Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.
This journal is © The Royal Society of Chemistry 2020

Supplementary information

Design and synthesis of phenylphosphine oxide-based polymer photocatalysts for highly efficient visible-light-driven hydrogen evolution

Wen-Hsin Wang,[‡] Li-Yu Ting,[‡] Jayachandran Jayakumar, Chih-Li Chang, Wei-Cheng Lin, Chih-Chia Chung, Mohamed Hammad Elsayed, Chia-Yeh Lu, Ahmed M. Elewa, and Ho-Hsiu Chou*[a]

[‡]These authors contributed equally

Department of Chemical Engineering, National Tsing Hua University, No. 101, Sec. 2, Kuang-Fu Rd., Hsinchu 30013, Taiwan

E-mail: hhchou@mx.nthu.edu.tw

General methods: All reagents were obtained from commercial suppliers and used without further purification. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di-n-octylfluorene (F-B),[1,2] were synthesized using previous literature procedures. All reactions were performed under a N_2 atmosphere using standard Schlenk techniques. UV–vis absorption spectra of the polymers were recorded using a Hitachi U-3300 spectrophotometer. Fluorescence spectra of the polymers were recorded using a Hitachi F-7000 spectrophotometer. TGA of the polymers was performed under N_2 using a TA Q600 instrument over the temperature range of 50–650 °C (heating rate: 10 °C min^{-1}). BET surface areas of polymers were measured using Micromeritics ASAP2020. The hydrodynamic diameter of the polymer was measured on a Zetasizer Nano ZS90 (Malvern Instruments Nordic AB). X-ray photoelectron spectra were collected using a ULVAC-PHI PHI 5000 Versaprobe II chemical analysis electron spectrometer (ESCA). Powder X-ray diffraction (PXRD) measurements were performed on a Bruker Instruments D2-Phaser. ^1H and ^{31}P NMR spectra were measured using a Bruker Avance 500 MHz NMR spectrometer. The molecular weights of the polymers were determined using GPC and polystyrene standards; the mobile phase was tetrahydrofuran (flow rate: 1 mL min^{-1}) at 40 °C. The energy levels of the HOMOs were measured using a photoelectron spectrometer (model AC-II). Optical bandgaps (E_g) were calculated from the onsets of the absorption spectra. The energy levels of the LUMOs were calculated by subtracting the E_g from the HOMO energy levels. Water for the H_2 evolution experiments was purified using an ELGA LabWater system. Absolute quantum yields (AQYs) were recorded using the Wrighton–Ginley–Morse method[3] and was determined under the same catalytic conditions stated above, with the light source is 350 W Xe-lamp with a single wavelength cutoff filter (λ = 420, 460, and 500 nm). Time-resolved transient PL spectra of the polymer photocatalysts were measured on a spectrometer (FLS980, Edinburgh Instruments) with a gated photomultiplier tube. The absorption spectroscopy using a LP980 transient absorption (TA) spectrometer equipped with a pulsed Xe lamp, a standard PMT-LP detector, and an ICCD detector was employed for the measurements. The molecular geometries of the polymers were optimized, and their orbital energies and charge distributions computed using DFT at the and B3LYP/6-31G** (H, C, O, P) levels.[4]

Experimental Section

Synthesis of 3,7-dibromo-5-phenylbenzo[*b*]phosphindole 5-oxide (BPO-Br):[5] To a two-neck reaction bottle (100 mL) containing 4,4'-dibromo-2,2'-diiodobiphenyl (564 mg, 1.0 mmol) in THF (10 mL) was evacuated and degassed under nitrogen for 30 minutes at room temperature. Then, n-Butyl lithium (0.84 mL, 2.1 mmol) was added slowly at -78 °C and stirred for 1 h at the same temperature. To this solution, $PPhCl_2$ (200 mg, 1.1 mmol) was added dropwise and the reaction mixture was allowed to stir for 12 h at room temperature. The organic layer was obtained by extracting with water and ether (3 × 40 mL). The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The un-oxidized compound was obtained by the column chromatography with n-hexane after the condensing. The compound was added with 10 mL DCM, stirred for 12 hours with 10 mL hydrogen peroxide and poured into the separatory funnel for extract the organic layer. 3,7-Dibromo-5-phenyl-5*H*-benzo[*b*]phosphindole 5-oxide was obtained after the condensing by ridding of water with anhydrous magnesium sulfate. (130 mg, 0.3 mmol, combined yield about 30%);^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (dd, *J* = 10 Hz, *J* = 2 Hz, 2H), 7.70 (d, *J* = 10 Hz, 2H), 7.59~7.66 (m, 4H), 7.54 (dt, *J* = 7.5 Hz, *J* = 1Hz, 1H), 7.42 (dt, *J* = 7.5 Hz, *J* = 1 Hz, 2H); ^{31}P NMR (202 MHz, $CDCl_3$, 295 K): δ 31.77 (s, 1P); **HRMS** (EI^+) calcd for $C_{18}H_{11}Br_2OP$ 433.8894, found 433.8887 and their another isomer 431.8913.

General procedure for Suzuki–Miyaura coupling polymerization: Toluene and water were injected into a sealed tube charged with the monomers, K_2CO_3, and $Pd(PPh_3)_4$. The mixture was degassed by bubbling with N_2 for 30 min and then heated at 120 °C for 72 h. After cooling to room temperature, bromobenzene was added and then the sealed tube was heated at 120 °C for 6 h, followed by the addition of phenylboronic acid and heating at 120 °C for another 6 h. The mixture was cooled to room temperature and poured into MeOH. The yellow-green precipitate was collected through membrane filtration. Purification of the polymer was performed through Soxhlet extraction with MeOH and hexane. Finally, the polymer was dissolved in hot $CHCl_3$, concentrated, and then precipitated in MeOH. The polymer was collected and dried under vacuum.

PFPh: Monomer F-B (2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di-n-octylfluorene, 643 mg, 1 mmol), 1,4-Dibromobenzene (Ph-Br) (236 mg, 1 mmol), Na_2CO_3 (2540 mg, 24 mmol), tetra-n-butylammonium bromide (TBAB, 13.0 mg, 0.04 mmol), $Pd(PPh_3)_4$ (55.0 mg, 0.048 mmol), toluene (40 mL), and water (10 mL) were used for polymerization. GPC (THF): Mw 6.936 kg mol^{-1}.

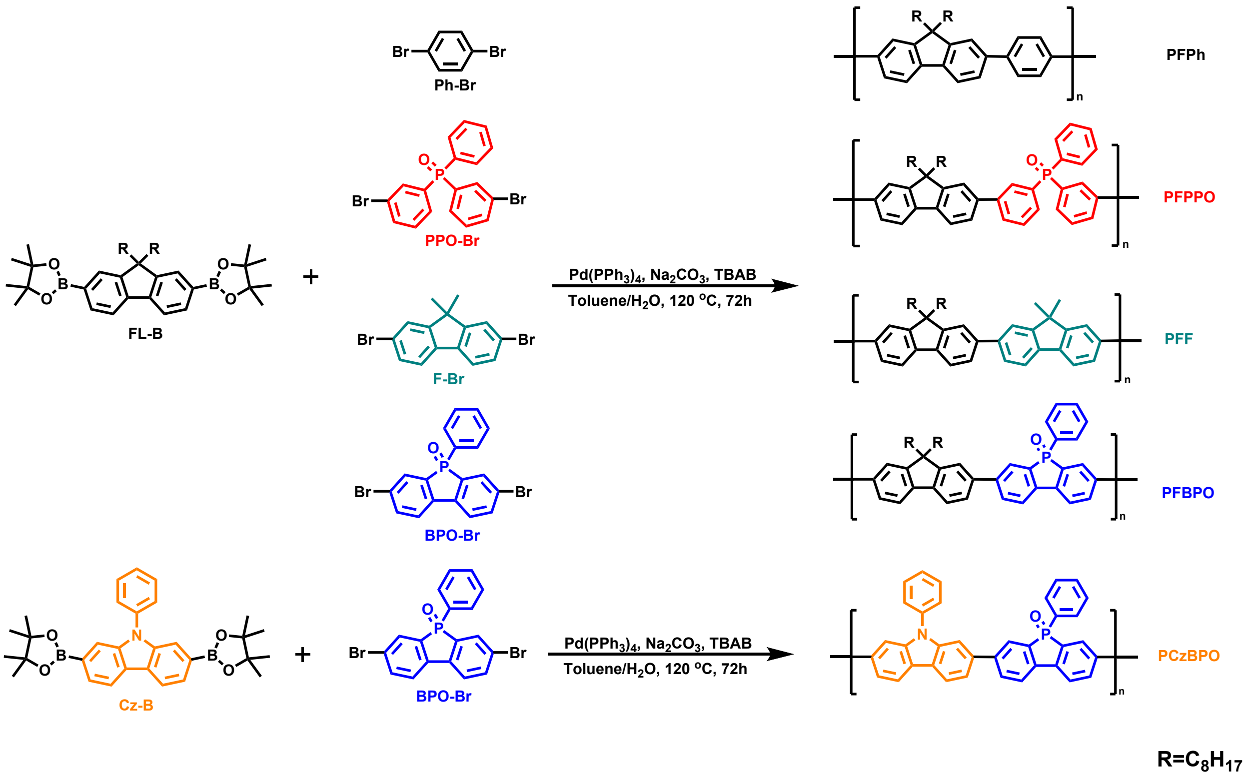
PFPPO: Monomer F-B (2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di-n-octylfluorene, 643 mg, 1 mmol), bis(3-bromophenyl)(phenyl)phosphine oxide (Br-PPO) (436 mg, 1 mmol), Na_2CO_3 (2540 mg, 24 mmol), tetra-n-butylammonium bromide (TBAB, 13.0 mg, 0.04 mmol), $Pd(PPh_3)_4$ (55.0 mg, 0.048 mmol), toluene (40 mL), and water (10 mL) were used for polymerization. GPC (THF): Mw 6.148 kg mol^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.16 (d, *J* = 7.5 Hz), 7.84 (d, *J* = 6 Hz), 7.76~7.79 (m), 7.72 (d, *J* = 7.5 Hz), 7.49~7.58 (m), 7.41~7.45 (m), 7.33~7.36 (m), 1.97 (t, *J* = 8 Hz), 1.33 (s), 0.99~1.24 (m), 0.72~0.75 (m), 0.60 (br); ^{31}P NMR (202 MHz, $CDCl_3$, 295 K): δ 29.77 (s), 28.11(s).

PFF: Monomer F-B (2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di-n-octylfluorene, 643 mg, 1 mmol), 2,7-Dibromo-9,9-dimethylfluorene (F-Br) (352 mg, 1 mmol), Na_2CO_3 (2540 mg, 24 mmol), tetra-n-butylammonium bromide (TBAB, 13.0 mg, 0.04 mmol), $Pd(PPh_3)_4$ (55.0 mg, 0.048 mmol), toluene (40 mL), and water (10 mL) were used for polymerization. GPC (THF): Mw 16.898 kg mol^{-1}.

