

Electronic Supporting Information

Pyrene- and 1,3,5-triazine-based D-A two-dimensional polymers for sunlight-driven hydrogen evolution: the influence of linking pattern

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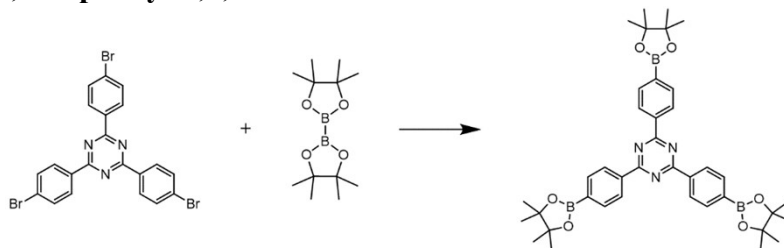
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Synthesis of 2,4,6-triphenyl-1,3,5-triazine boronate.



A mixture of 2,4,6-tris(4-bromophenyl)-1,3,5-triazine (2.40 g, 4.40 mmol), bis(pinacolato)diboron (3.80 g, 14.60 mmol), potassium carbonate (1.20 g, 13.20 mmol), and Pd(dppf)Cl₂ (204 mg, 0.278 mmol) in dry 1,4-dioxane (70 mL) was refluxed under N₂ for 24 h. After cooling to room temperature, the mixture was poured into water (250 mL). The aqueous phase was separated and extracted with CH₂Cl₂ (3 × 80 mL). The combined organic extracts were dried with anhydrous Na₂SO₄, and concentrated under reduced pressure. The resultant residue was subjected to column chromatography (petroleum ether/CH₂Cl₂, 1:1) to give the title compound (1.55 g, 50%) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.75–8.77 (d, *J* = 8.0 Hz, 6H), 8.01–8.03 (d, *J* = 8.4 Hz, 6H).

Methods

¹H and ¹³C NMR analyses were performed on 700 MHz spectrometers (Bruker AVANCE NEO 400 Ascend) in the indicated solvents at room temperature.

High resolution solid-state NMR spectra were recorded on an Agilent NMR spectrometer (60054-ASC) using a standard CP pulse sequence probe with 4 mm (outside diameter) zirconia rotors.

Scanning electron microscope (SEM) images were collected using scanning electron microscope (JEOL, JSM-7500F) at an accelerating voltage of 5.0 kV. Transmission electron microscope (TEM) was performed on a JEM-2100 electron microscope with an accelerating voltage of 200 kV.

TGA was carried out on an American TA-Q20 in nitrogen atmosphere using a 10 °C/min ramp without equilibration delay. The Solid-state UV-Vis absorbance was measured by UV spectrophotometer (HITACHI, U-3900).

Powder X-ray diffraction (PXRD) patterns were obtained on a PANalytical Empyrean X-ray diffractometer with Cu Kα line focused radiation at 40 kV and 40 mA from 2θ = 1° up to 40° with 0.02° increment by Bragg-Brentano. The powdered sample was added to the glass and compacted for measurement.

N₂ adsorption isotherms were measured up to 1 bar at 77 K using a Micrometrics ASAP 2460 surface area analyzer. Prior to measurements, samples (ca. 100 mg) were degassed for over 12 h at 120 °C. UHP grade N₂ and He were used throughout the adsorption experiments. Oil-free vacuum pumps and oil-free pressure regulators were used for measurements to prevent contamination of the samples during the degassing process and isotherm measurement.

In density functional theory (DFT) calculations, structural optimization of the two structural units of TzSPy and TzPy was performed using Gaussian software with a B3LYP/6-31+G(d,p) basis set and an implicit SMD solvent model.

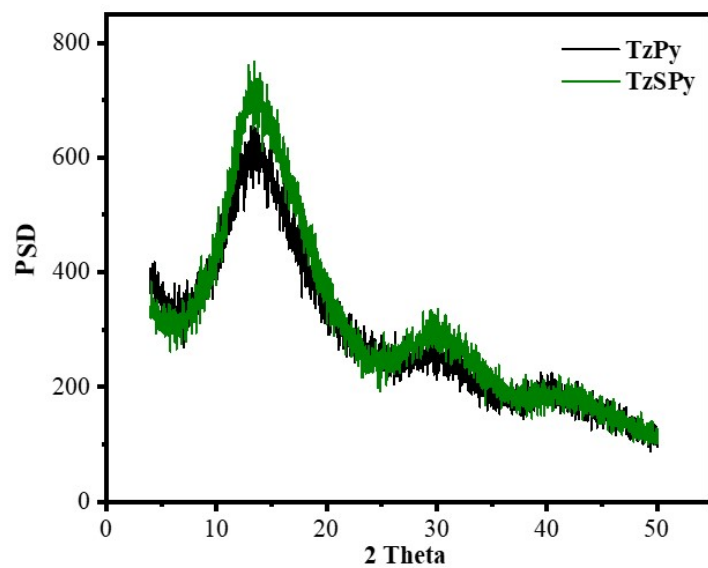
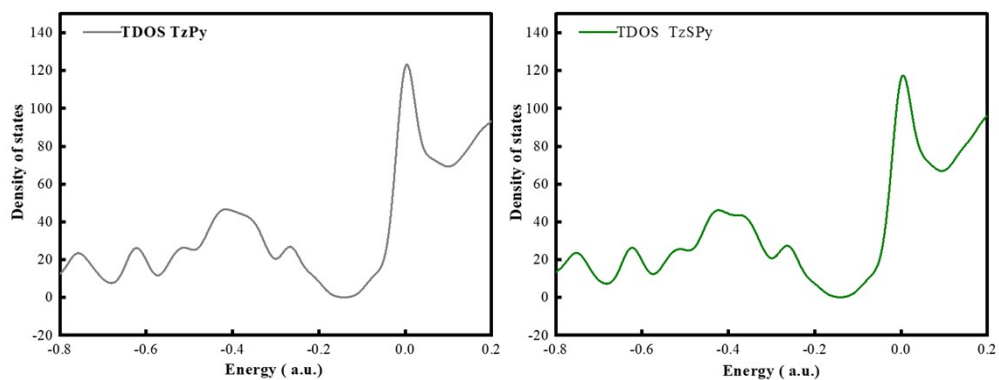


