahydrofuran, dried under vacuum at 120 °C overnight. Yield, 75%. Anal. Calcd for $(C_{78}H_{42}N_6O_6S_3)_n$ (%): C, 74.64; H, 3.34; N, 6.69. Found：C, 72.96; H, 4.94; N, 4.90. The residual Pd content was found to be 0.40 wt % from ICP-MS.

Synthesis of Triazine-Th-CPP.

Triazine-Th-CPP was synthesized and purified according to the similar procedure of Triazine-Ph-CPP. Yield, 55%. Anal. Calcd for $(C_{66}H_{30}N_6O_6S_9)_n$ (%): C, 61.38; H, 2.34; N, 6.51. Found : C, 55.58; H, 2.96; N,7.21. The residual Pd content was found to be 2.20 wt% from ICP-MS.

Hydrogen Evolution Experiments.

All photocatalytic experiments were performed in a reaction cell, and the reaction temperature was maintained at 5 °C by a water-cooling system. For Triazine- Ph-CPP, photocatalyst is dispersed in 7 mL triethanolamine (TEOA) and 15 mL water. For Triazine- Th-CPP, photocatalyst is dispersed in 22 mL water with 220 mg ascorbic acid. The suspended solution was ultrasonicated several hours. After evacuated the air of the reaction system, the reaction suspension was irradiated by a 300 W Xe lamp at 17A current (Beijing Perfect Light Co.) with stirring. The amount of hydrogen was measured with an online gas chromatography (TCD detector, N_2 carrier).

The apparent quantum yield measurement

The apparent quantum yield (AQY) was measured at a distance 10 cm from the light source with monochromatic light at wavelength of 365 nm, 420 nm, 450 nm and 500 nm, and their intensities were 5.67, 28.28, 37.02, 38.32 mW/cm^2, respectively. The top illumination surface was controlled as 9.61 cm^2. In general, an aqueous suspension of Triazine-Ph-CPP (32 mg) and triethanolamine was illuminated for six hours, and the amount of the hydrogen was determined by gas chromatography. AQY was calculated according to the following equation:

$$\eta=2\times\frac{N}{N_0}\times 100\% = 2\times\frac{M\times N_A\times h\times c}{S\times P\times t\times\lambda}\times 100\%$$

Where, M is the amount of H_2 (mol), N_A is Avogadro constant (6.022×10^{23}/mol), h is the Planck constant (6.626×10^{-34} J.s), c is the speed of light (3×10^{8} m/s), S is the irradiation area (cm^2), P is the intensity of light (mW/cm^2), t is the illumination time (s), λ is the wavelength of the monochromatic light (m).

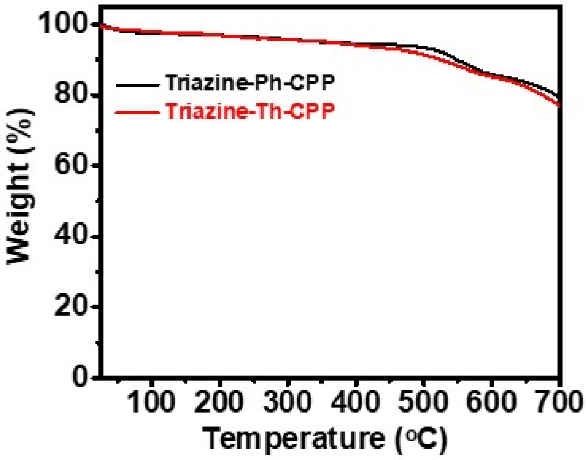


Fig. S1 TGA curves of Triazine-Ph-CPP and Triazine-Th-CPP.

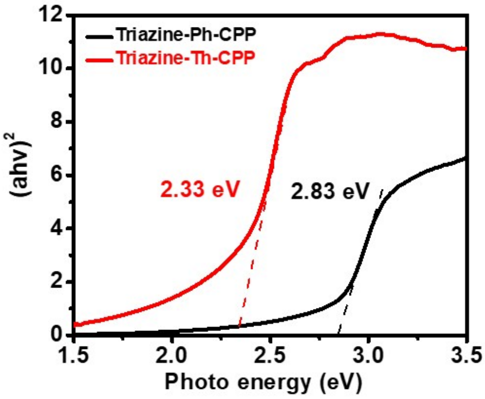


Fig. S2 Bandgaps of Triazine-Ph-CPP and Triazine-Th-CPP calculated by Tauc-plot.