PFBPO: Monomer F-B (2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di-n-octylfluorene, 643 mg, 1 mmol), 3,7-dibromo-5-phenylbenzo[b]phosphindole 5-oxide (Br-BPO) (434 mg, 1 mmol), Na_2CO_3 (2540 mg, 24 mmol), tetra-n-butylammonium bromide (TBAB, 13.0 mg, 0.04 mmol), $Pd(PPh_3)_4$ (55.0 mg, 0.048 mmol), toluene (40 mL), and water (10 mL) were used for polymerization. GPC (THF): Mw 16.070 kg mol^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, *J* = 10.5 Hz), 7.93 (dd, *J* = 19 Hz, *J* = 7.5 Hz), 7.75~7.81 (m), 7.66 (d, *J* = 7.5 Hz), 7.55~7.60 (m), 7.49~7.52 (m), 7.43~7.47 (m), 1.97~2.03 (m), 1.13 (t, *J* = 6.5 Hz), 0.73~0.78 (m), 0.64 (br); ^{31}P NMR (202 MHz, $CDCl_3$, 295 K) : δ 33.80 (s).

PCzBPO: 9-Phenyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (495 mg, 1 mmol), 3,7-dibromo-5-phenylbenzo[b]phosphindole 5-oxide (Br-BPO) (434 mg, 1 mmol), Na_2CO_3 (2540 mg, 24 mmol), tetra-n-butylammonium bromide (TBAB, 13.0 mg, 0.04 mmol), $Pd(PPh_3)_4$ (55.0 mg, 0.048 mmol), toluene (40 mL), and water (10 mL) were used for polymerization. GPC (THF): Mw 2.467 kg mol^{-1}, Mn 1.429 kg mol^{-1}, polydispersity index = 1.73.

^1H NMR (500 MHz, $CDCl_3$): δ 8.15-8.65 (m), 7.94-7.96 (m), 7.80-7.85 (m), 7.55-7.65 (m), 7.34-7.58 (m). ^{31}P NMR (202 MHz, $CDCl_3$): δ 32.77 (s), 33.45 (s), 33.73 (s).



Scheme S1. General synthetic routes of all polymer photocatalysts.

The AQY measurement and wavelength experiment:[6] The AQY for H_2 evolution was measured using monochromatic visible light (420 ± 1.0 nm) at ambient temperature (27.0 ± 1.0 °C). Depending on the amount of hydrogen gas produced by the photocatalytic reaction over an average of one hour, the AQY was calculated by using the following equations:

$$\eta_{AQY} = \frac{2 \times M \times N_A \times \hbar \times c}{S \times P \times t \times \lambda} \times 100\% \qquad \text{Eq S-1}$$

where M = amount of H_2 (mol), N_A = Avogadro constant (6.022×10^{23} mol^{-1}),

Ђ = Planck constant (6.626×10^{-34} J s), S = irradiation area (cm^2), P = intensity of irradiation light ($W\ cm^{-2}$), t = photoreaction time (s), and λ = wavelength of the monochromatic light (m).

Photocatalytic H_2 evolution: The polymer powder (5 mg) and 10 mL of a mixture of water, TEA, and methanol (1:1:1) were inserted into a reaction glass, which was then closed with a septum. The resulting mixture was ultra-sonicated and degassed completely by Ar bubbling prior to irradiation. The suspension was illuminated with a 350 W Xe lamp (AM1.5, 1000 W m^{-2}, $\lambda > 420$ nm) at a constant temperature of 27.0 ± 1.0 °C under atmospheric pressure and the space between the reaction mixture and the light source was fixed at a specific distance. Hydrogen samples were taken with a gas-tight syringe and injected into a Shimadzu GC-2014 gas chromatograph with Ar as the carrier gas. Hydrogen was detected with a thermal conductivity detector, with standard hydrogen gas of known concentration as a reference. The increase in pressure from the evolved hydrogen is neglected in the calculations.

Photocurrent method; Photocurrent measurements were performed on a Zahner Zennium E workstation equipped with a three-electrode cell including a Pt wire counter electrode, Ag/AgCl as a reference electrode (3M NaCl) and a fluorine-doped tin oxide (FTO) glass as a working electrode. About 5 mg of polymers were dispersed into a tetrahydrofuran solution (1 mL) and sonicate for 1 h. After that, 200 µL of as-prepared suspension was spin-coated on FTO glass with an active area of 6.875 cm^2. Here, 0.5 M Na_2SO_4 aqueous solution was prepared as an electrolyte. 1.5 V constant potential was applied with the 20 s light on-off after a certain time interval to record the photo and dark current under LED light irradiation

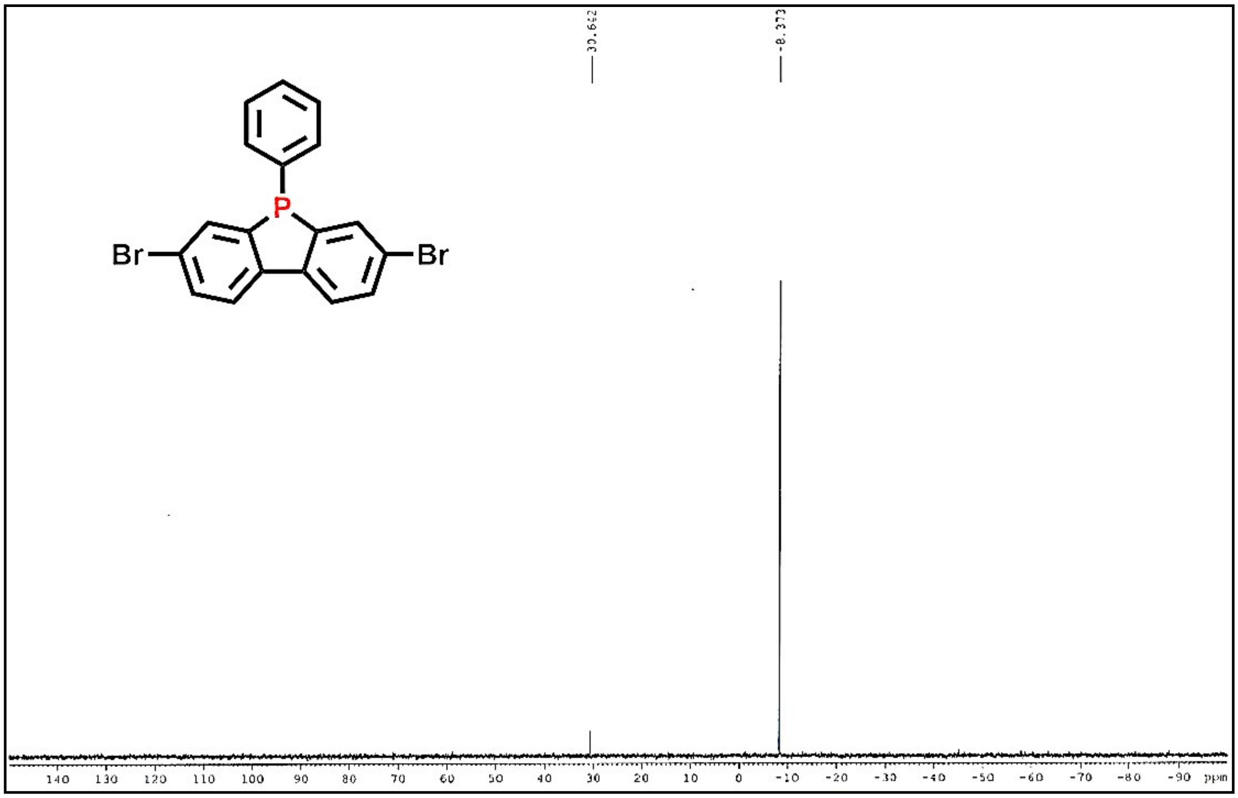
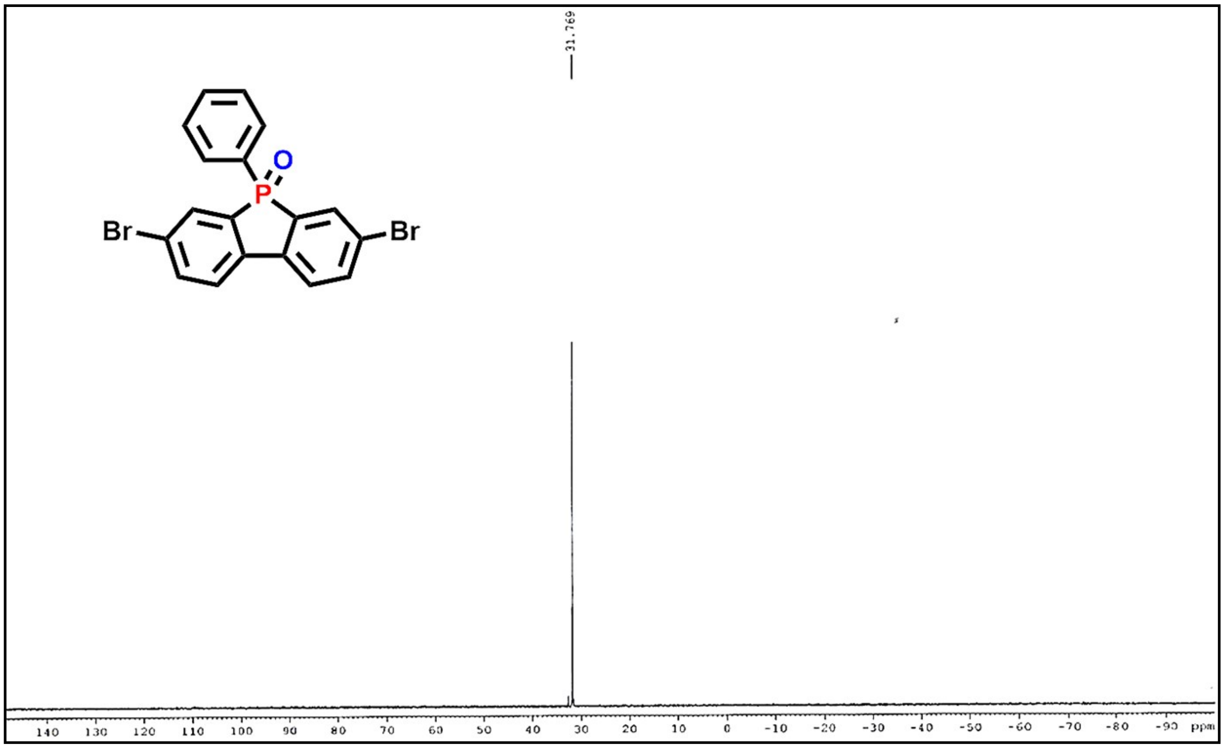
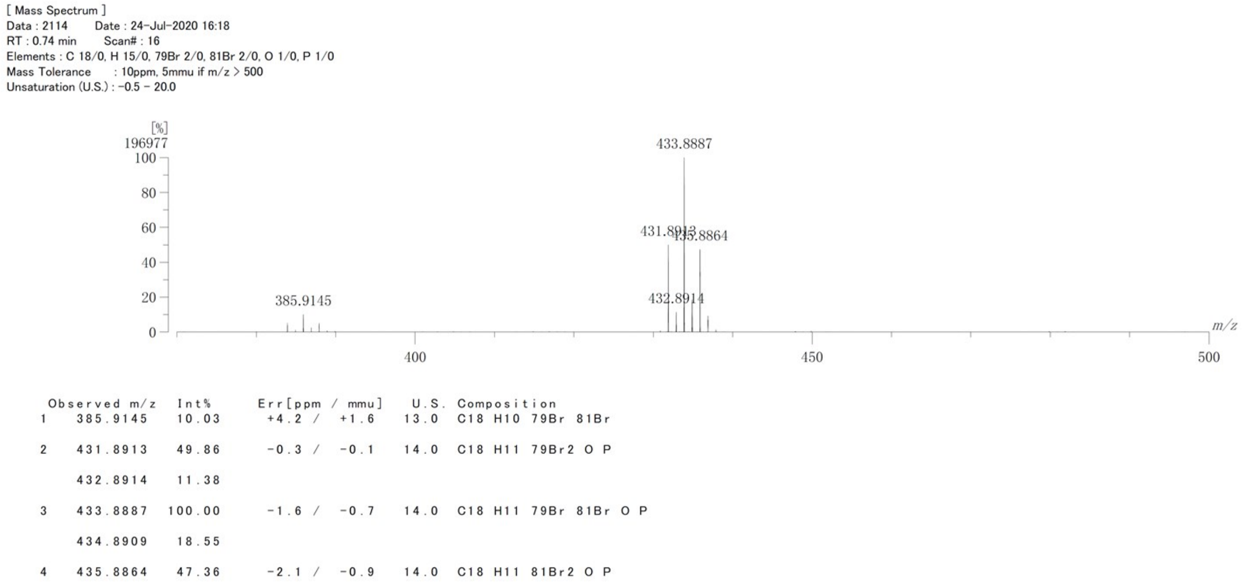


