

Electronic Supporting Information

1,3,5-triazine and dithienothiophene-based conjugated polymers for highly effective photocatalytic hydrogen evolution

Jie Yang,^{a,b} Yahu A. Liu,^c Ming-Ming Zhai,^a Jun-Jie Qin,^b
Wei-Bo Hu,^{*b} Hui Yang^{*a,b} and Ke Wen^{*a,b}

^a School of Physical Science and Technology, ShanghaiTech University,
Shanghai 201210, P. R. China

^b Shanghai Advanced Research Institute, Chinese Academy of Science,
Shanghai 201210, P. R. China

^c Medicinal Chemistry, ChemBridge Research Laboratories,
San Diego, California, 92127, United States

*Corresponding Authors

Wei-Bo Hu, PhD
E-Mail: huwb@sari.ac.cn

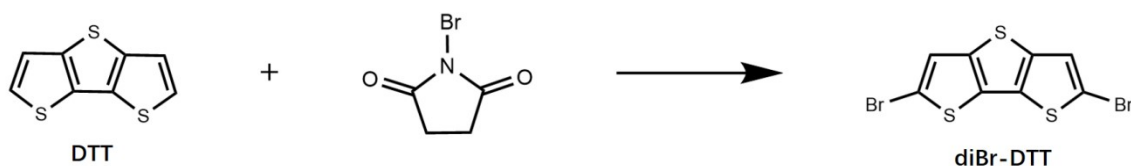
Hui Yang, PhD
E-Mail: yangh@sari.ac.cn

Ke Wen, PhD
E-Mail: wenk@sari.ac.cn

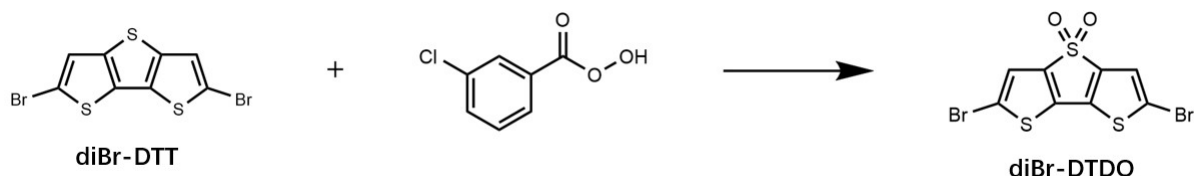
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Synthesis of diBr-DTT and diBr-DTDO



diBr-DTT. To a solution of dithieno[3,2-b:2',3'-d]thiophene (7.0 mmol) in a mixed solvent of CHCl_3 and AcOH (54 mL, 1:1, v/v) was added NBS (2.74 g, 15.4 mmol) portionwise at 0 °C to result in a mixture which was warmed to at 25 °C and stirred for 3 h. The reaction mixture was poured into ice-water (300 mL) and extract with CHCl_3 (3×80 mL). The combined organic extracts were washed with saturated aqueous NaHCO_3 solution (20 mL) and brine (20 mL), dried over Na_2SO_4 , and concentrated under reduced pressure to afford a residue which was subjected to a column chromatography on silica gel with DCM as eluent. The product obtained from the chromatography was recrystallized from a DCM/hexanes solution to furnish **diBr-DTT** as an off-white solid. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.28 (s, 2H).



diBr-DTDO. To a solution of DTT (177.0 mg, 0.5 mmol) in DCM (15 mL) was added 3-chloroperoxybenzoic acid (216.0 mg, 80% purity, 1.0 mmol) to result in a mixture which was heated under gentle reflux for 2 d, cooled to the reaction mixture, poured into a concentrated aqueous NaHSO_3 solution (150 mL), and extracted with DCM (3×40 mL). The combined organic extracts were washed with 5% aqueous NaHCO_3 solution (10 mL) and water (mL), dried over anhydrous MgSO_4 , and concentrated under reduced pressure. The residue was subjected to a column chromatography on silica gel with a mixed solvent of DCM/PE(1:4) as eluent to afford a product which was recrystallized from a solution in MeCN to furnish **diBr-DTDO** as a yellow solid (90 mg, 47%). $^1\text{H NMR}$ (400 MHz, CDCl_3): 7.21 (s, 2H).

Methods

^1H and ^{13}C NMR analyses were performed on a 500 MHz spectrometer (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. 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 on a UV spectrophotometer (HITACHI, U-3900). Powder X-ray diffraction (PXRD) patterns were obtained on a PANalytical Empyrean X-ray

diffractometer with Cu K α line focused radiation at 40 kV and 40 mA from $2\theta = 1^\circ$ up to 30° 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 TzDTDO and TzDTT was performed using Gaussian software with a B3LYP/6-31+G(d,p) basis set and an implicit SMD solvent model

The apparent quantum yield measurement

The AQY was measured at selected wavelengths enabled by different band pass filters (400, 420, 450, 500, 550, and 600 nm) with the intensities calibrated as 25, 4.6, 21, 20, 27 and 28 mW cm⁻¹, respectively, using a power meter (CEL-FZ-A, China Education Au-light). The AQY at a given wavelength was calculated by the following equation.

$$\text{AQY} = \frac{2 \times M \times N_A \times h \times c}{S \times P \times t \times \lambda}$$

Where M is the amount of H₂ (mol), N_A is the Avogadro constant (6.022×10^{23} /mol), h is the Planck constant (6.626×10^{-34} J·s), c is the speed of light in vacuum, S is the irradiation area (9 cm² in our experiment), P is the intensity of irradiation light (W cm⁻²), t is the irradiation time(s), and l is the wavelength of the monochromatic light (m).