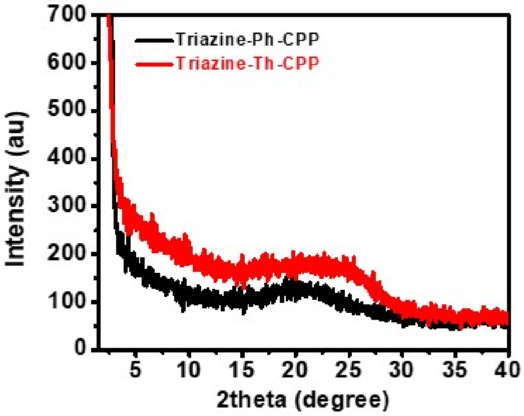


Fig. S3 Powder XRD patterns of Triazine-Ph-CPP and Triazine-Th-CPP.

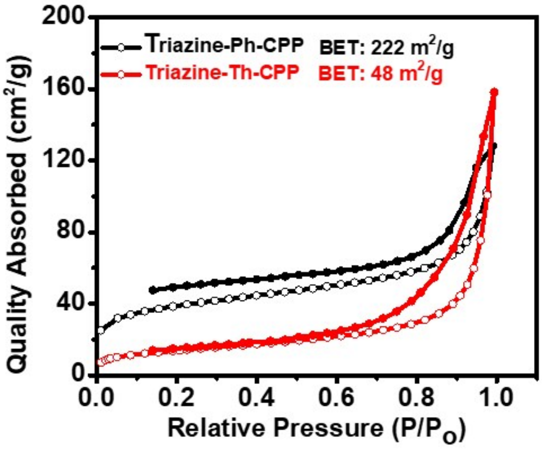


Fig. S4 Nitrogen adsorption/desorption isotherms of Triazine-Ph-CPP and Triazine-Th-CPP.

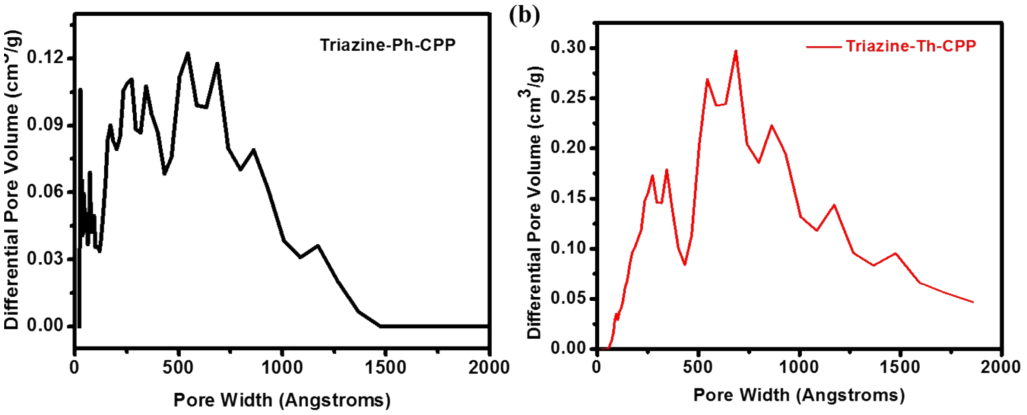


Fig. S5 Pore size distribution curves for Triazine-Ph-CPP and Triazine-Th-CPP.