Fig. S1. ^{31}P NMR spectra of BP-Br monomer.





```
[ Mass Spectrum ]
Data : 2114        Date : 24-Jul-2020 16:18
RT : 0.74 min      Scan# : 16
Elements : C 18/0, H 15/0, 79Br 2/0, 81Br 2/0, O 1/0, P 1/0
Mass Tolerance      : 10ppm, 5mmu if m/z > 500
Unsaturation (U.S.) : -0.5 - 20.0
```

```
   Observed m/z   Int%     Err[ppm / mmu]    U.S.  Composition
1    385.9145     10.03     +4.2 /  +1.6     13.0  C18 H10 79Br 81Br

2    431.8913     49.86     -0.3 /  -0.1     14.0  C18 H11 79Br2 O P

     432.8914     11.38

3    433.8887    100.00     -1.6 /  -0.7     14.0  C18 H11 79Br 81Br O P

     434.8909     18.55

4    435.8864     47.36     -2.1 /  -0.9     14.0  C18 H11 81Br2 O P
```

Fig. S2. ^{31}P NMR and mass spectra of BPO-Br monomer.

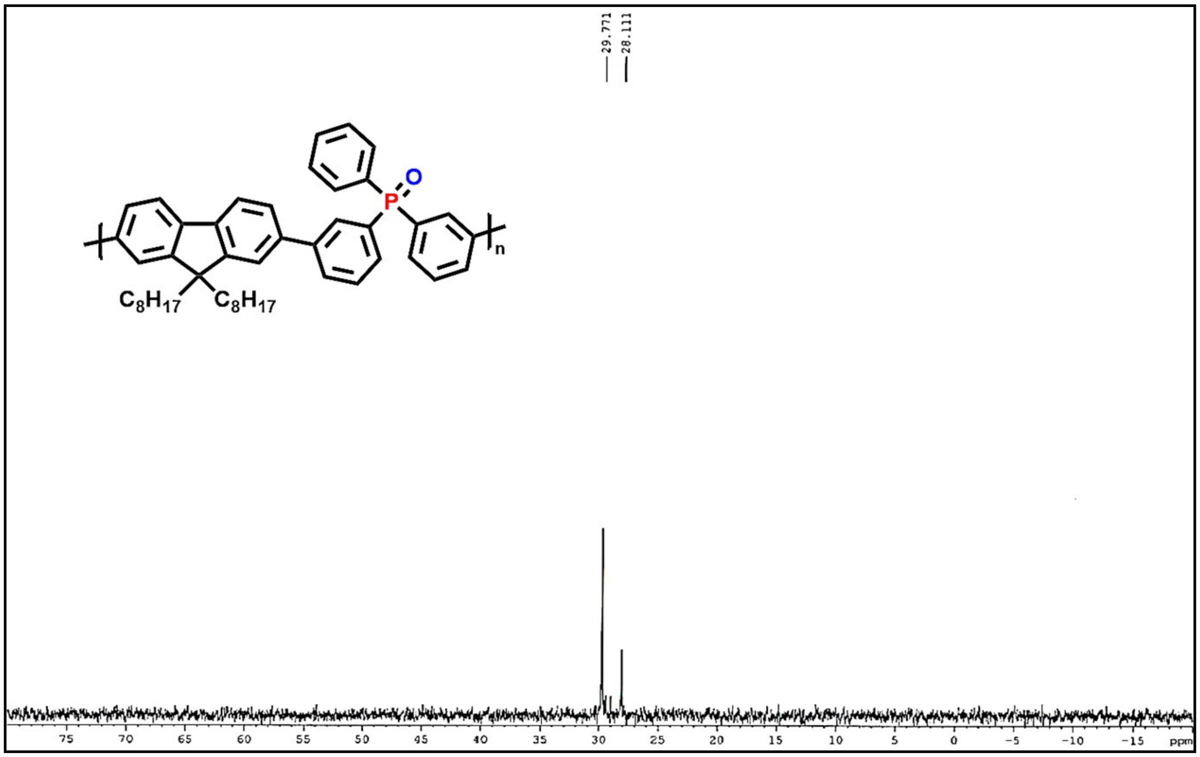


Fig. S3. ^{31}P NMR spectra of PFPPO polymer.

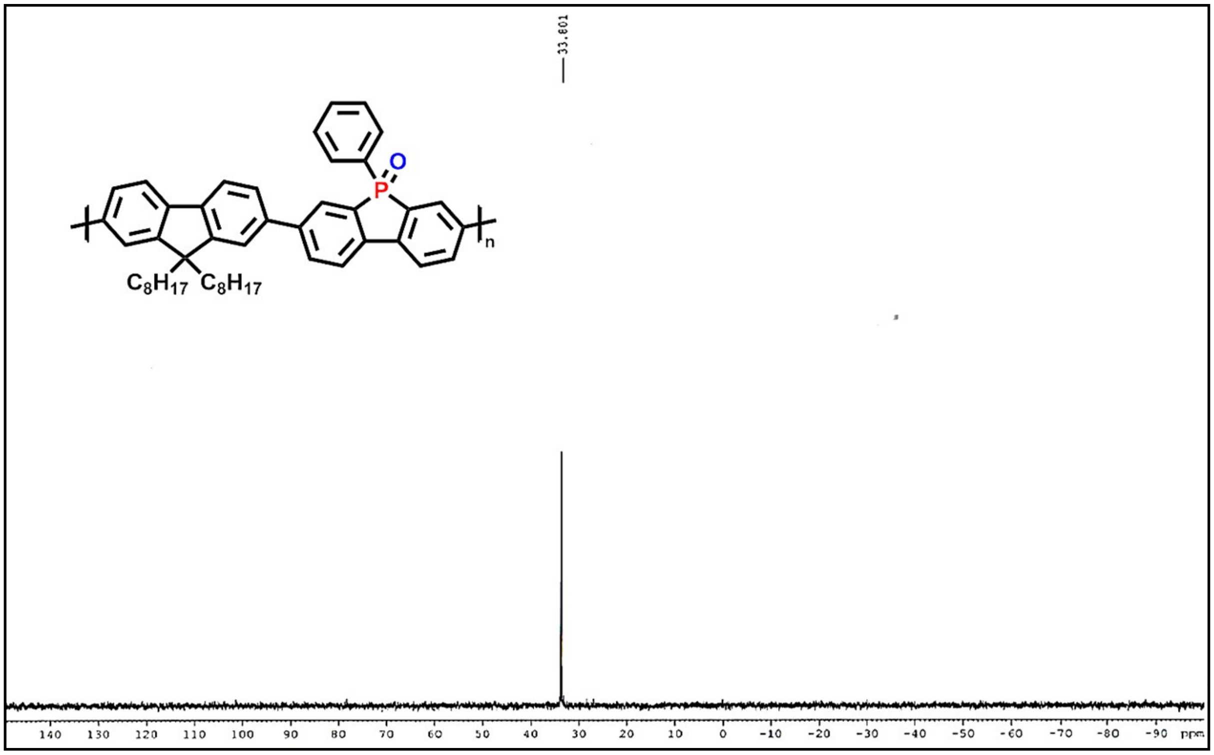


Fig. S4. ^{31}P NMR spectra of PFBPO polymer.

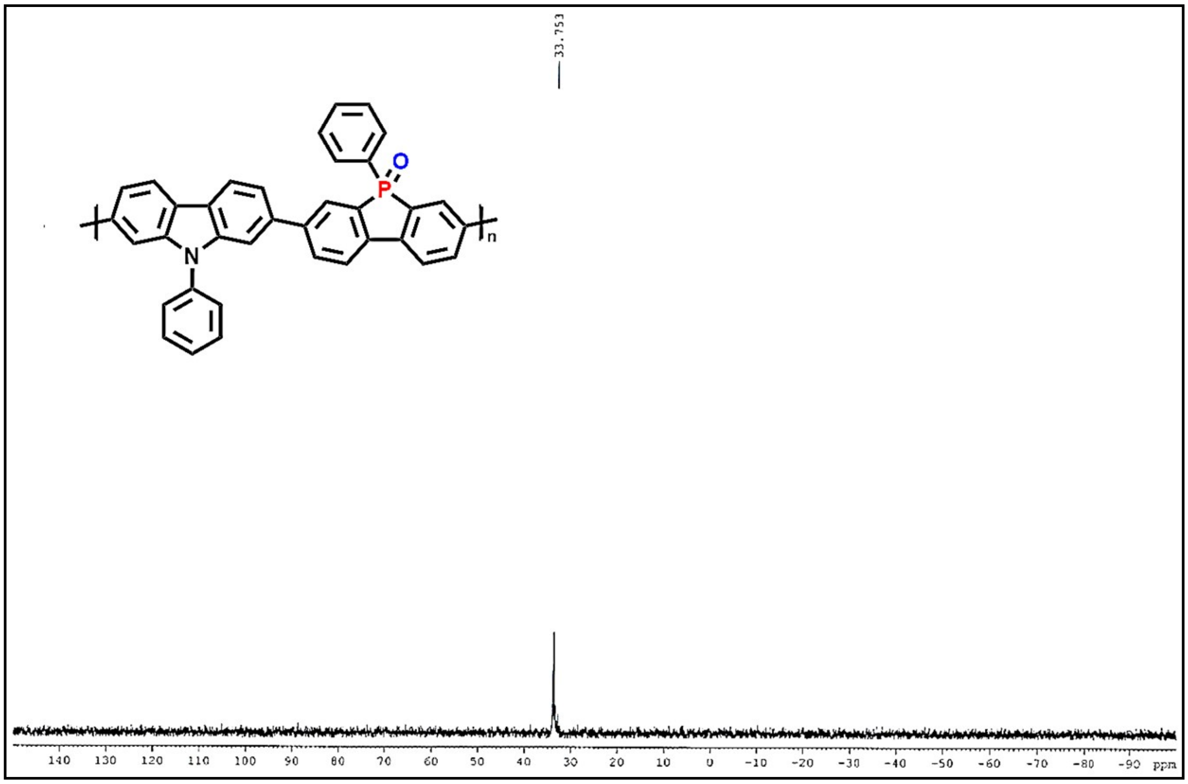


Fig. S5. ^{31}P NMR spectra of PCzBPO polymer.