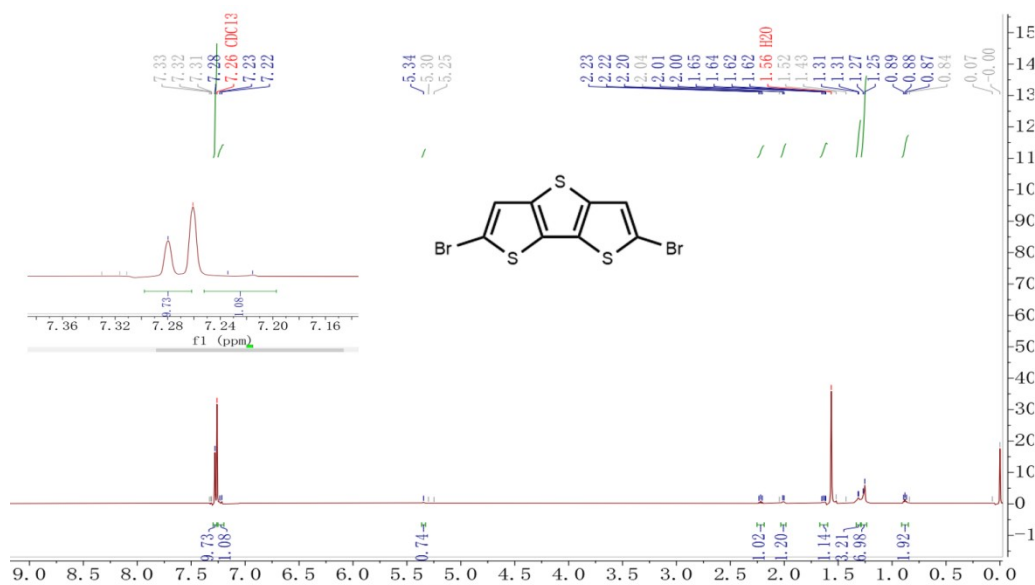


Figure S1. ^1H NMR (500 MHz, CDCl_3) of **TzDTT**.

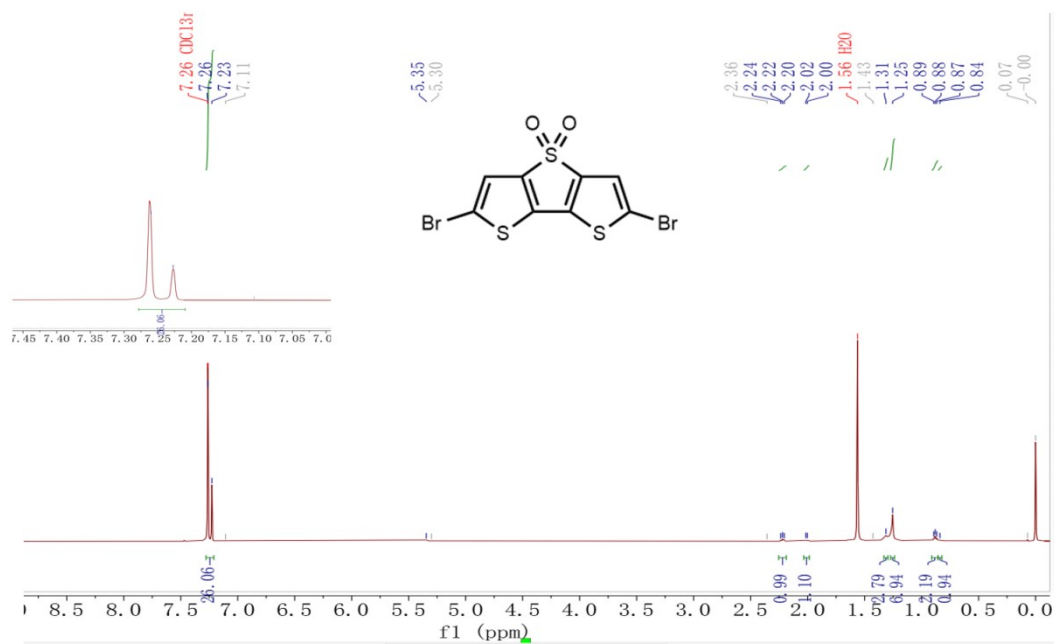


Figure S2. ^1H NMR (500 MHz, CDCl_3) of **TzDTDO**.

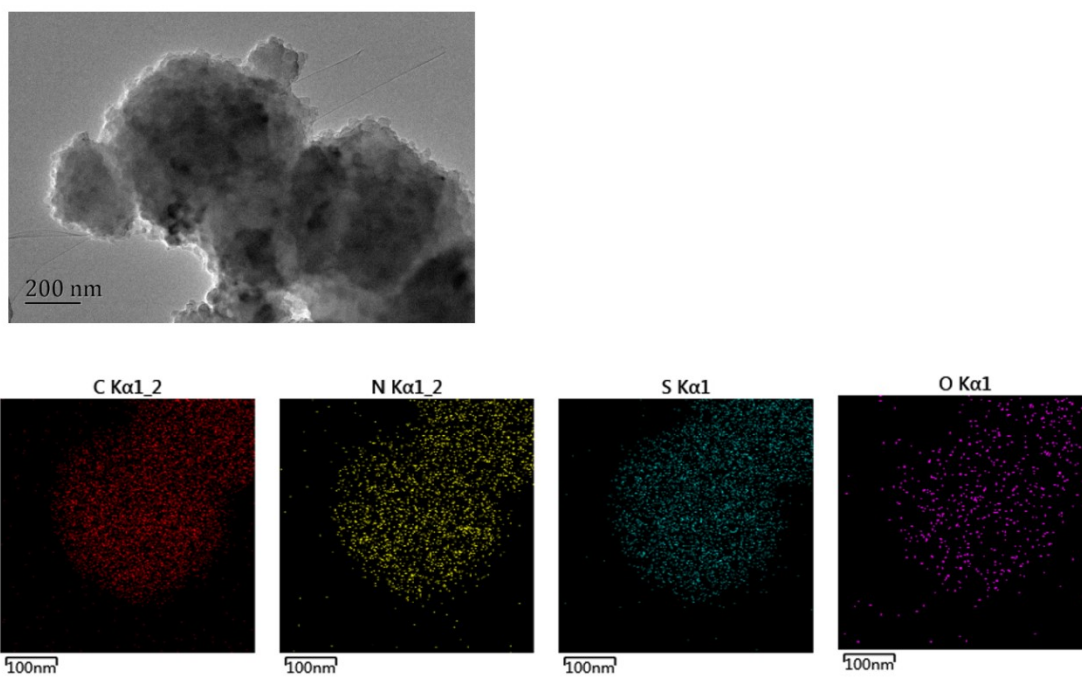


Figure S3. The elemental mapping of TzDTT.