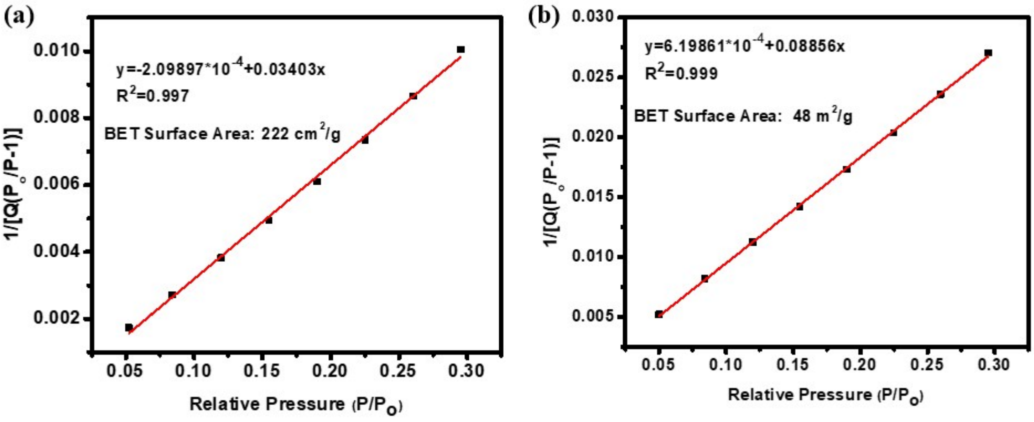


Fig. S6 BET surface area plots for (a)Triazine-Ph-CPP and (b)Triazine-Th-CPP.

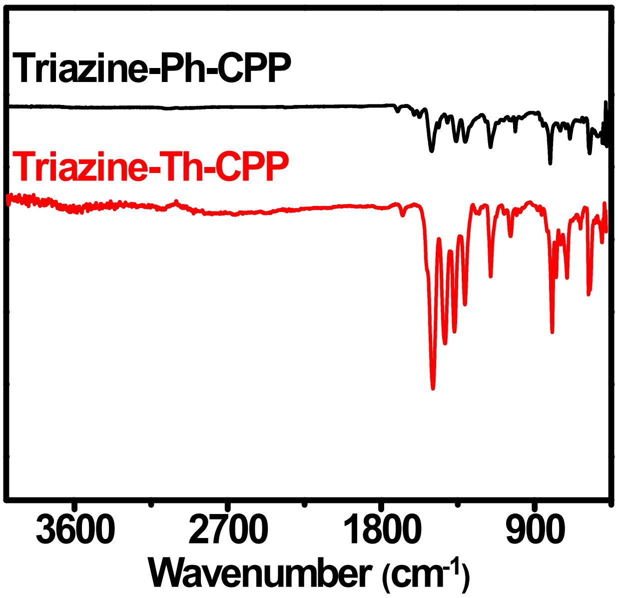


Fig. S7 IR spectra of Triazine-Ph-CPP and Triazine-Th-CPP.

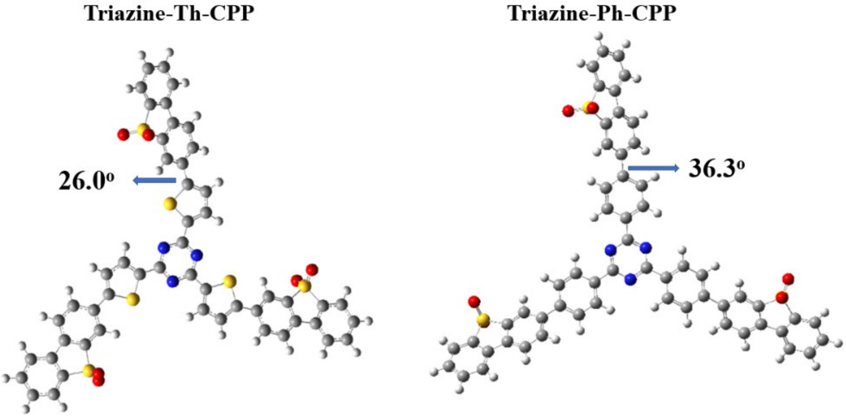


Fig. S8 DFT geometry optimizations and the dihedral angles of Triazine-Th-CPP and Triazine-Ph-CPP.