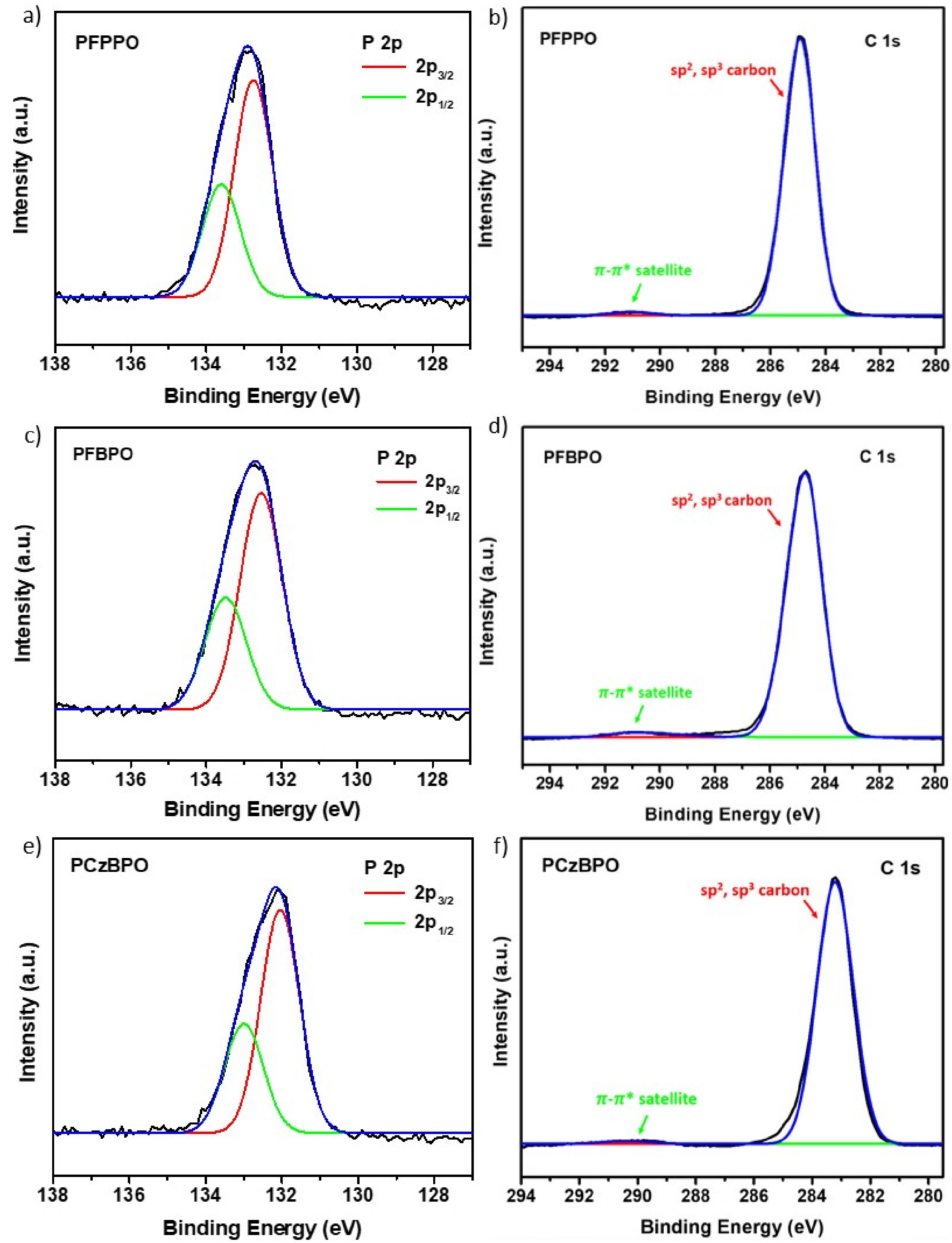


Fig. S6. High-resolution XPS spectra: (a and b) P 2p, C 1s for PFPPO; (c and d) P 2p, C 1s for PFBPO; P 2p, C 1s for PCzBPO.

Table S1. Photophysical, thermal properties and palladium content of polymer photocatalysts.

Photocatalysts	Emisson [nm][a]	M_w [amu][b]	PDI [M_w/M_n][b]	T_d [°C][c]	Pd-content [wt %)][d]
PFPh	413	6936	2.02	353	0.5001
PFPPO	395	6148	1.73	374	0.0395
PFF	418	16898	1.93	403	0.0808
PFBPO	434	16070	1.84	413	0.0374
PCzBPO	438	2467	1.73	525	0.0441

[a]Emission measured in dichloromethane solution (0.05 mg/mL). [b]Molecular weight and PDI were determined by gel permeation chromatography in THF at 40 °C. [c]The decomposition temperature was determined by thermogravimetric analysis. [d]The Pd contents were determined by ICP-OES.

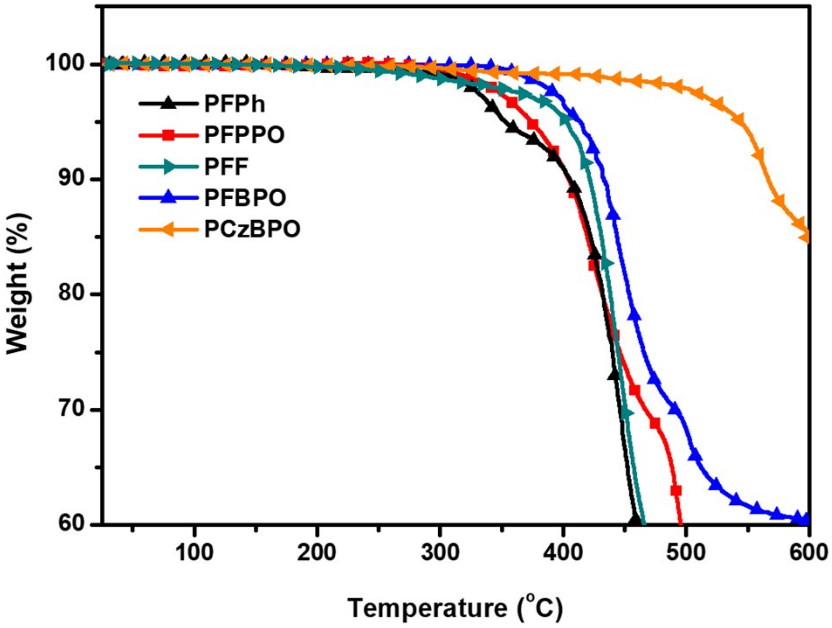


Fig. S7. Thermogravimetric analysis(TGA) of polymer photocatalysts.

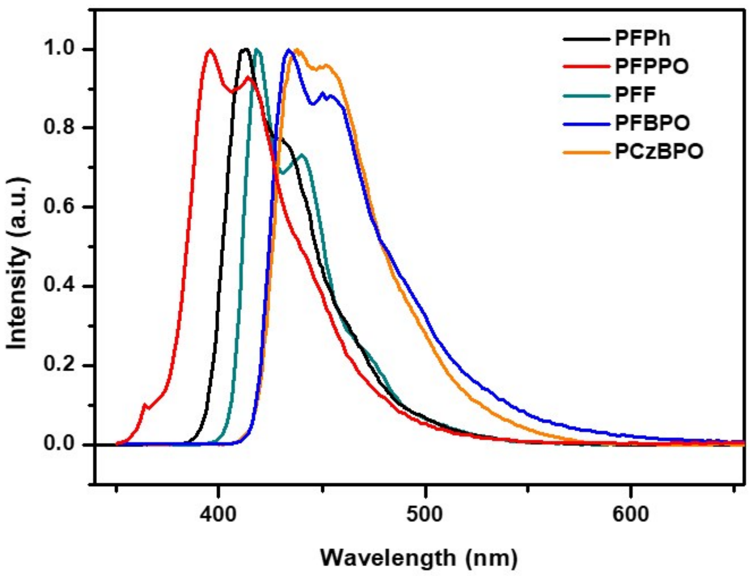


Fig. S8. Emission spectra of copolymers measured in DCM (0.05 mg/mL) at room temperature.

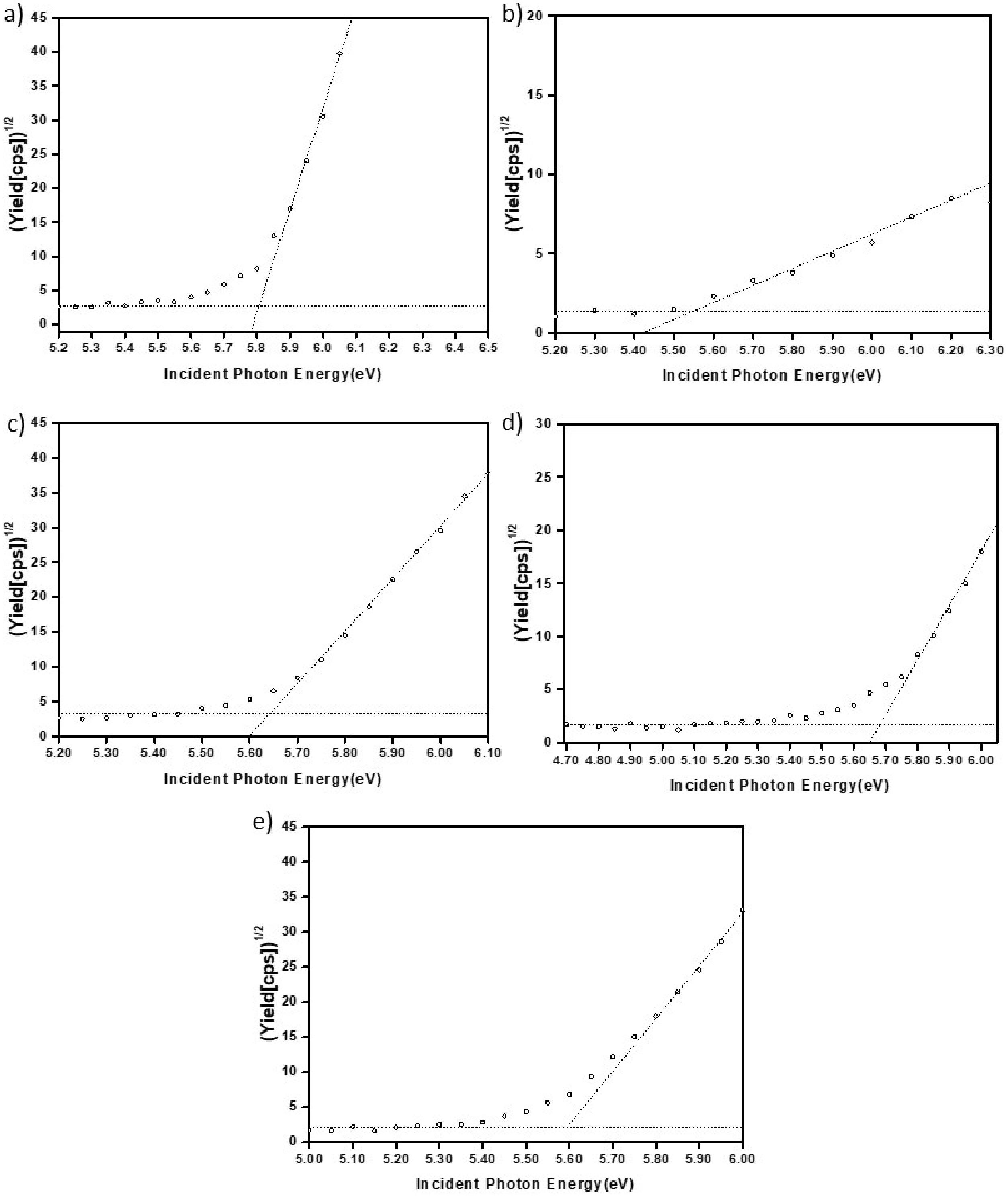


Fig. S9. Calculated HOMOs of polymer photocatalysts a) PFPh, b) PFPPO, c) PFF, d) PFBPO, e) PCzBPO by photoelectron spectroscopy (Model: AC-II).