Figure S1. Powder XRD patterns of TzPy and TzSPy.

Figure S2. Scanning electron microscope images of TzPy (a, c) and TzSPy (b, d).



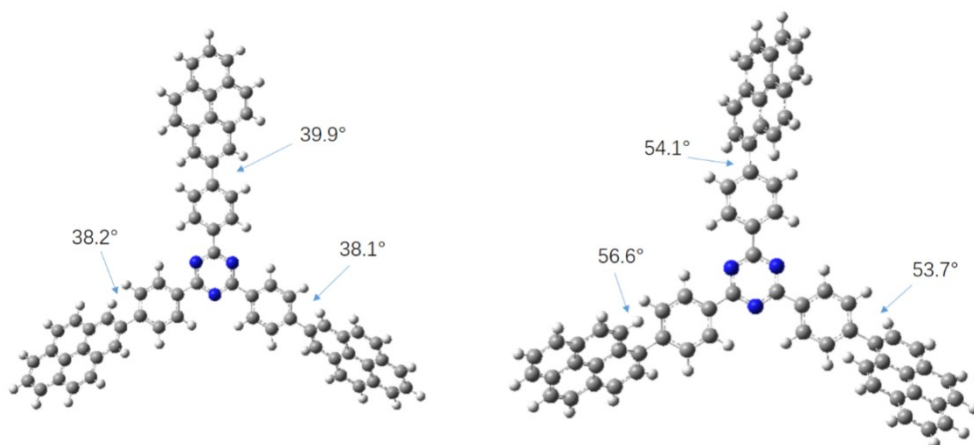


Figure S3. The DOS curves, DFT geometry optimizations and the dihedral angles of the polymers.

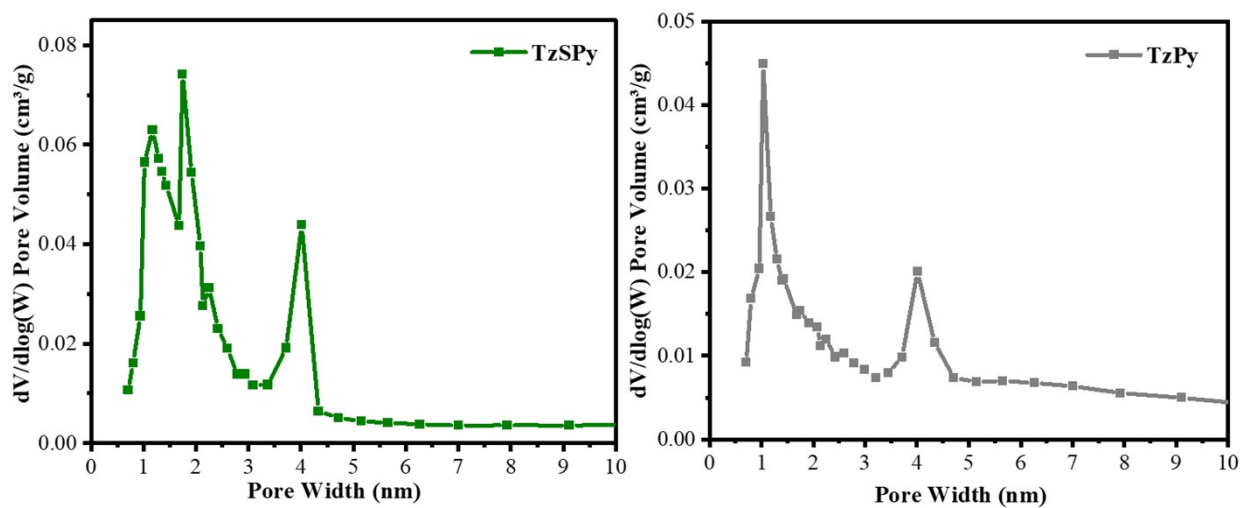


Figure S4. Pore size distribution.