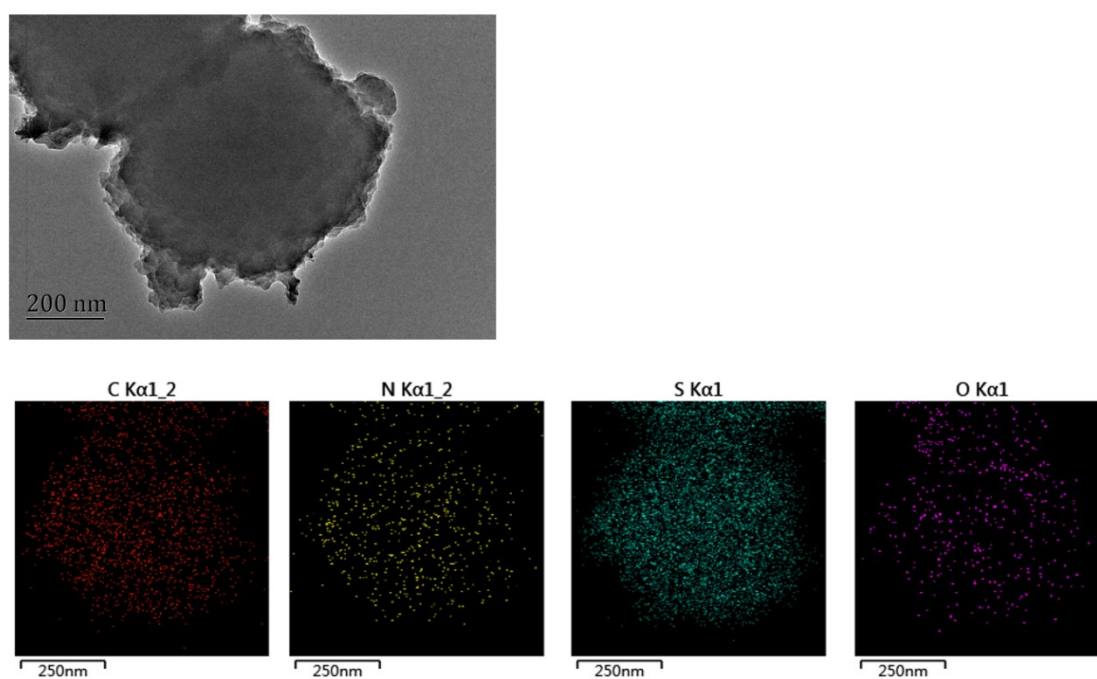


Figure S4. The elemental mapping of TzDTDO.

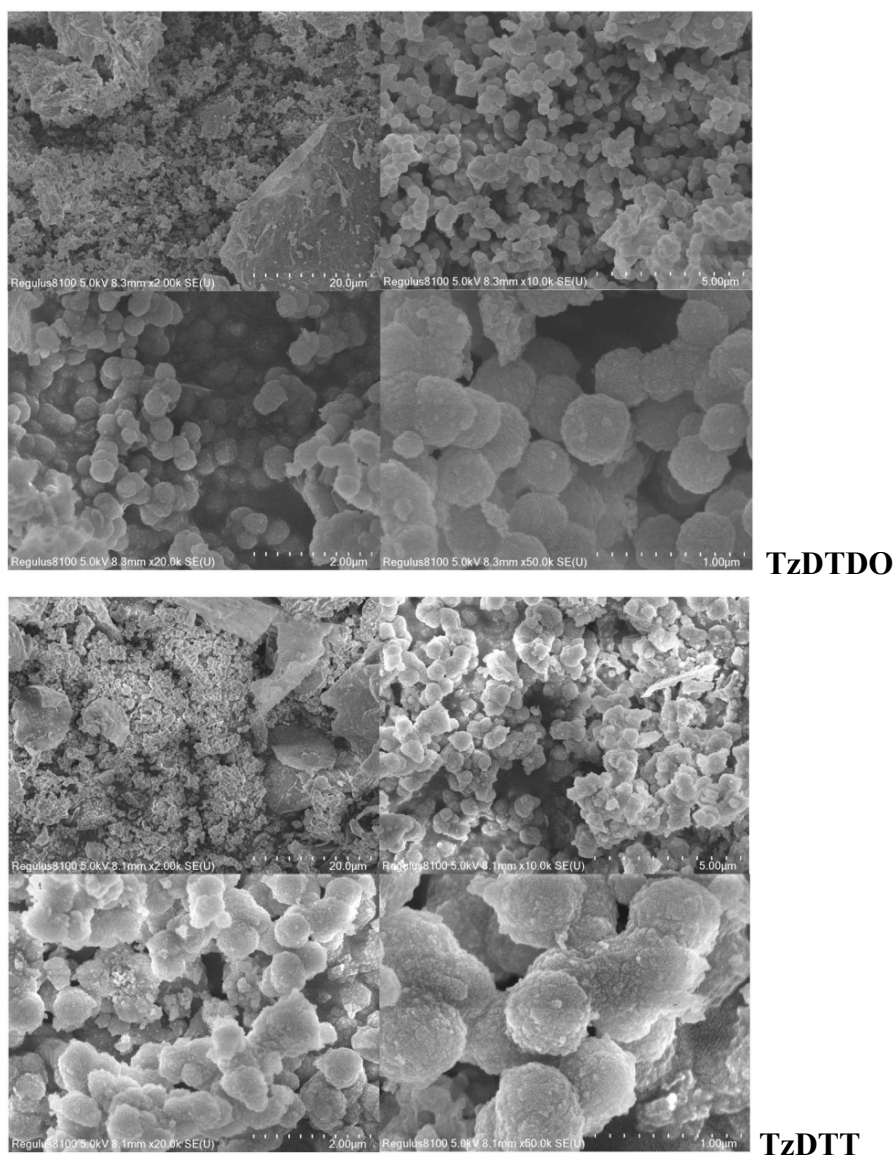


Figure S5. Scanning electron microscope images of **TzDTDO** and **TzDTT**

Table S1. Element analysis of obtained polymers

sample	composition	C (%)	H (%)	N (%)	S (%)	O (%)	B, Pd, Br, or P (%)	C : N	C : S
TzDTDO	Calculated	61.38	2.34	6.51	22.34	7.34	—	9.43	2.75
	Found	47.85	2.52	4.76	14.6	16.1	14.17	10.1	3.28
TzDTT	Calculated	66.31	2.53	7.03	24.31	—	—	9.43	2.73
	Found	51.47	2.43	5.42	14.89	11.05	14.74	9.49	3.46