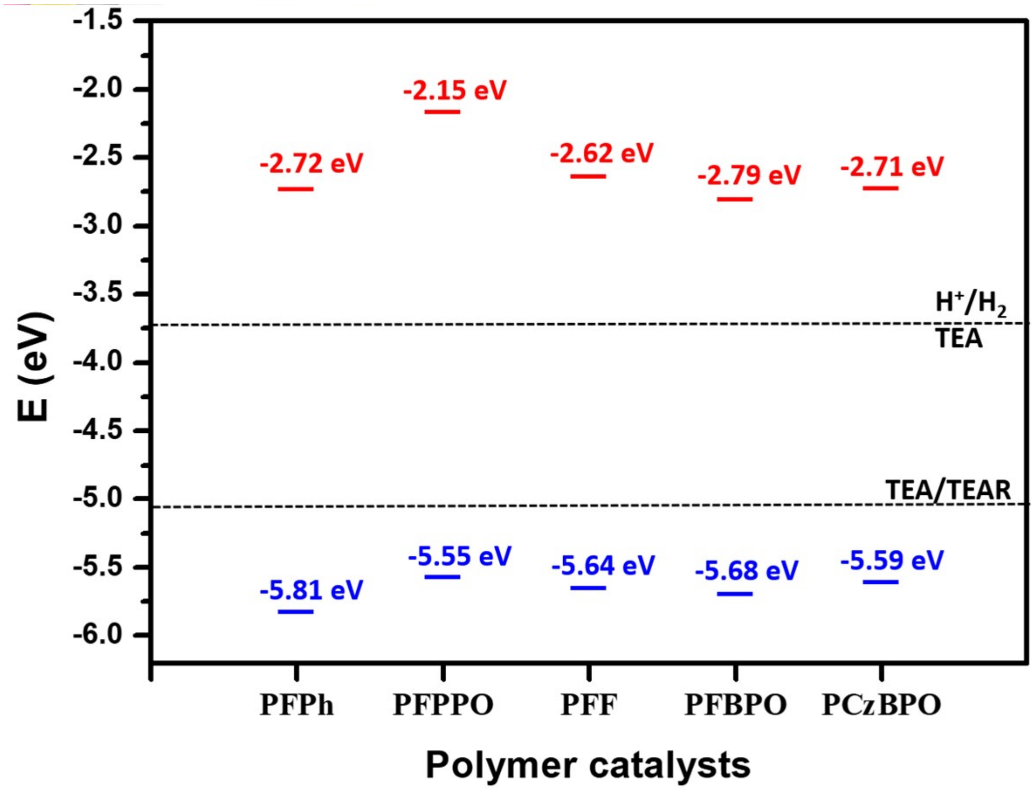
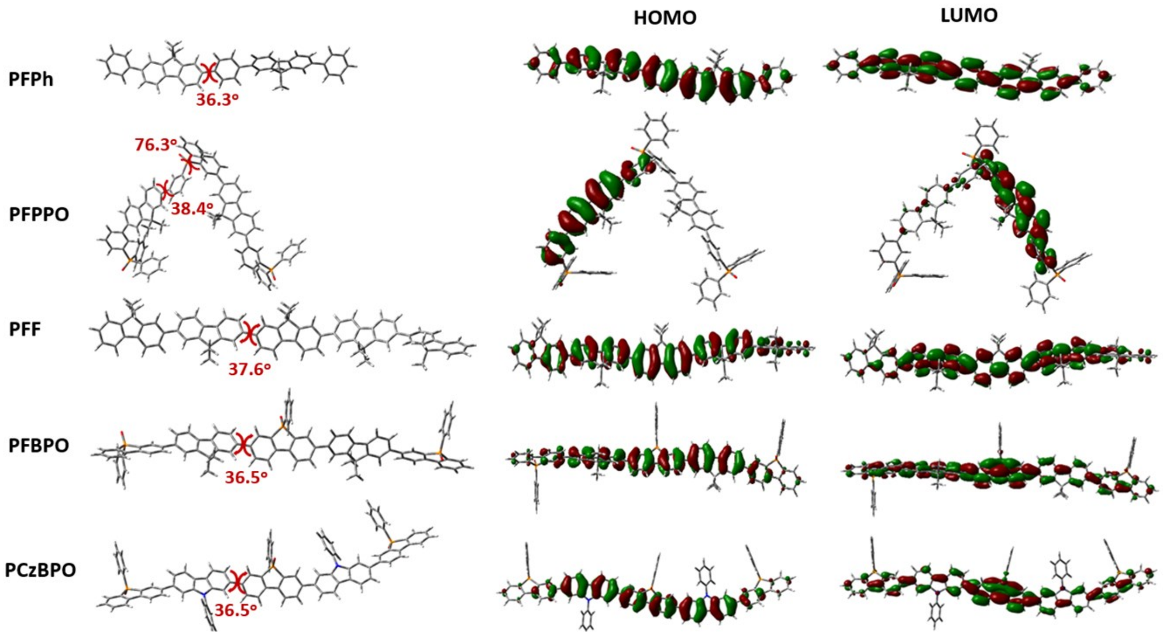
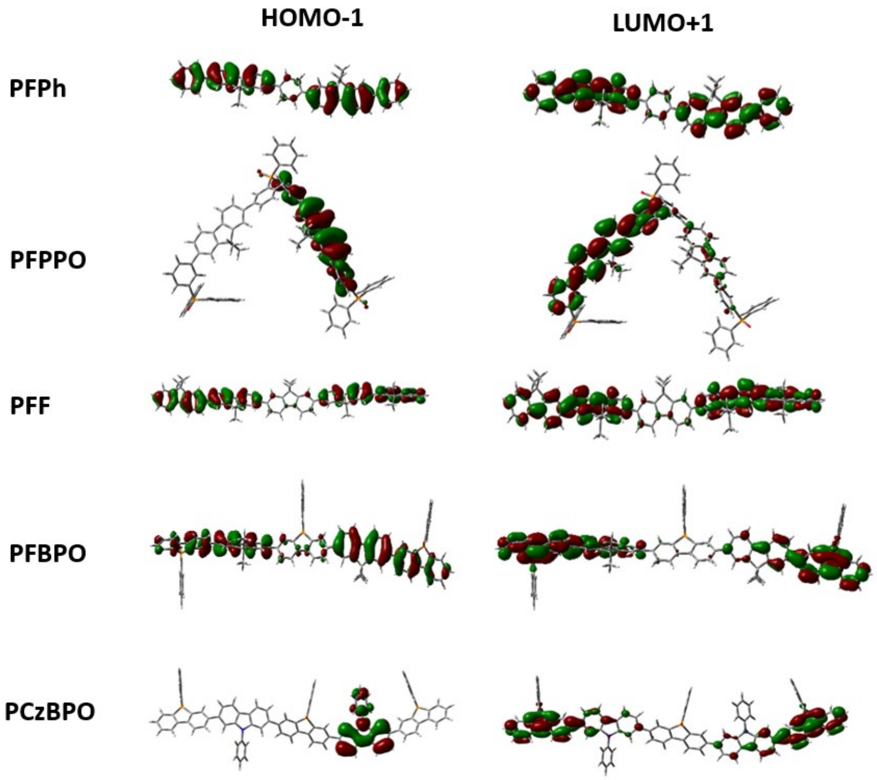


Fig. S10. Energy level diagram for the polymers.


HOMO
LUMO
PFPh
36.3°
PFPPO
76.3°
38.4°
PFF
37.6°
PFBPO
36.5°
PCzBPO
36.5°


HOMO-1
LUMO+1
PFPh
PFPPO
PFF
PFBPO
PCzBPO

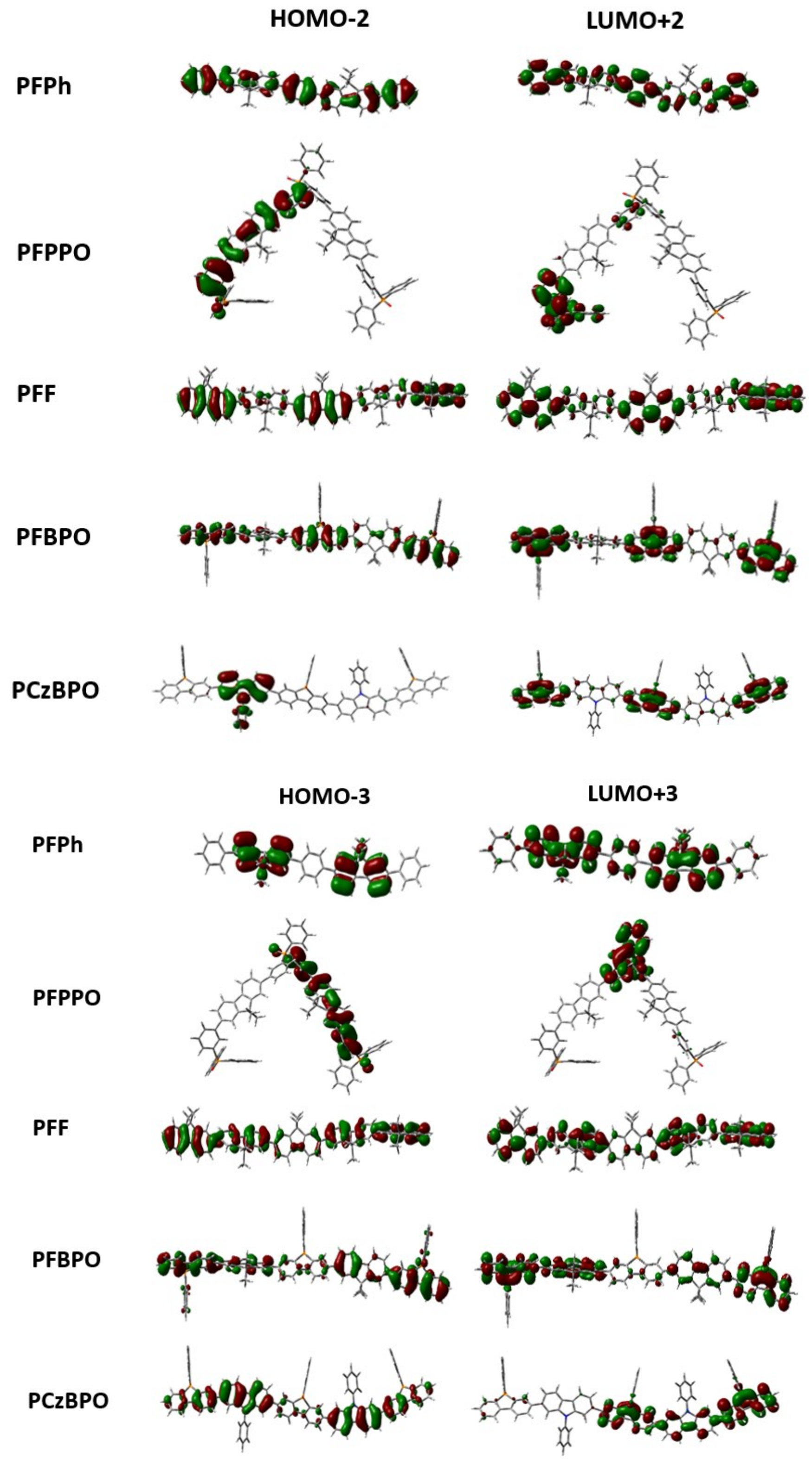


Fig. S11. Optimized structures and the HOMO and LUMO distribution of PFPh, PFPPO, PFF, PFBPO and PCzBPO.