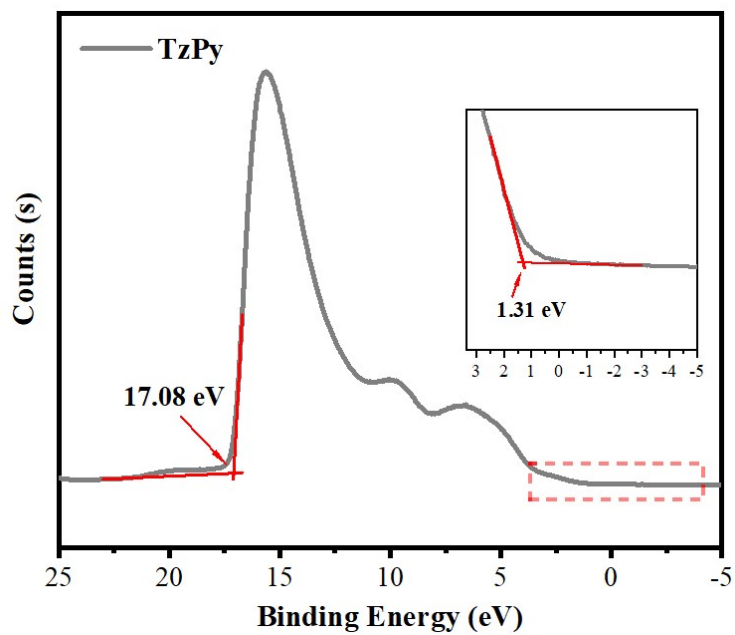


Figure S5. High-resolution valence band UPS spectrum of TzPy.

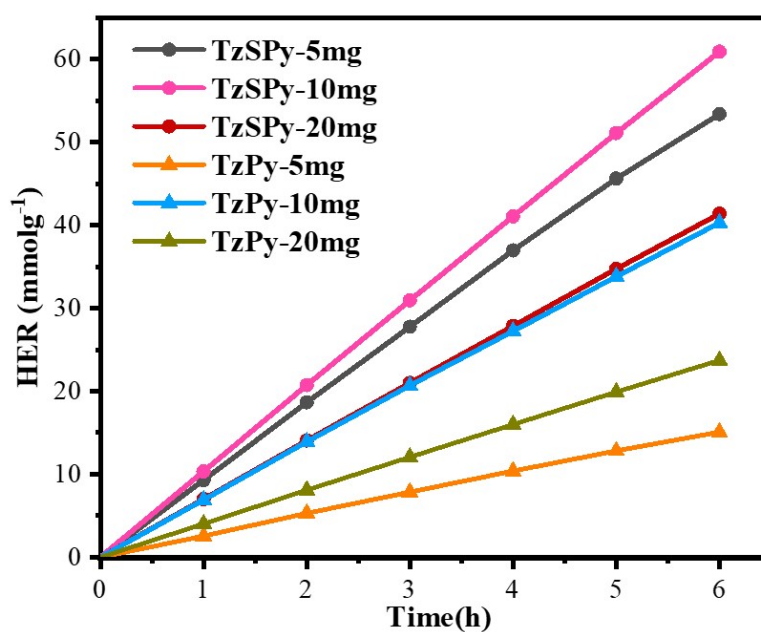


Figure S6. Hydrogen evolution rates (HER) of TzPy and TzSPy in the presence of 3 wt% Pt under simulated sunlight (AM1.5G).

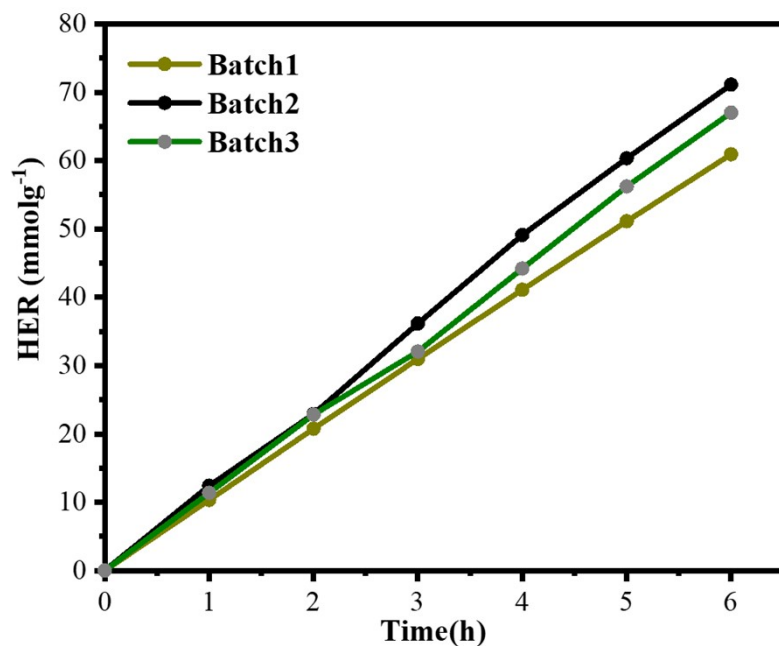


Figure S7. HER as a function of reaction time (10 mg of TzSPy from three different batches) under simulated sunlight (AM1.5G).