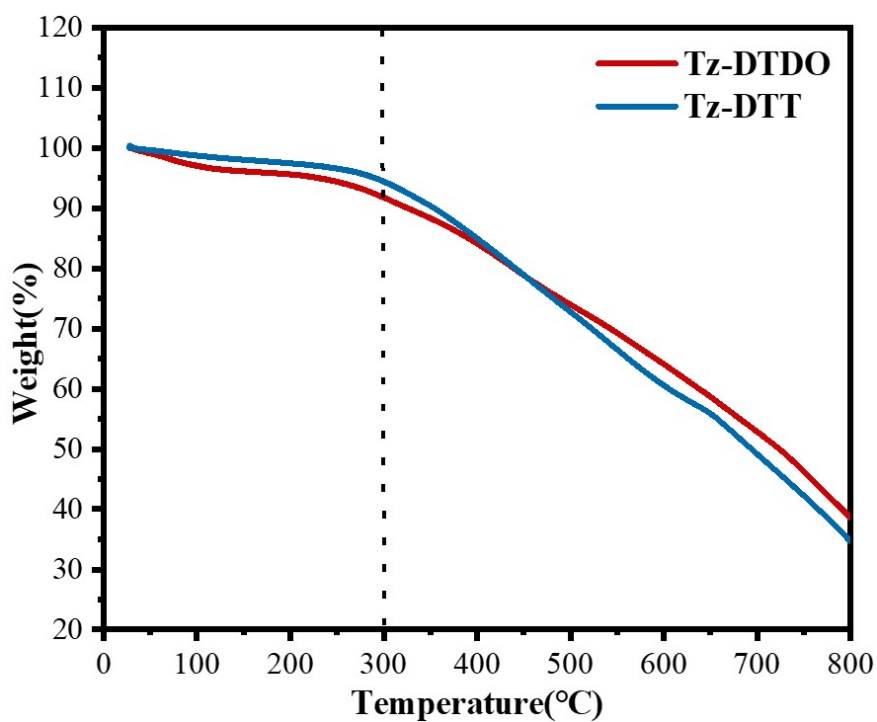


Figure S6. Thermogravimetric analysis(TGA) profile of polymers under N₂ atmosphere.

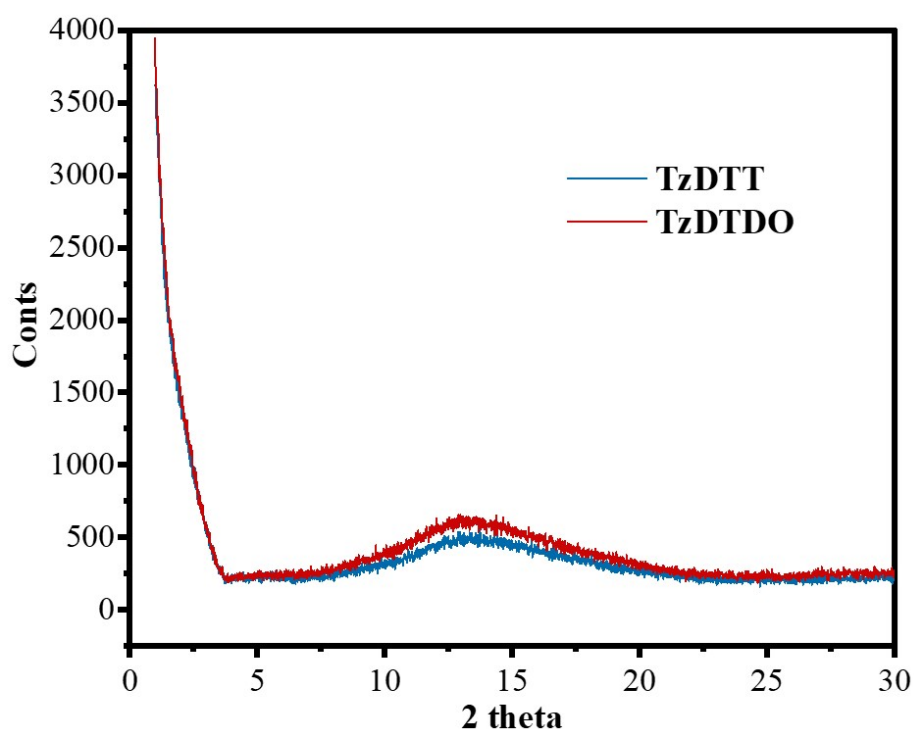


Figure S7. Powder XRD patterns of TzDTT and TzDTDO.

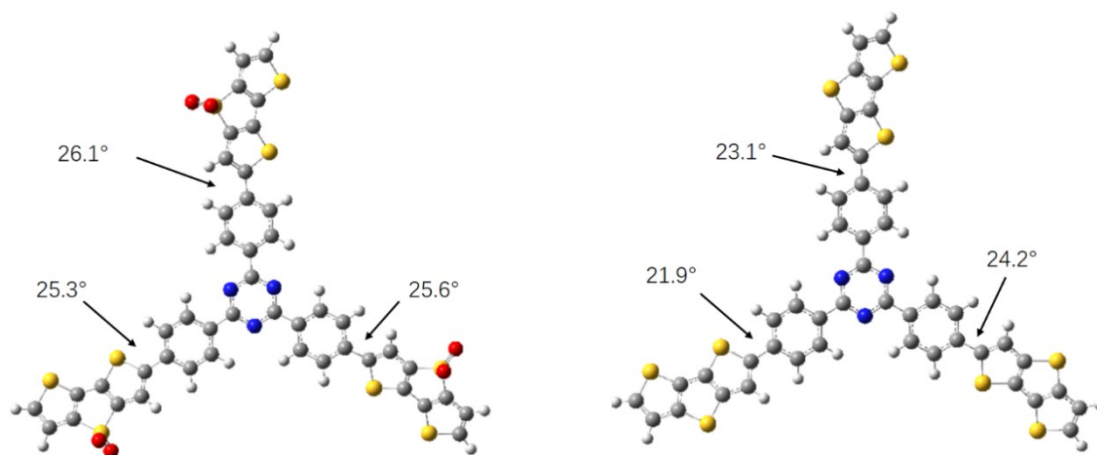
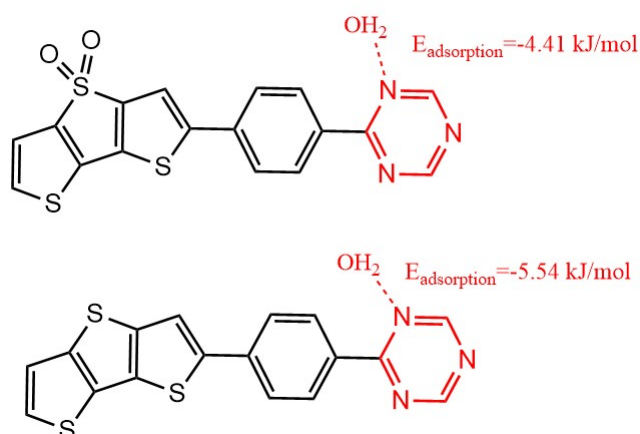