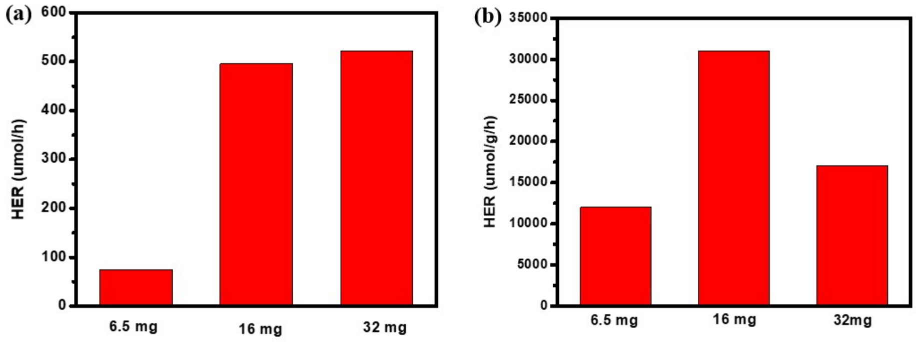


Fig. S9 HER of Triazine-Ph-CPP with different units (a) µmol/h and (b) µmol/g h

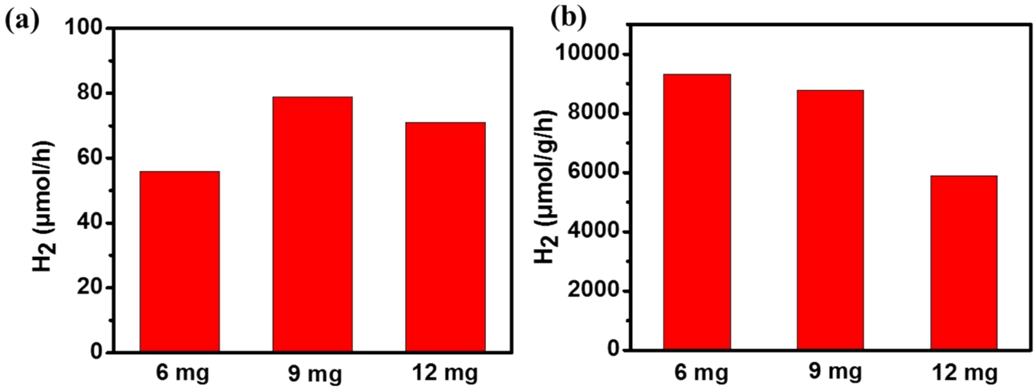


Fig. S10 HER of Triazine-Th-CPP with different units (a) µmol/h and (b) µmol/g h

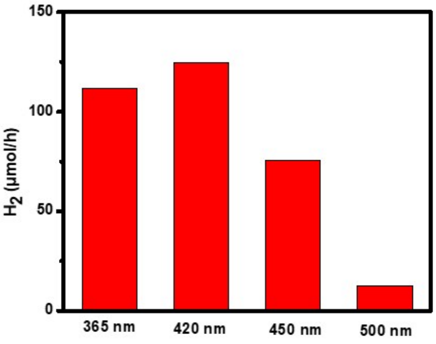


Fig. S11 Wavelength-specific hydrogen production of Triazine-Ph-CPP (32 mg)