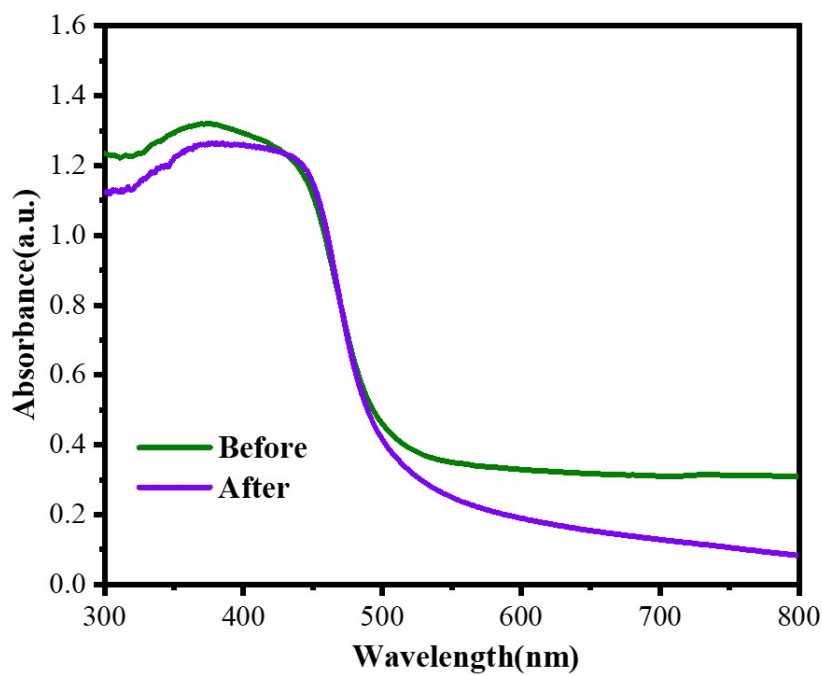


Figure S8. Solid UV/vis absorption spectra of the polymer TzSPy before and after photocatalytic H₂ evolution reaction in a TEOA/water/MeCN mixture under simulated sunlight(AM1.5G) for 24 h.

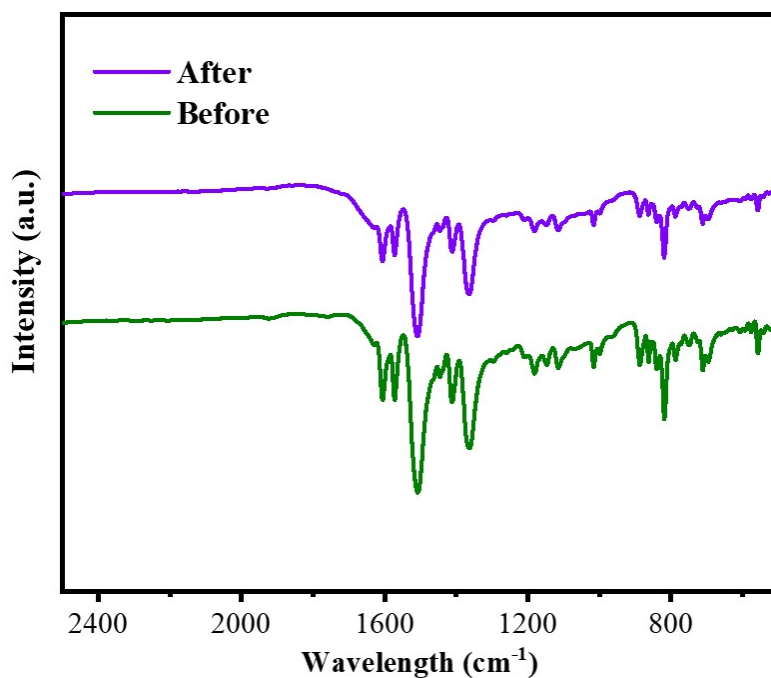


Figure S9. FT-IR spectra of the polymer TzSPy before and after photocatalytic H₂ evolution reaction in a TEOA/water/MeCN mixture under simulated sunlight (AM1.5G) for 24 h.