Figure S8. DFT geometry optimization and the dihedral angles of the polymers.



Theoretical and experimental level distribution and the adsorption energy of water molecules

CMPs	$E_{CB}(eV)$	$E_{VB}(eV)$	$E_{g,opt}(eV)$	$LUMO_{cal}(eV)$	$HOMO_{cal}(eV)$	$E_{g,cal}$	$E_{adsorption}(kJ/mol)$
TzDTDO	-3.17	-5.37	2.20	-2.82	-6.06	3.24	-4.41
TzDTT	-2.77	-5.01	2.24	-5.60	-5.60	3.19	-5.54

Figure S9. The Models of the two polymers and water molecule calculated by DFT theory.

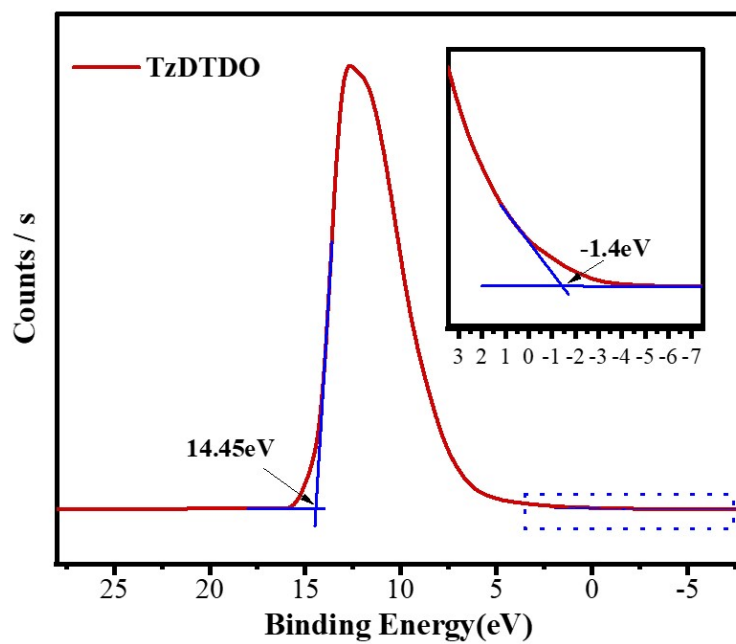


Figure S10. UPS spectrum of TzDTDO.

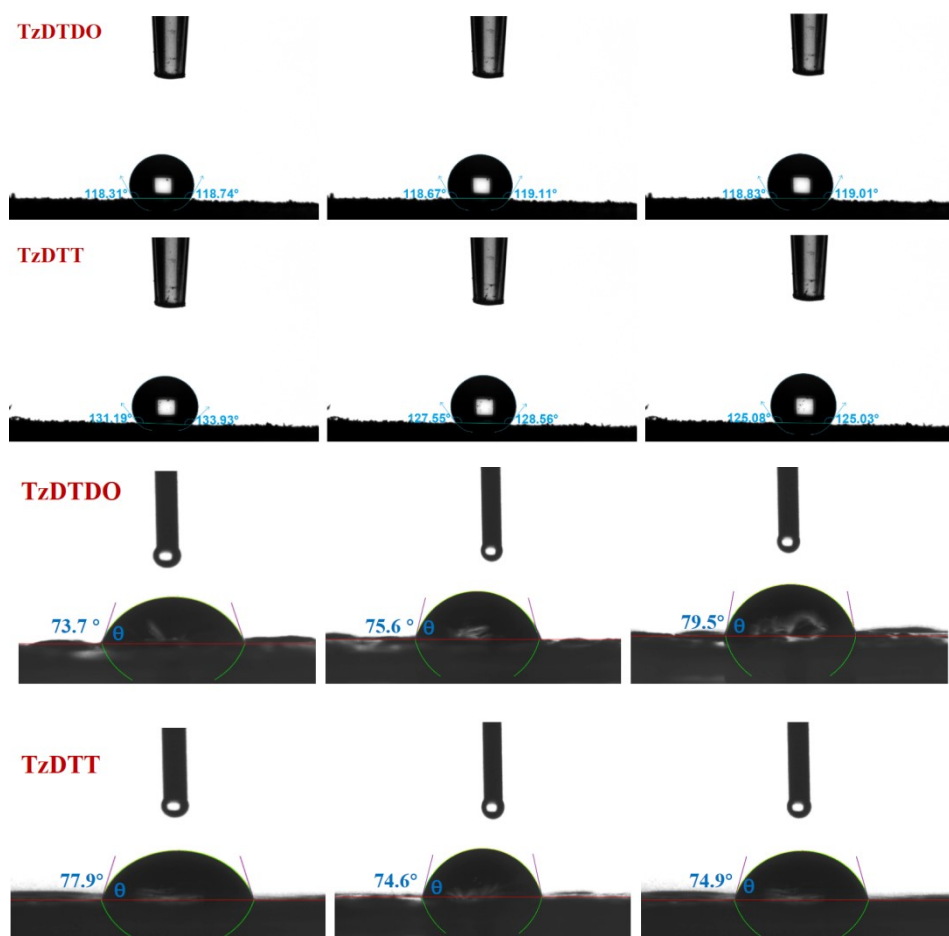


Figure S11. The contact angles of the two polymers.