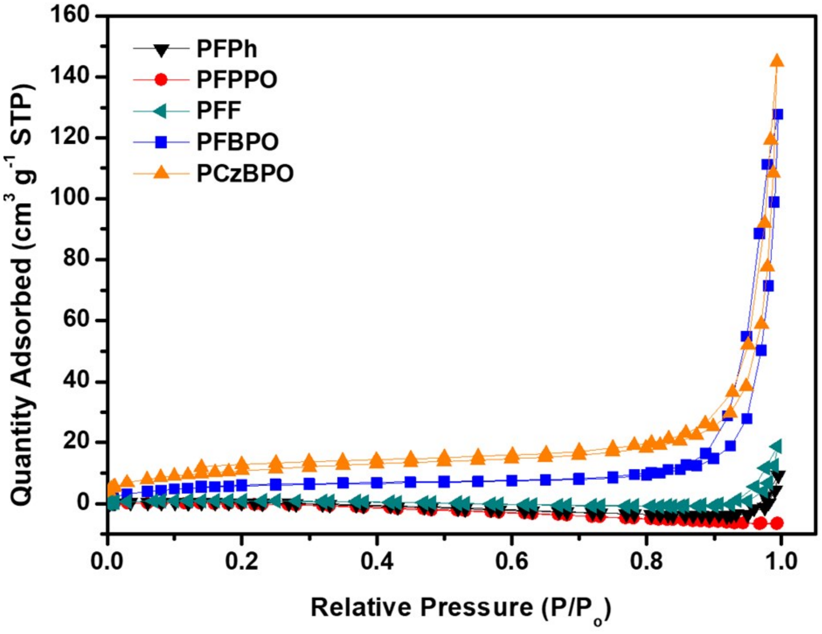


Fig. S12. Nitrogen sorption isotherms for the polymers collected at 77.3 K.

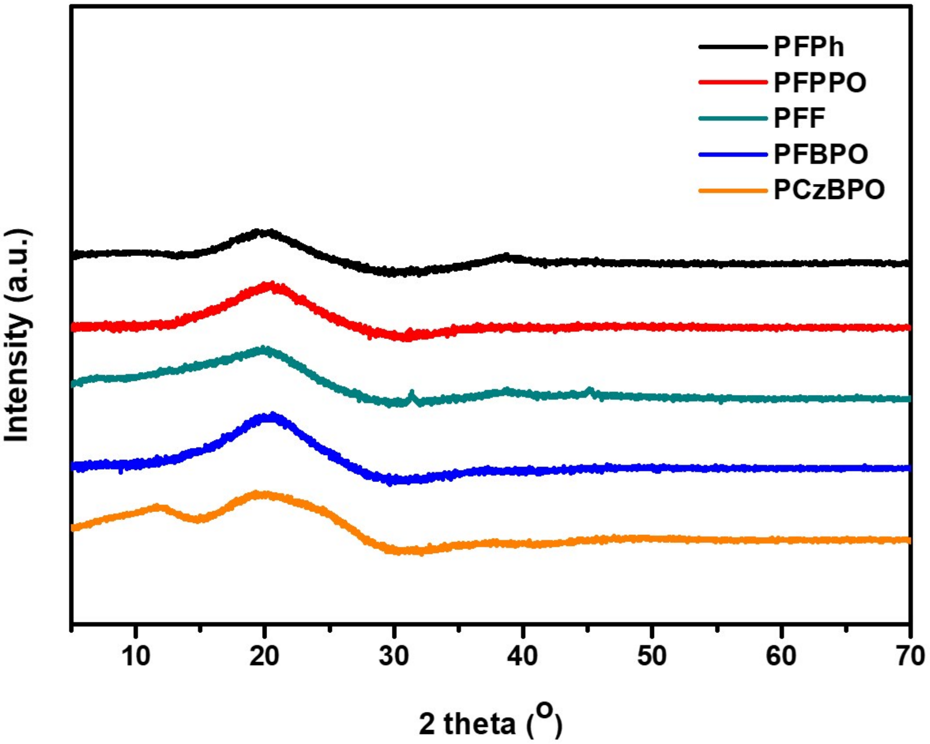


Fig. S13. Powder XRD patterns for the polymers.

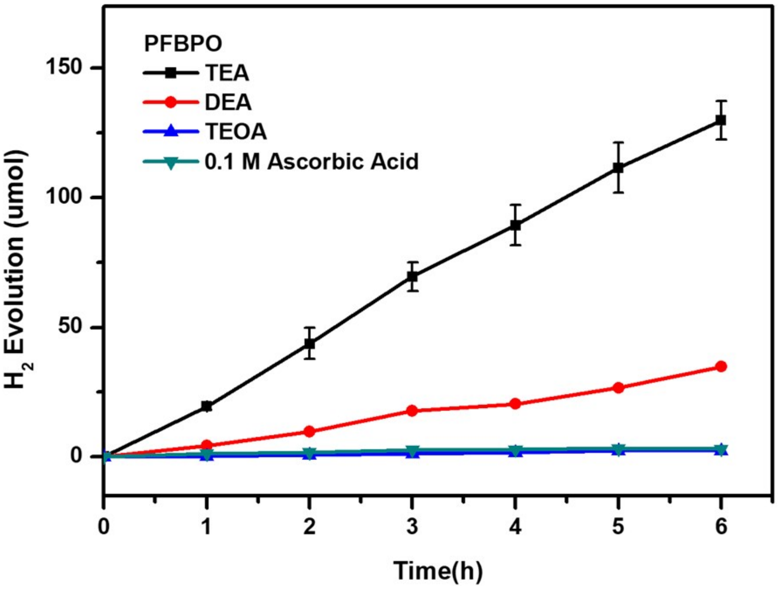


Fig. S14. Optimization of photocatalytic activities for PFBPO using different sacrificial agents.

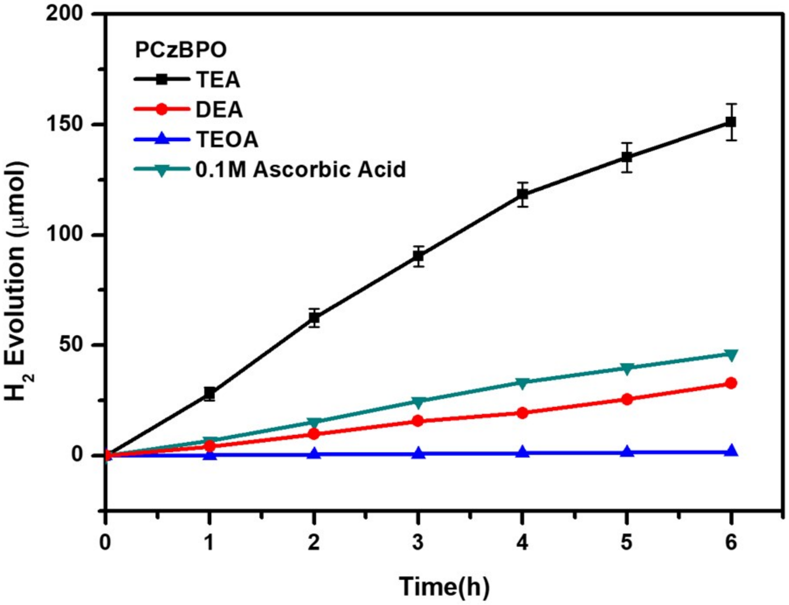


Fig. S15. Optimization of photocatalytic activities for PCzBPO using different sacrificial agents.

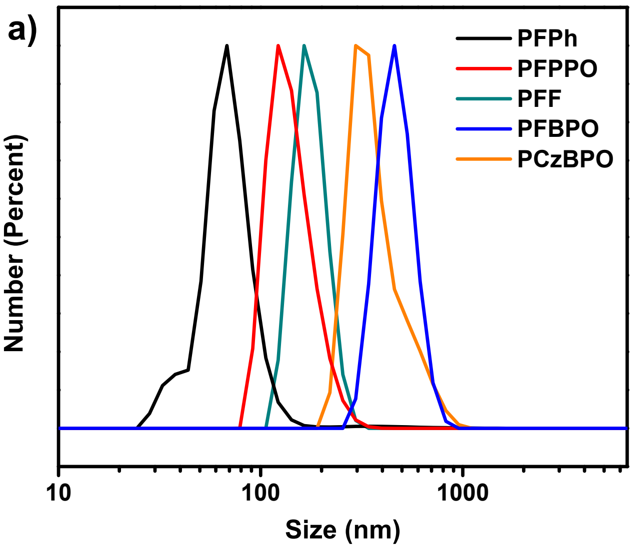


Fig. S16. Hydrodynamic diameter for all polymers are measured by DLS

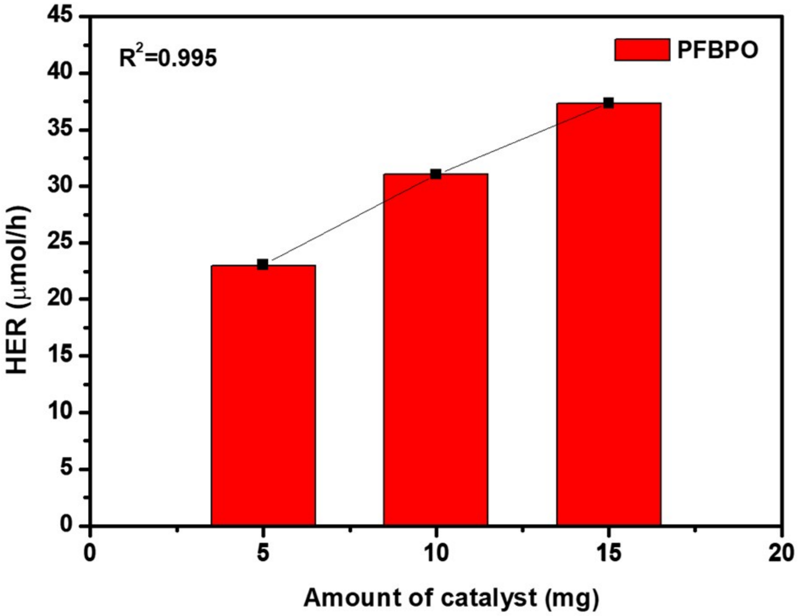
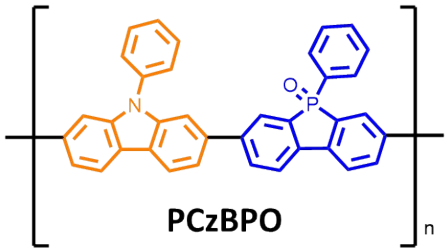
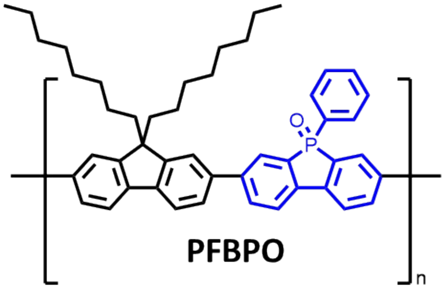


Fig. S17. Effect of photocatalyst amount on the hydrogen production activity of PFBPO in a solution of H_2O/methanol/TEA under λ > 400 nm irradiation.