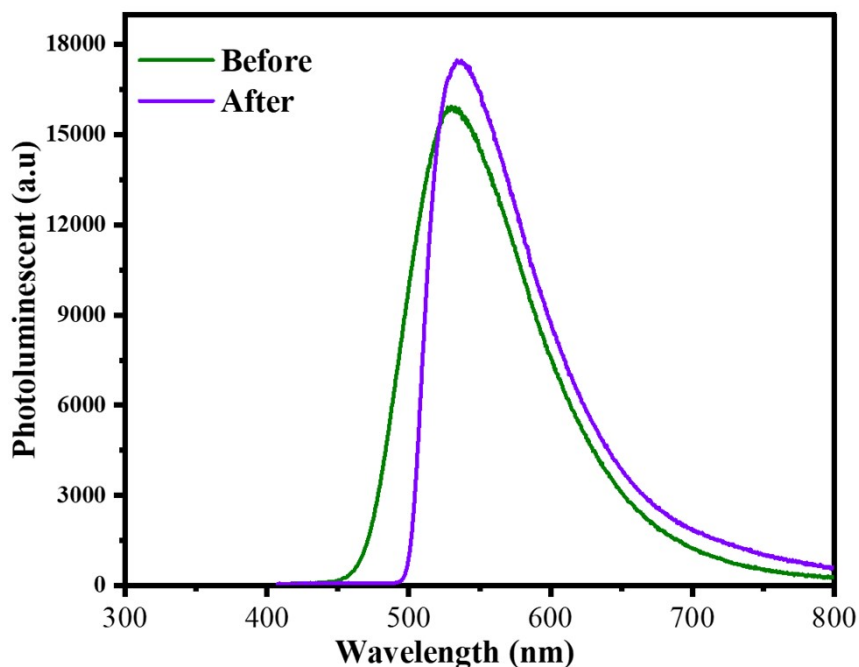


Figure S10. Photoluminescence spectra of the polymer TzSPy before and after photocatalytic H₂ evolution reaction in a TEOA/water/MeCN mixture under simulated sunlight (AM1.5G) for 24 h.

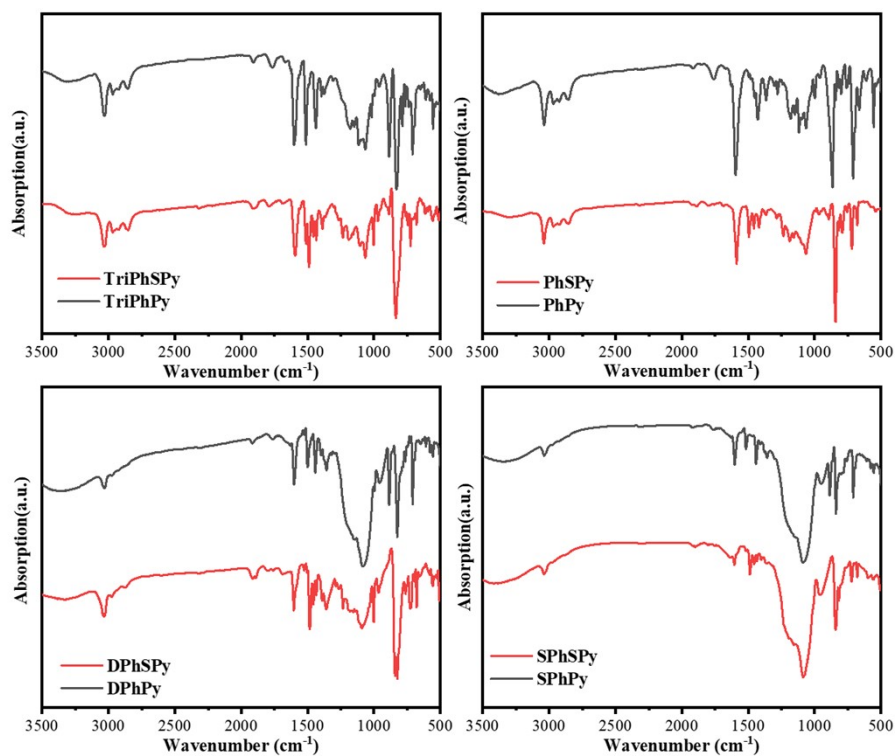


Figure S11. FT-IR spectra of additional four groups of polymers.

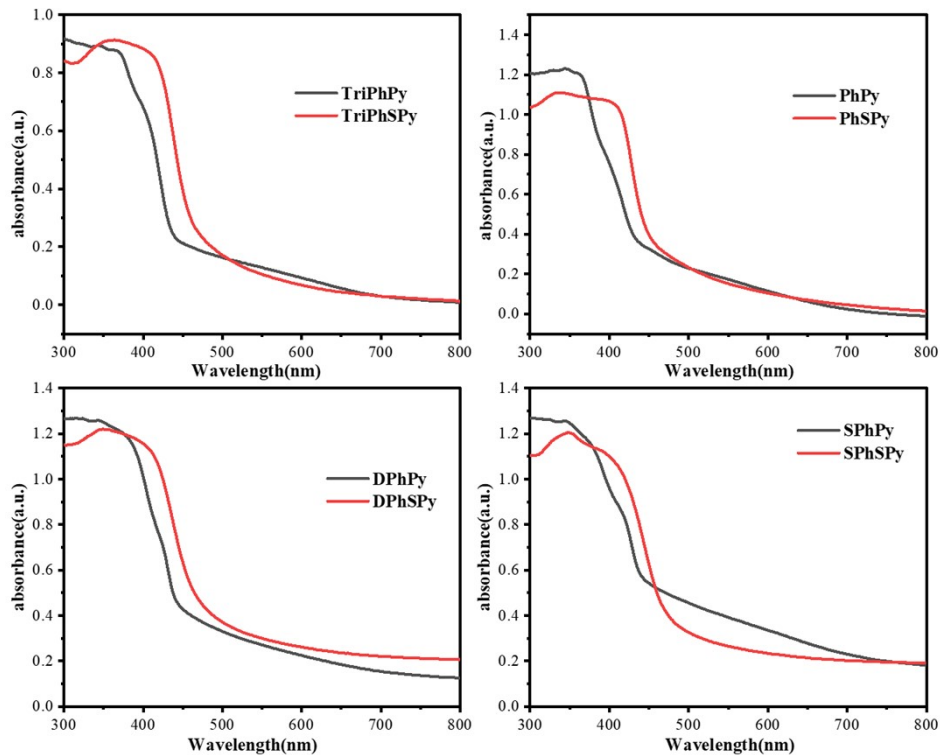


Figure S12. Solid UV/vis absorption spectra of the four groups of polymers.