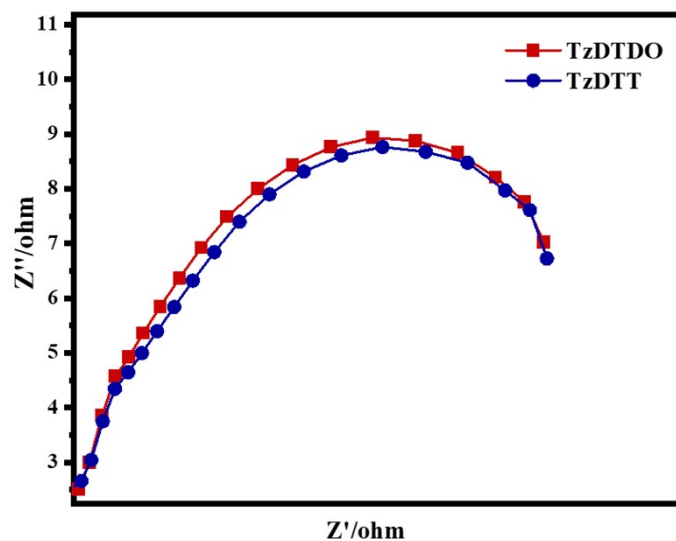


Figure S12. Electrochemical impedance spectroscopy (EIS) Nyquist plots of the polymers.

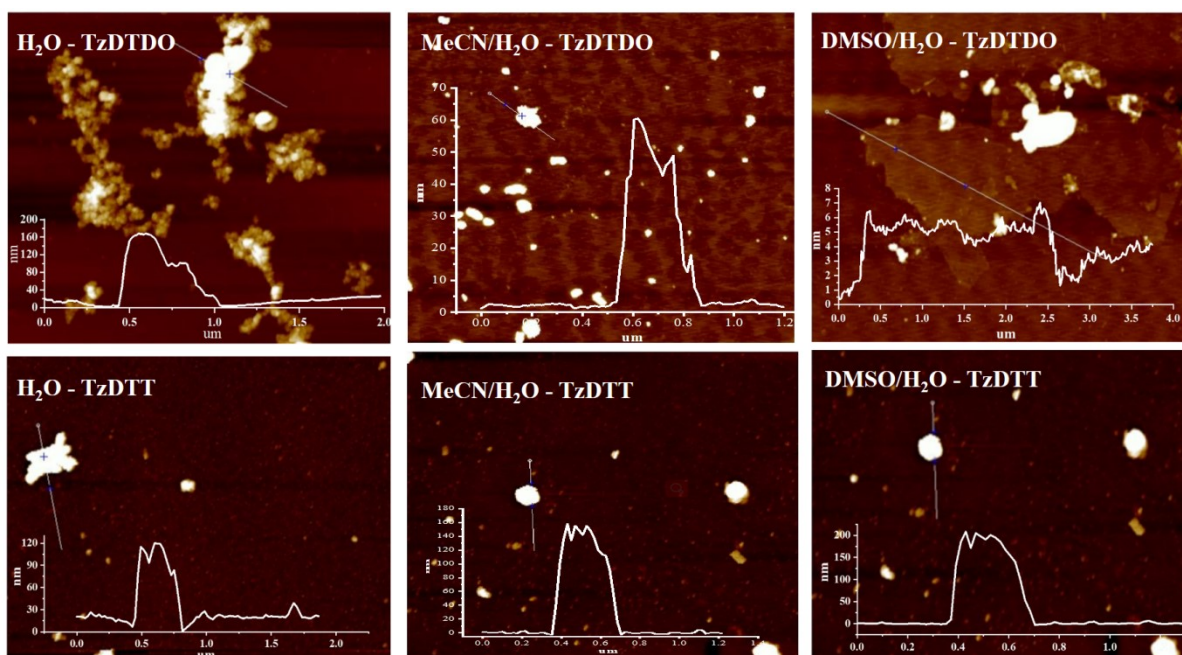


Figure S13. The AFM image of the two polymers dispersed ultrasonically in H₂O, MeCN/H₂O (1:2) and DMSO/H₂O (1:2), respectively.

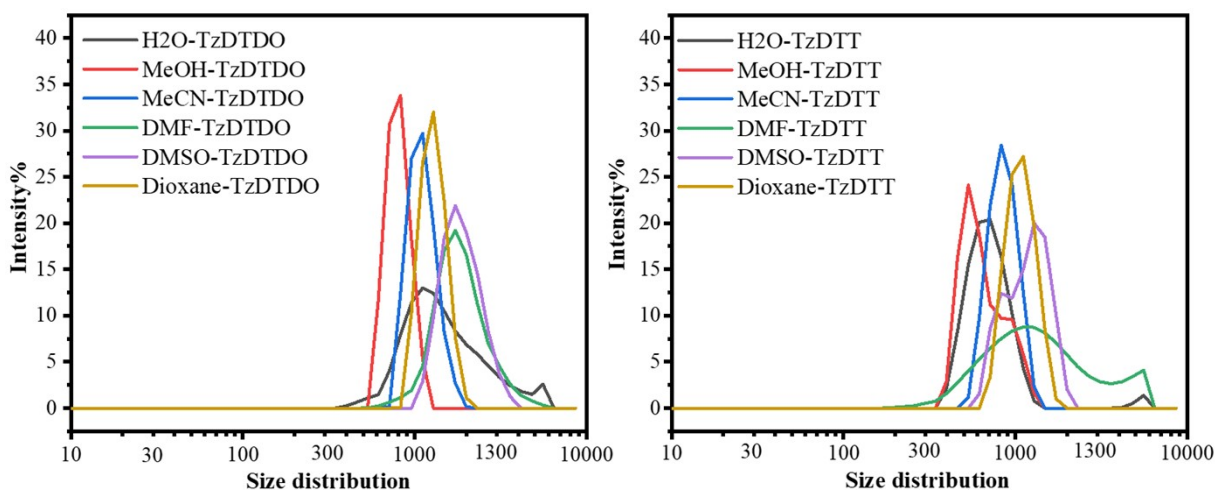


Figure S14. The size distribution of the two polymers measured by dynamic light scattering (DLS).