Conc. of Pd	HER (µmol h^{-1}) (>420 nm)
Residual Pd (441 ppm Pd)	30.09
Add 3.0 % Pd(PPh$_3$)$_4$ in 5mg polymer	31.20

Conc. of Pt	HER (µmol h^{-1}) (>420 nm)
1 % Pt	34.53
1 % Pt	33.73
3 % Pt	38.08
5 % Pt	30.46



Conc. of Pt	HER (µmol h^{-1}) (>420 nm)
1 % Pt	36.76
5 % Pt	36.54

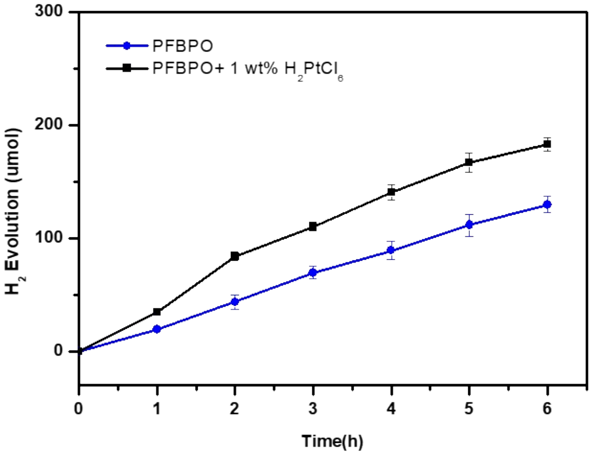


Fig. S18. Pictorial diagram of hydrogen evolution reactions optimized with different concentrations of Pd and Pt.

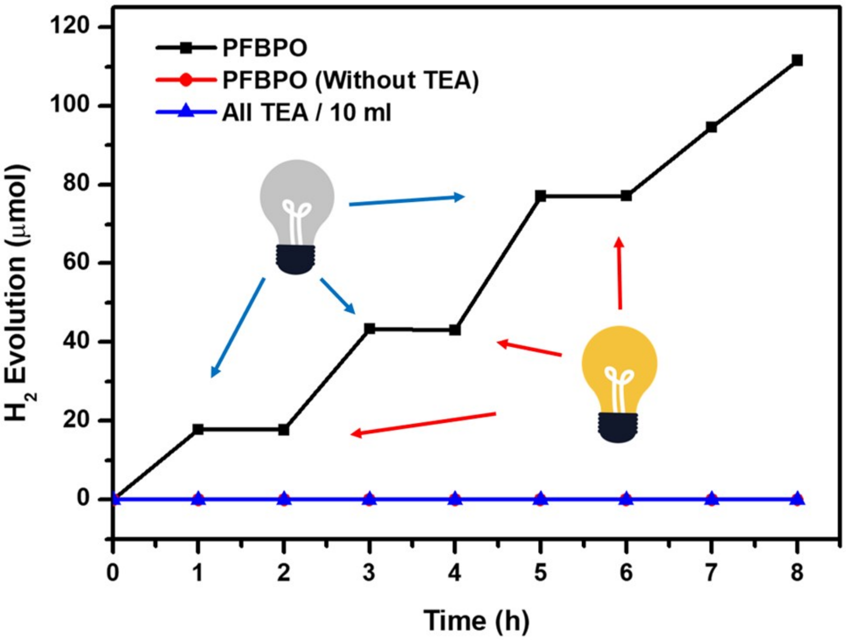


Fig. S19. Control experiment of PFBPO.

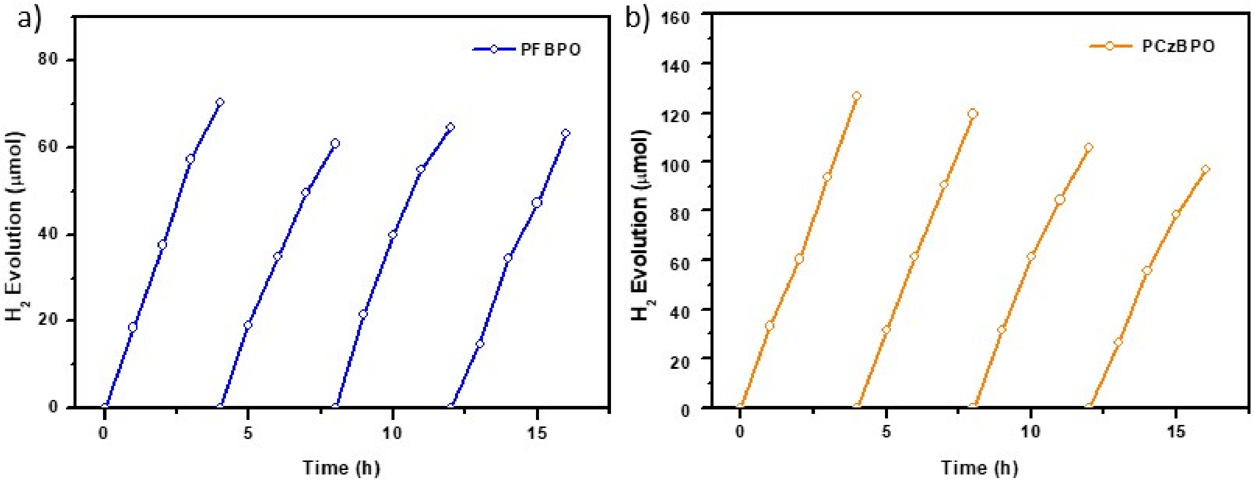


Fig. S20. Long-term stability tests for PFBPO and PCzBPO. Photocatalytic test conditions: 5 mg PFBPO and PCzBPO as photocatalyst; 10 mL solution of H_2O/methanol/TEA under the irradiation of visible light (>400 nm).

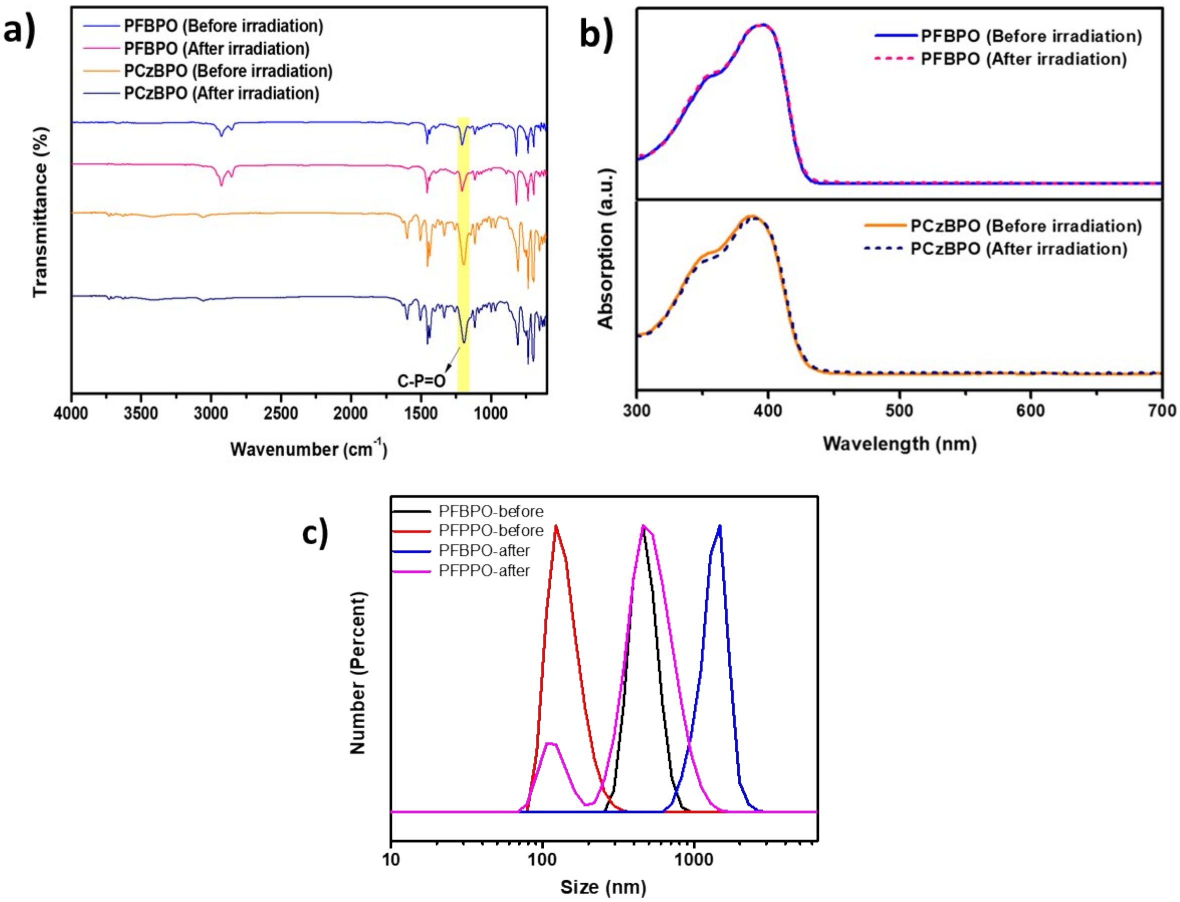


Fig. S21. FT-IR (a), UV-vis and DLS spectra of PFBPO, PCzBPO sample before and after photocatalytic hydrogen evolution.

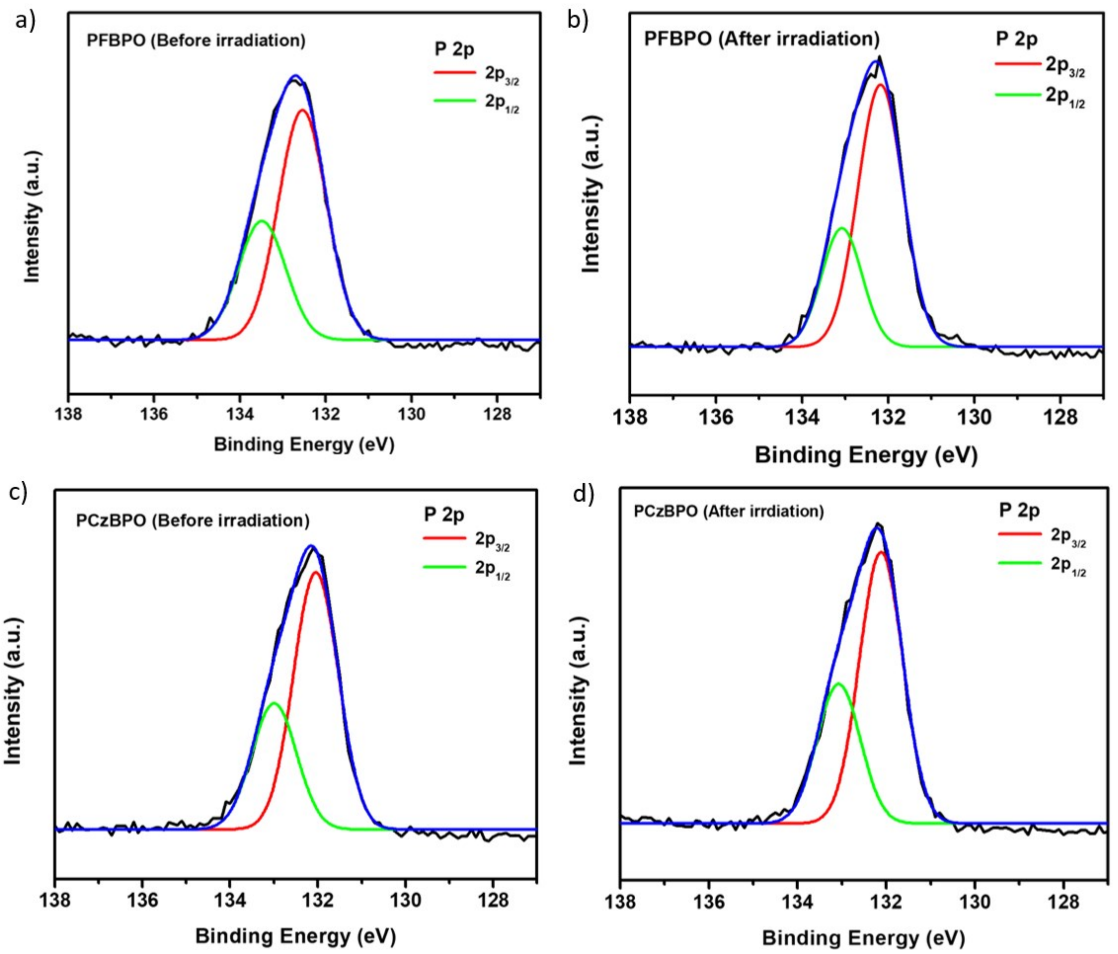


Fig. S22. XPS spectra of P 2p, C 1s for (a and b) PFBPO sample, (c and d) PCzBPO before and after photocatalytic hydrogen evolution