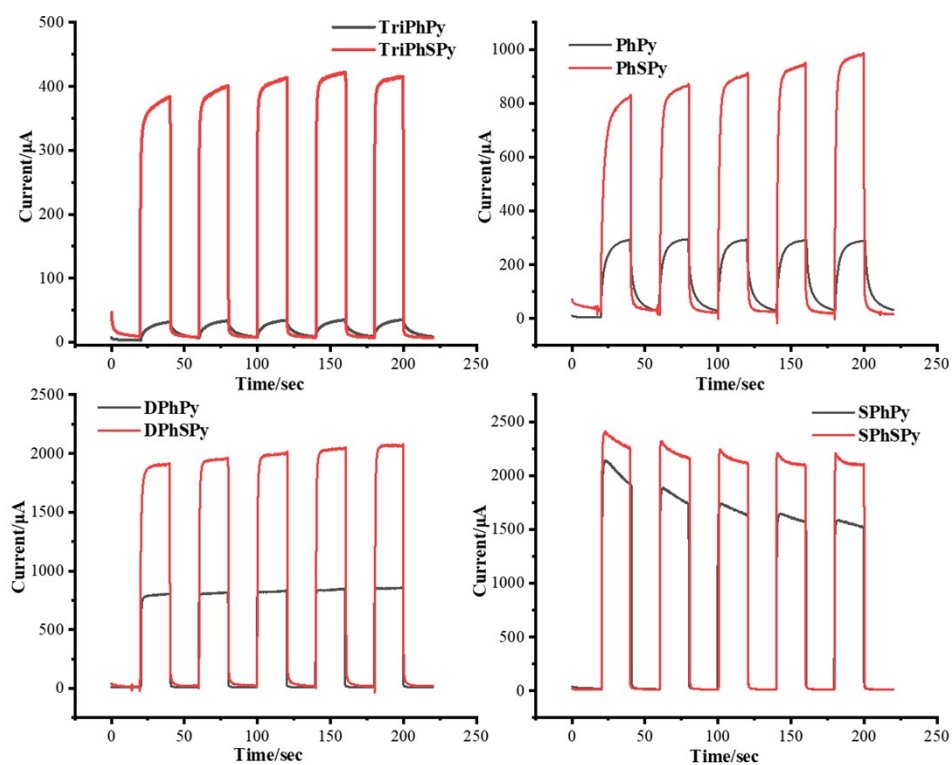


Figure S13. Photocurrent response curves of the four groups of polymers.

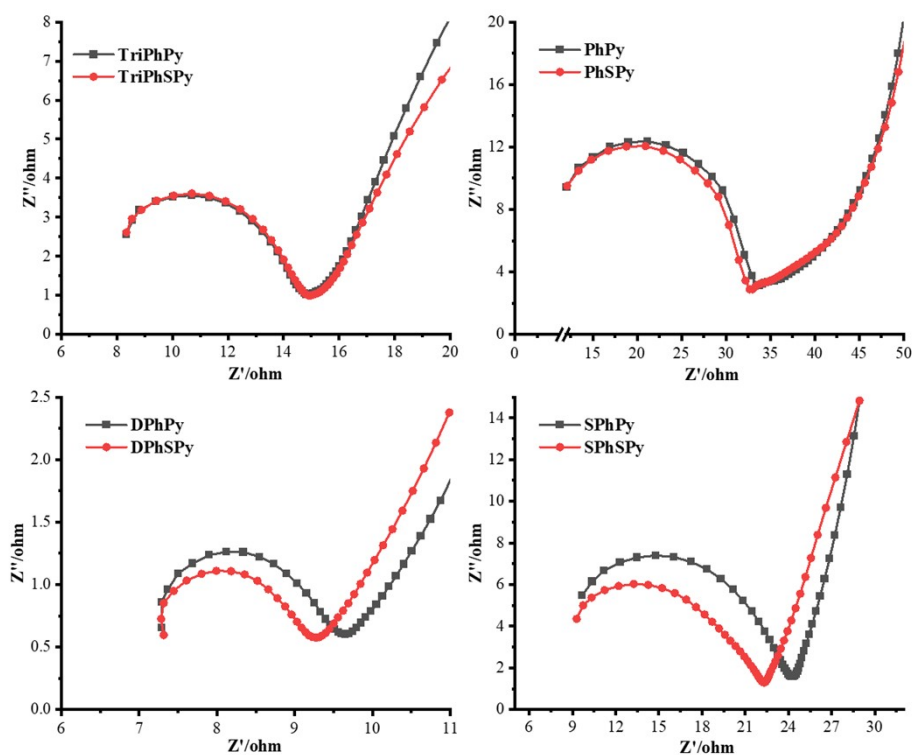
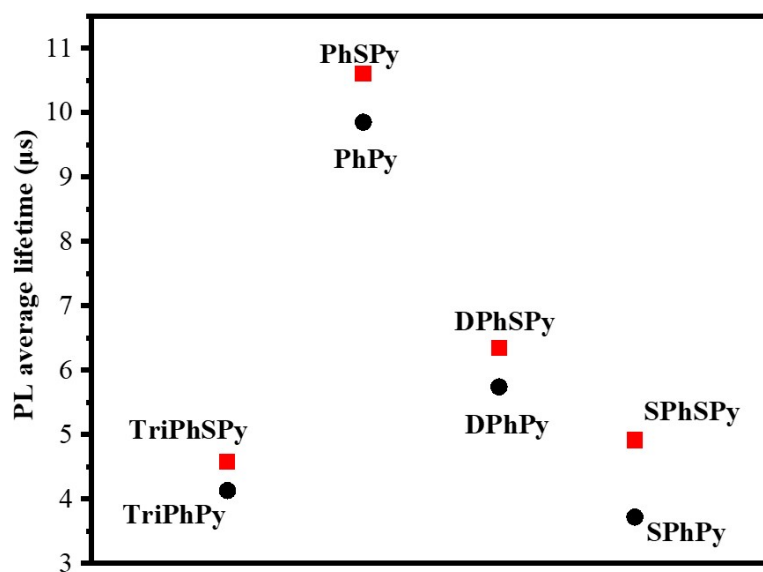