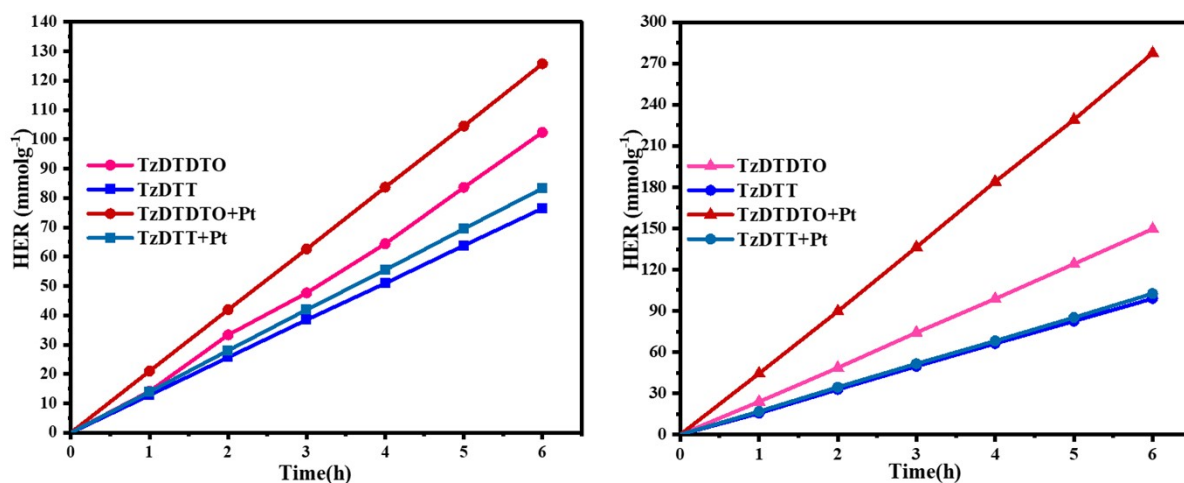


Figure S15. The HER performance of the two polymers under the light irradiation of >420 nm (left) and AM1.5G (right figure) with AA as the electron sacrificial agent (right).

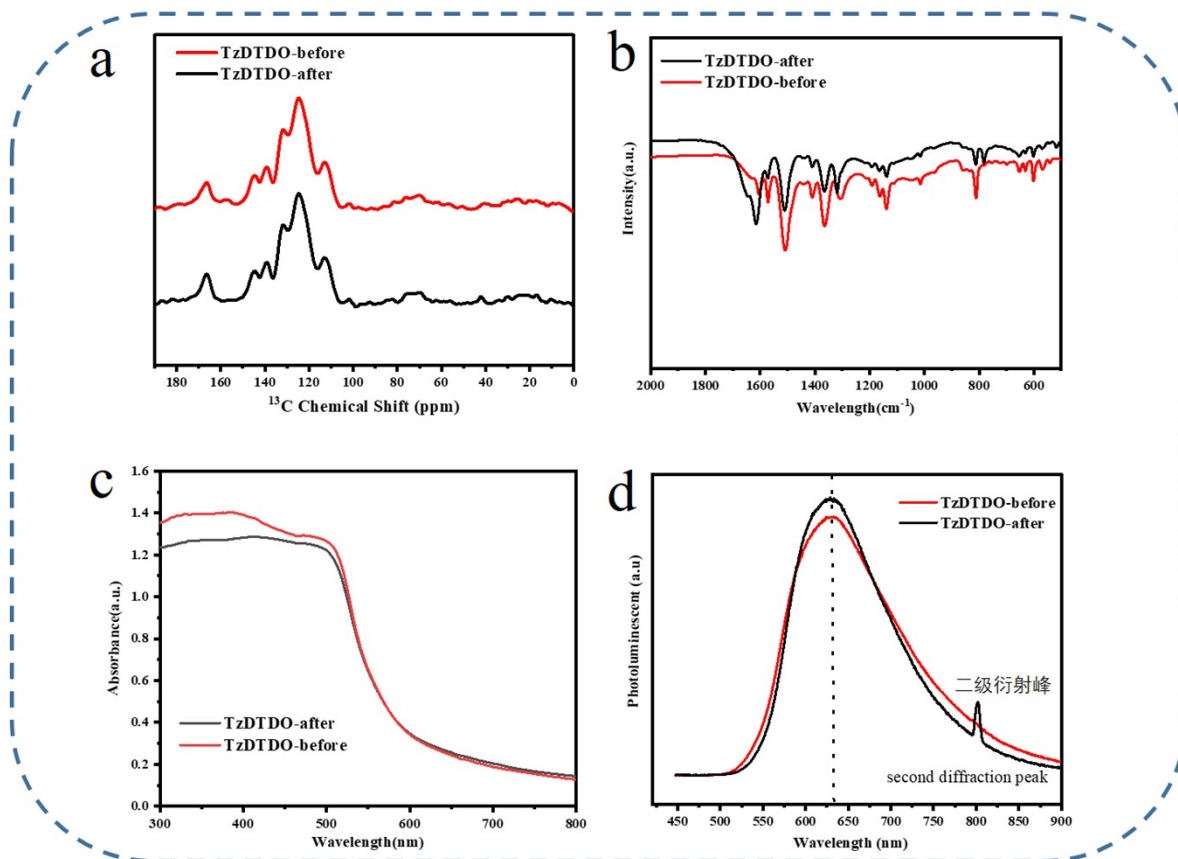


Figure S16. (a)The solid ^{13}C NMR, (b)FT-IR, (c)solid UV/Vis and (d)PL spectra of TzDTDO before/after PHP in $\text{H}_2\text{O}/\text{AA}$ for 24 h.