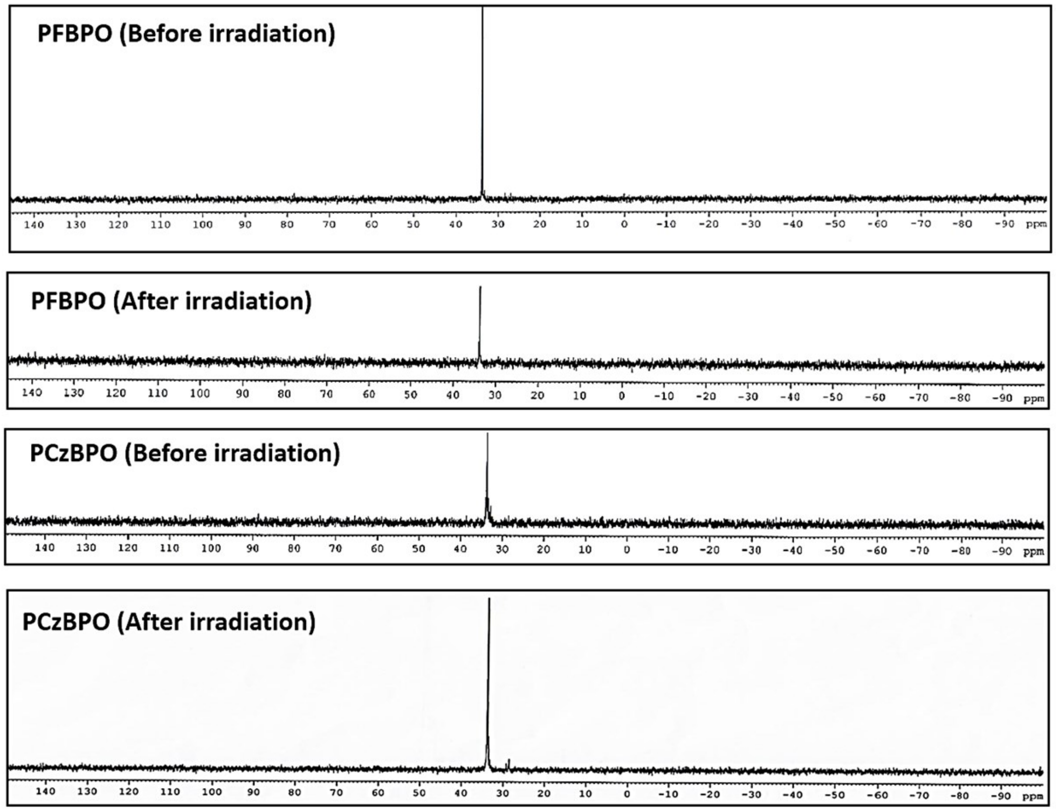


Fig. S23. ^{31}P NMR spectra of PFBPO and PCzBPO sample before and after photocatalytic hydrogen evolution

Table S2. Compared the photophysical, HERs and AQYs of various photocatalysts in the known literature.

Polymer Catalysts	**Metal Co-Catalysts**	**HER**$^{a)}$ $\lambda > 420$ nm **(mmol h^{-1}g^{-1})**	**AQY (%)** @ λ at 420/460/500 nm	**Conditions** @ λ > 420 nm	**References**
P7	Pd-residue	3.68	2.25/- /-	Water/MeOH/TEA	*Angew. Chem. Int. Ed.* **2016** *55*, 1792-1798
PCP4e	2 wt% Pt	1.9 (400 nm)	-/ -/ -	Water/MeOH/ 20%TEA	*J. Am. Chem. Soc.* **2016** *138,* 7681-7686
PCP11	2 wt% Pt	2.59	1.93/ -/ -	Water/MeOH/ 20%TEA	*Macromolecules* **2016,** 49, 6903−6909
CTFS10	1 wt% Pt	2.00	-/ -/ -	Water/ 10 vol% TEOA	*J. Mater. Chem. A,* **2016,** *4,* 12402–12406
CTF-HUST 2	Pt	2.65	-/ -/ -	Water/ 20 vol% TEOA	*Angew. Chem. Int. Ed.* **2017,** *56*, 14149 –14153
DBTD-CMP1	3 wt% Pt	4.6	-/ -/ - 3.3 (400 nm)	Water/ 20 vol% TEOA	*ACS Catal.* **2018,** *8*, 8590−8596
	Pd-residue	2.46	-/ -/ -	Water/ 20 vol% TEOA	
OB-POP-3	3 wt% Pt	0.91	2.0/ -/ -	Water/ 20 vol% TEOA	*Adv. Funct. Mater.* **2018,** *27*, 1703146

PyBT-2	3 wt% Pt	1.06	-/ -/ -	20 vol% TEOA	*Appl. Catal. B: Environ.* **2018** 228, 1-9
CTF-1-100W	3 wt% Pt	5.50	6.0 @ 420nm 3.6 @ 460nm 0.7 @ 500nm	Water/ 10 vol% TEOA/ 3% MeOH	*Energy Environ. Sci.* **2018**, *11*, 1617-1624
FS-COF+WS5F	8 wt% Pt	16.3	7.3/ -/ -	Water/ L-AA (0.1 M)	*Nat. Chem.,***2018**, *10,* 1180
P10	Pd-residue	3.26	11.6/ -/ -	Water/MeOH/TEA	*Nat. Commun.,* **2018***, **9**,* 4968
P28	Pd-residue	0.96	6.7 @ 420nm 4.6 @ 460nm 0.8 @ 500nm	Water/MeOH/TEA	*Chem. Mater.* **2018,** *30*, 5733−5742
SNP-BTT1	3 wt% Pt	3.16	4.5/ -/ -	Water/acetonitrile/TEOA	*Angew. Chem. Int. Ed.* **2018***, 57*, 14188-14192
	Pd-residue	0.49	-/ -/ -	Water/acetonitrile/TEOA	
F8T2-Pdots/g-C_3N_4	-	0.93	5.7 @ 420nm 4.0 @ 460nm 2.2 @ 500nm	Water/ 10 vol% TEOA	*J. Mater. Chem. A,* **2019**, *7,* 303–311
PFN-Br	Pd-residue	0.68	-/ -/ -	Water/TEA	*Nano Energy.***2019**, *60*, 775–783
	3 wt% Pt	4.60	-/ -/ -	Water/TEA	
N-PDBT-O	Pd-residue	12.2	3.7 @ 420nm 2.4 @ 460nm 1.5 @ 500nm	Water/ 10%TEOA	*Macromol. Rapid Commun.* **2019**, *40*, 1800494
S-CMP3	2.1 wt% Pt	3.11	13.2 @ 420nm 5.7 @ 460nm 1.5 @ 500nm	Water/MeOH/TEA	*Chem. Mater.***2019**, *31,* 305−313
Cu_3P−FCN	1.0 wt% Cu	0.28	3.74	Water/ 10%TEOA	*ACS Appl. Mater. Interfaces* **2019**, 11, 16527−16537
P64	Pd-residue	3.53	20.7 @ 420m NA @ 460nm NA @ 500nm	Water/MeOH/TEA	*J. Am. Chem. Soc.* ***2019**, 141, 9063-9071*
P62	Pd-residue	3.50	15.1 @ 420nm NA @ 460nm NA @ 500nm	Water/MeOH/TEA	
CPF-1	Pd-residue	0.033	**-/ -/ -**	Water/ 10%TEOA	*Chem. Eur. J.* **2019**, *25*, 12342 – 12348
2CzPN	1.0 wt% Pt	3.67	7.5 @ 420m 6.1 @ 475nm 0.8 @ 550nm	10%MeOH/ 10%TEOA/0.5M AA	*ChemSusChem* **2019***, 12, doi.org/10.1002/cssc.201902553*
PSO-FS	Pd-residue	3.4	6.8/ -/ -	Water/ 10 vol% TEOA	*Angew. Chem. Int. Ed.* **2019**, 58, 10236-10240.
P35	Pd-residue	0.83	-/ -/ -	Water/MeOH/TEA	*Chem. Mater.* **2019**, 31, 305- 313.
PB2S	Pd-residue	8.92	0.01/ -/ -	Water/MeOH/TEA	*ACS Energy Lett.* **2020**, 5, 669−675

p-FuS	Pd-residue	5.88	-/ -/ -	Water/MeOH/TEA	*J. Mater. Chem. A,* **2020**,8, 8700-8705
PS-TEG	Pd-residue	2.9	-/ -/ -	Water/MeOH/TEA	*Energy Environ. Sci.*, **2020**, 13, 1843-1855
PFPPO	**Pd-residue**	**0.03**	**0.03/ -/ -**	Water/MeOH/TEA	**This work**
PFBPO	**Pd-residue**	**4.60**	**12.79 @ 420m** **11.76 @ 460nm** **3.16 @ 500nm**	Water/MeOH/TEA	**This work**
PCzBPO	**Pd-residue**	**6.13**	**14.92 @ 420nm** **14.88 @ 460nm** **1.81 @ 50nm**	Water/MeOH/TEA	**This work**

[a)] Hydrogen evolution rate (light source, $\lambda > 420$ nm).

References:

1. H.-Y. Liu, P.-J. Wu, S.-Y. Kuo, C.-P. Chen, E.-H. Chang, C.-Y. Wu and Y.-H. Chan, *J. Am. Chem. Soc.* **2015**, *137*, 10420-10429.

2. M. S. Wrighton, D. S. Ginley and D. L. Morse, *J. Phys. Chem.* **1974**, *78*, 2229-2233.

3. A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652.

4. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O¨. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, **2013**.

5. a) A. Bruch, A. Fukazawa, E. Yamaguchi, S. Yamaguchi and A. Studer, *Angew. Chem., Int. Ed.*, 2011, **50**, 12094. b) Z. Tian, X. Yang, B. Liu, D. Zhong and G. Zhou, *J. Org. Chem.*, 2019, **895**, 28-36.

6. S. Chen, Y. Li and C. Wang, *RSC Adv.*, 2015, **5**, 15880-5885.