Figure S14. Electrochemical impedance spectroscopy (EIS) Nyquist plots of the four groups of polymers.



Polymer	τ_1 (μs)	τ_2 (μs)	T_{average} (μs)
TzPy	1.43 ns	/	1.43 ns
TzSPy	1.82 ns	/	1.82 ns
TriPhPy	1.35	10.37	4.13
TriPhSPy	1.31	11.73	4.57
PhPy	1.87	21.64	9.85
PhSPy	1.55	21.26	10.60
DPhPy	1.49	15.06	5.74
DPhSPy	1.536	14.45	6.36
SPhPy	1.16	7.12	3.72
SPhSPy	0.979	8.849	4.91

Figure S15. Fitted decay time of the four groups of polymers.

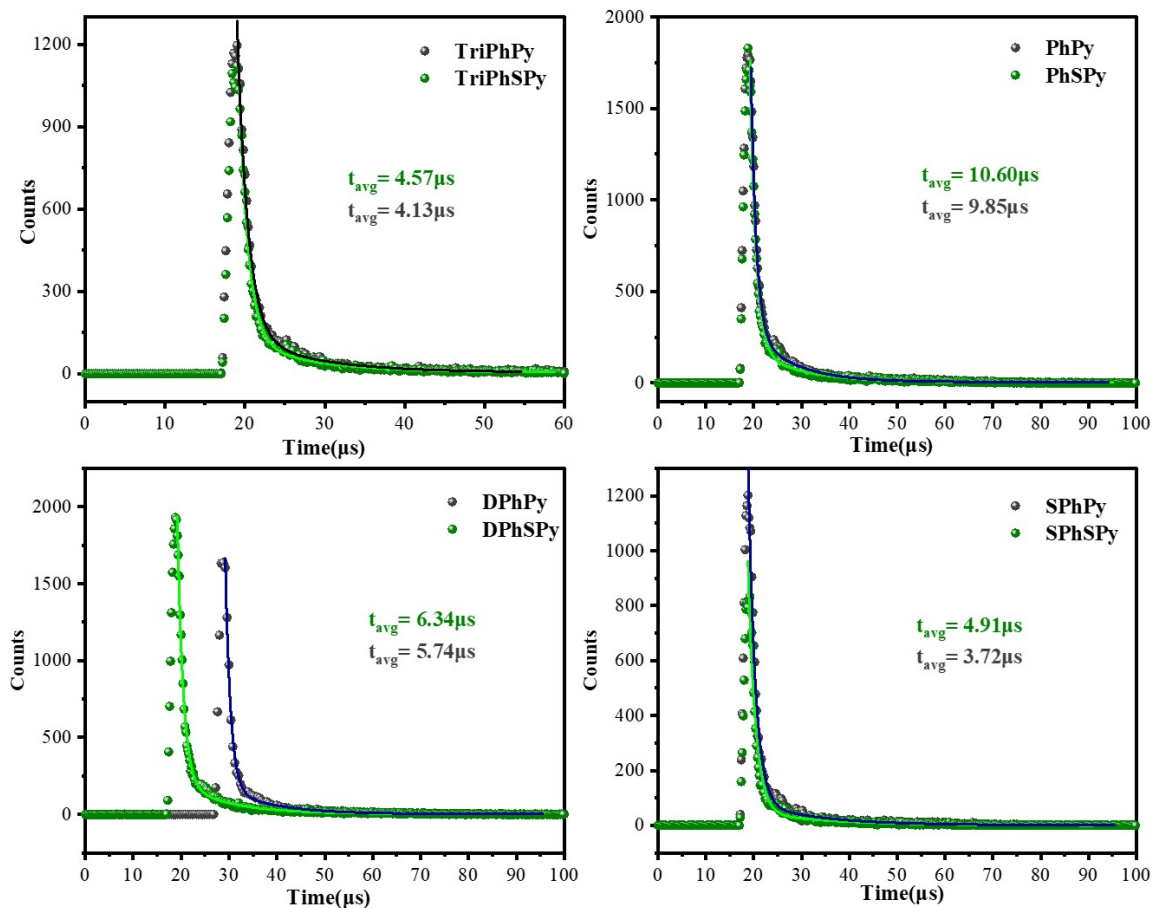


Figure S16. Time-resolved photoluminescence spectra of the four groups of polymers.

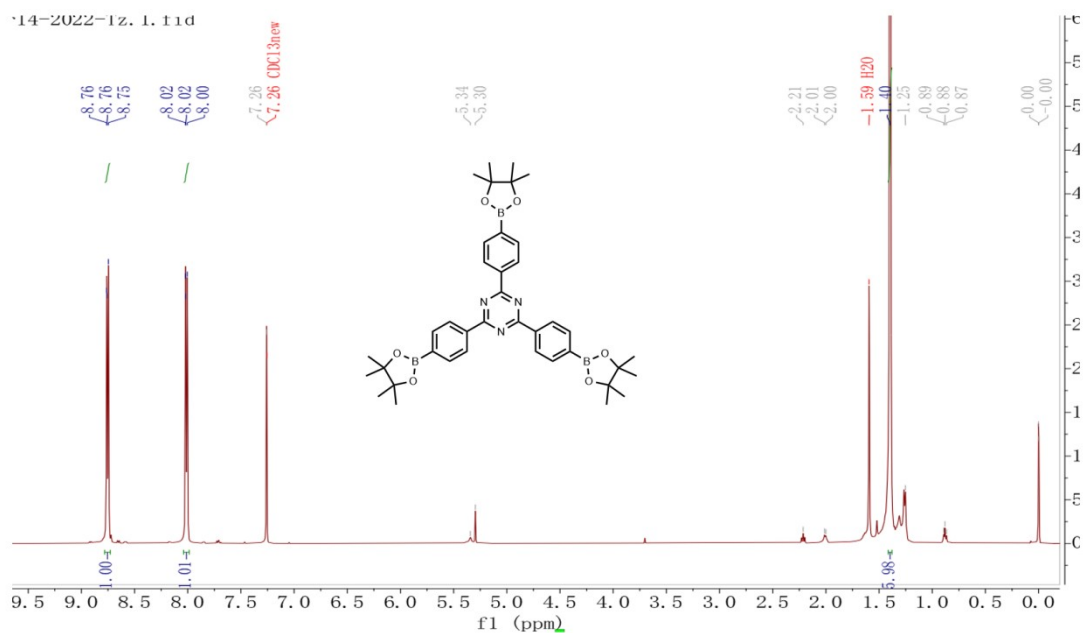


Figure S17. 1H NMR (700 MHz, $CDCl_3$) of 2,4,6-triphenyl-1,3,5-triazine boronate.

Table S1 the contrast of PHP Performance of TzSPy and other reported CMPs

Photocatalyst	cocatalyst	PHP	Irradiation	AQY%	Reference