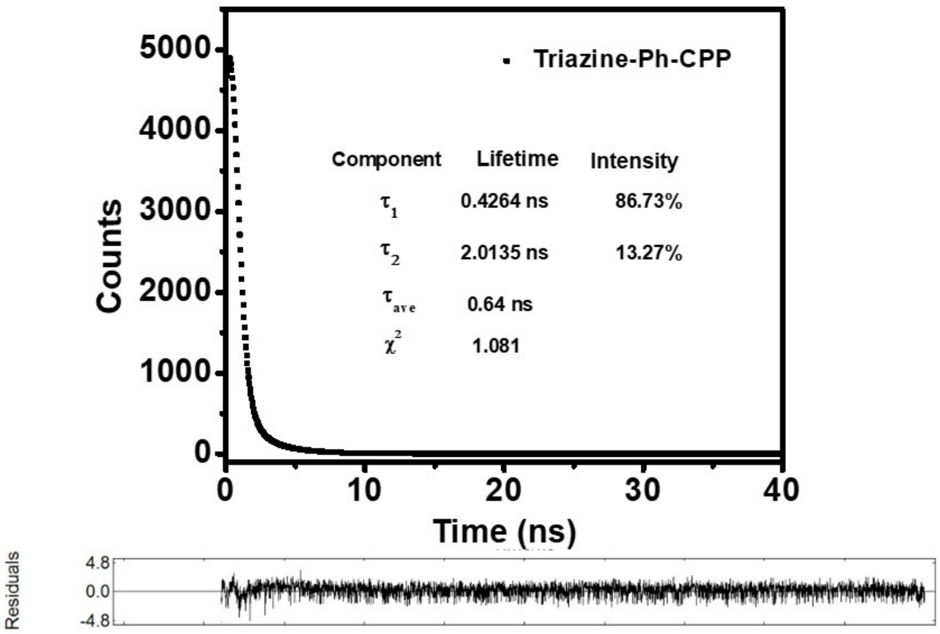


Fig. S12 Fitting curve of fluorescence life-time for Triazine-Ph-CPP

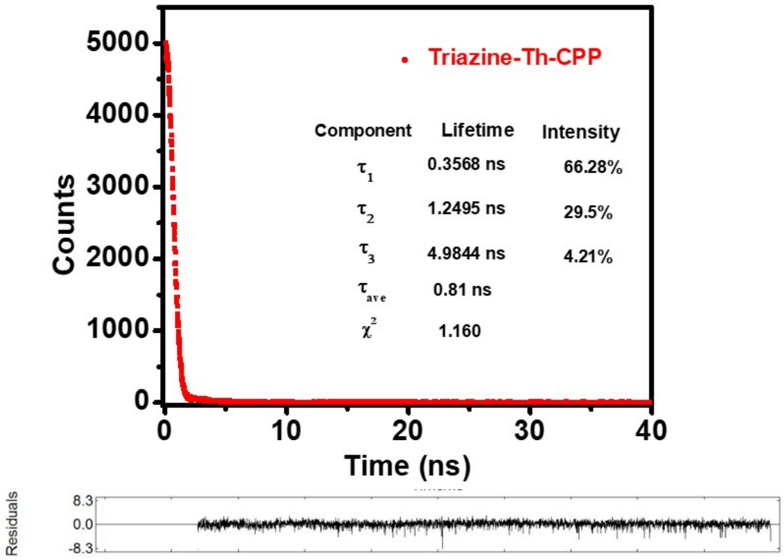


Fig. S13 Fitting curve of fluorescence life-time for Triazine-Th-CPP.

Table. S1 Photocatalytic performance of the reported organic photocatalysts.

Photocatalyst	Photocatalytic conditions	HER (μmol h^{-1})	AQY(%)	Reference
g-CN-1	50 mg, 3 wt.% Pt 10 vol% TEOA, λ > 420 nm	73.6	50.7 (405 nm)	ACS Catal. 2016, 6, 3921-3931
ter-CTF-0.7	50 mg, ~2 wt% Pt 10 vol% TEOA λ > 420 nm	966	22.8% (420 nm)	ACS Catal. 2019, 9, 9438−9445
N_3-COF	5mg, 0.86wt%Pt 1 vol% TEOA λ > 420 nm	9	0.45% (450 nm)	Nat. Commun, 2015, 6, 8508-8516.
PyDOBT-1	, 50 mg, 3wt% Pt, 10 vol% TEOA λ > 420 nm	426	6.1% (400 nm)	Macromolecules. 2018, 51, 9502-9508.
FS-COF	5 mg, 0.038 wt% Pt Ascorbic acid λ > 420 nm,	505	3.2% (420 nm)	Nat. Chem. 2018, 10, 1180-1189
PCP4e	3.5 mg 20 vol% TEA λ > 420 nm	6.65	0.34 (350 nm)	J. Am. Chem. Soc. 2016, 138, 7681-7686.
CTF-BT/Th	50 mg, 3 wt.% Pt 10 vol% TEOA λ > 420 nm	330	7.3% (420 nm)	Angew. Chem. Int. Ed. 2019, 58, 8676-8680
DBTD-CMP1	50 mg, 3wt% Pt, 10 vol% TEOA λ > 300 nm	460	3.3% (400 nm)	ACS Catal. 2018, 8, 8590−8596
Triazine-Ph-CPP	32 mg, 30 vol% TEOA λ > 300 nm	521	61.5% (365 nm) 7.7% (420 nm)	This work

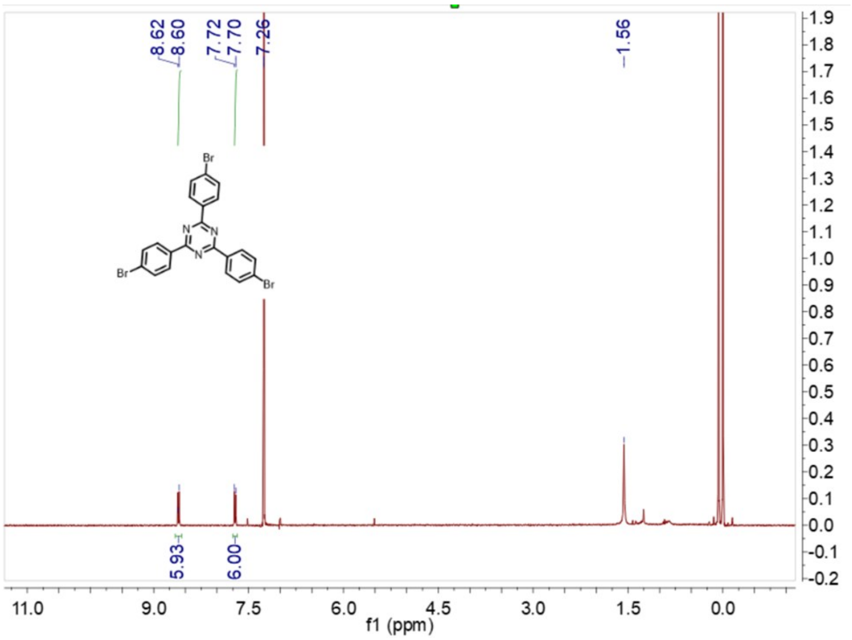


Figure. S14 ^{1}H NMR of compound 2.

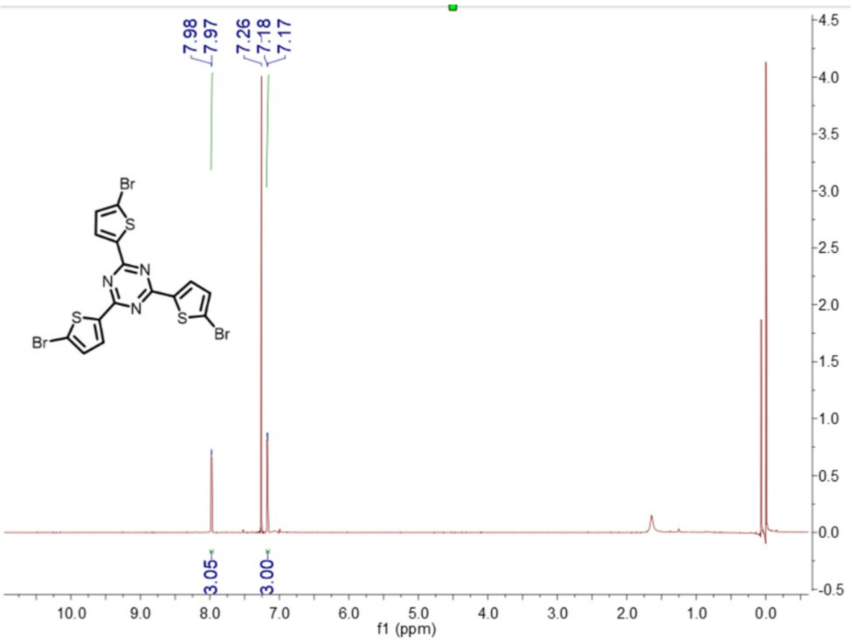


Figure. S15 ^{1}H NMR of compound M3.