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		(mmolg ⁻¹ h ⁻¹)	light		
TzSPy	3 wt% Pt	10.3	AM1.5	n/d*	This work
P-CTF	3 wt% Pt	0.659	AM1.5	2.11@50mg	1
PEG@BT-COF	3 wt% Pt	11.14	>420 nm	11.2@420 nm	2
TFPT-COF	2.2 wt%Pt	1.97	>420 nm	2.2	3
N ₃ -COF	0.68 wt%Pt	1.70	>420 nm	n/d*	4
Sp ² c-COF _{ERDN}	3 wt%Pt	2.12	>420 nm	0.48	5
TpPa-COF-(CH ₃) ₂	3 wt%Pt	8.33	>420 nm	n/d*	6
COF-alkene	3 wt%Pt	2.33	>400 nm	6.7	7
CTF-HUST-C1	3 wt%Pt	5.1	>420 nm	n/d*	8
COP-TP _{3:1}	3 wt%Pt	4.2	>400 nm	1.5	9
Py-CITP-BT-COF	5 wt%Pt	8.875	>420 nm	8.45	10
NUS-55	Co(bpy ₃)Cl ₂ 8.4 uM	2.48	>420 nm	1.55	11
PyTz-COF	3 wt% Pt	2.07	AM1.5	No	12
BTH-3	No	15.1	>420 nm	1.256@500nm	13
FS-COF	3 wt% Pt	10.1	AM1.5G	7.8@420 nm	14
PyTA-BC-Ph COF	3.7 wt%Pt	2.76	>420 nm	1.83	15

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