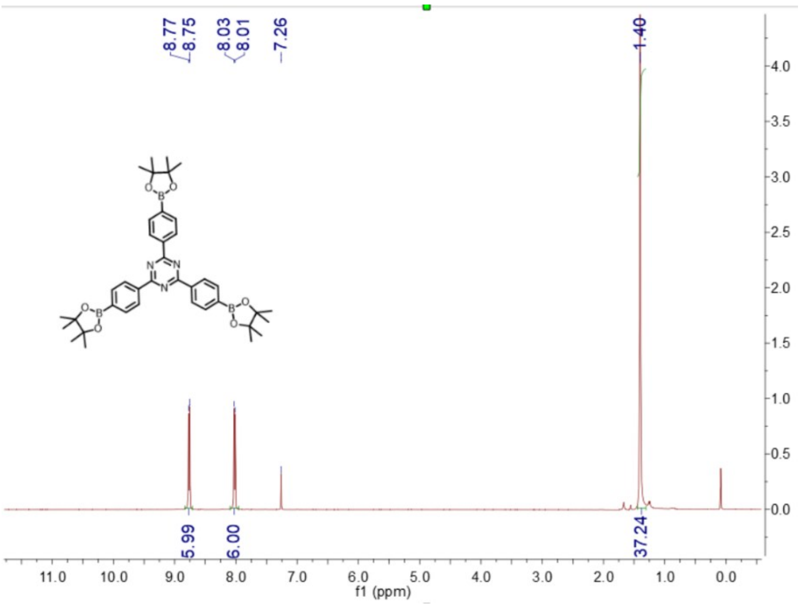


Figure. S16 ^{1}H NMR of compound M1.

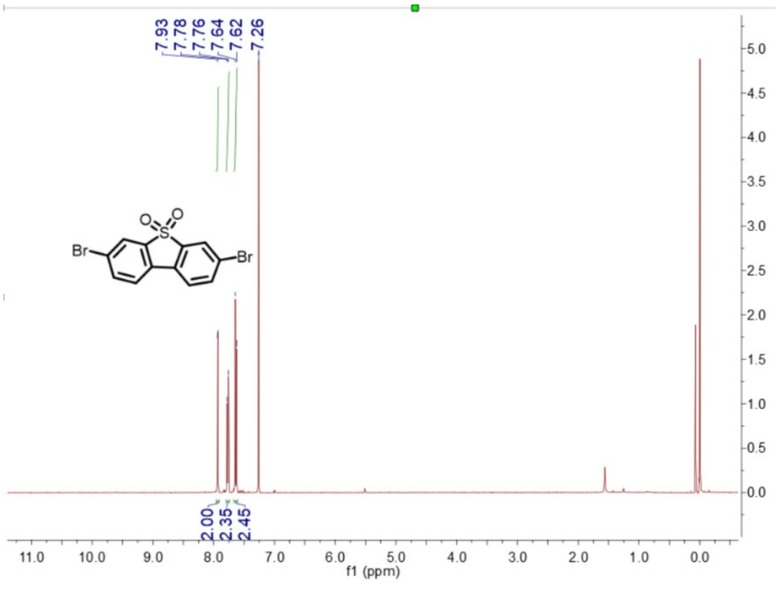


Figure. S17 ^{1}H NMR of compound M2.

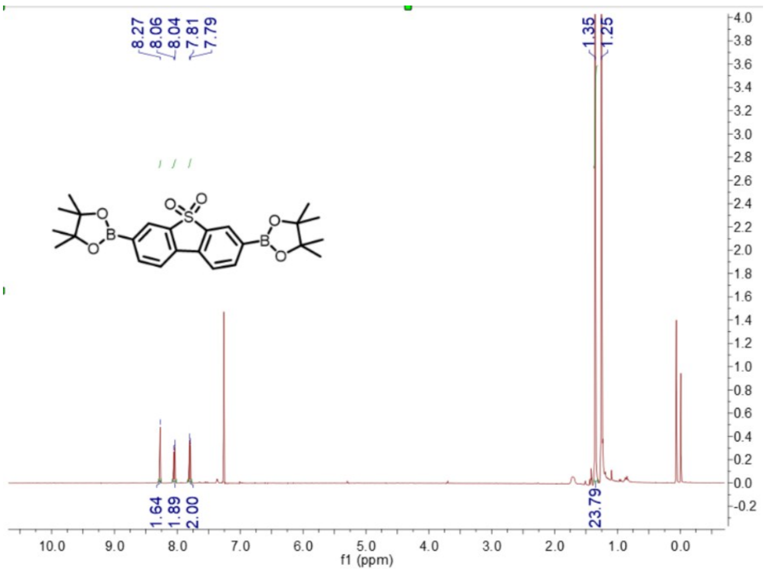


Figure. S18 ^{1}H NMR of compound M4.