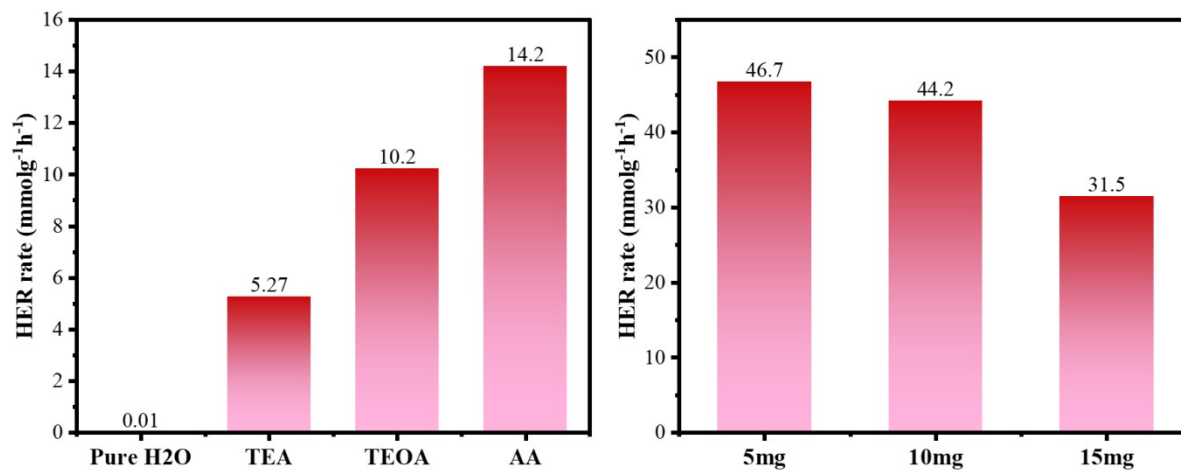


Figure S17. The HER rates of TzDTDO with different electron sacrificial agent (left) and in the presence of different amounts of photocatalyst (right).

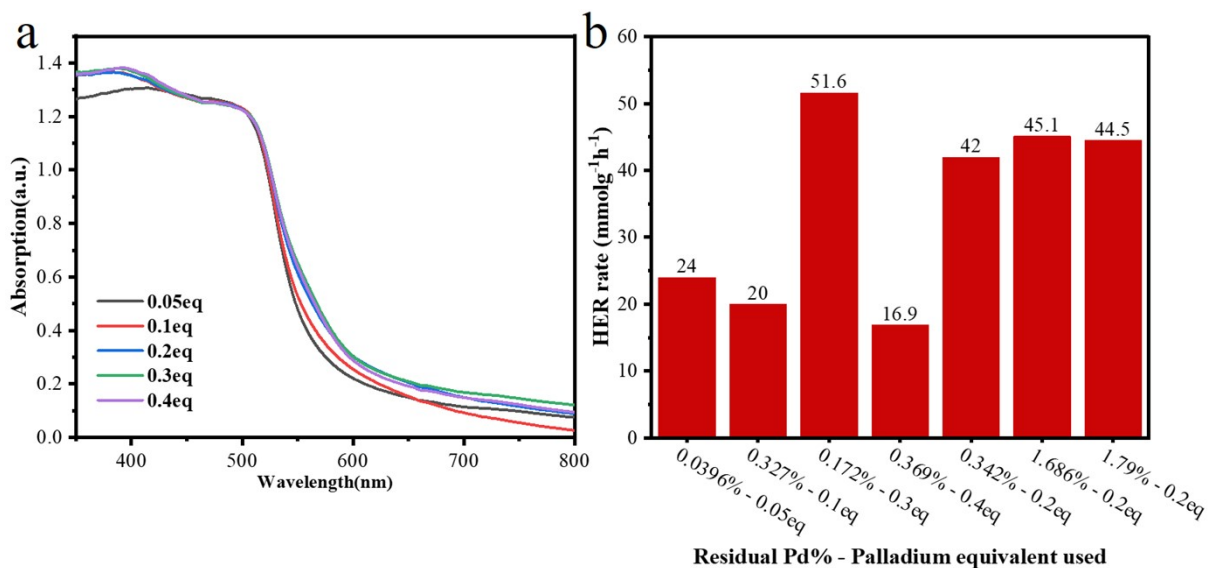


Figure S18. (a) DRS UV/Vis spectra of **TzDTDO** samples which were synthesized in the presence of various equivalents of catalyst $\text{Pd}(\text{PPh}_3)_4$. (b) HER performance of **TzDTDO** samples with residual Pd in various different masses.

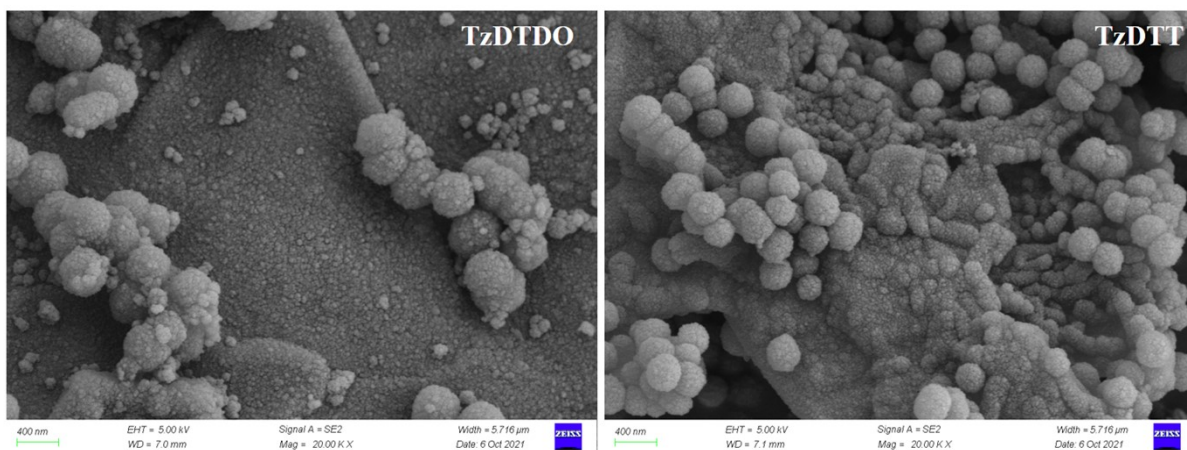


Figure S19. Morphology characterizations (SEM) after 24 h HER stability test.

Table S2. Fitted decay time in TRPL spectra of the two CMPs.

The fitting equation: $y = A + B_1 \cdot \exp(-x/\tau_1) + B_2 \cdot \exp(-x/\tau_2) + B_3 \cdot \exp(-x/\tau_3)$

sample	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	A	B ₁ %	B ₂ %	B ₃ %	Chi.sq(variance)
TzDTDO	0.167845	0.0446838	0.589145	3.44187	49.82	37.08	13.10	1.136915
TzDTT	0.0888652	0.096708	0.0966508	1.55839	0.36	49.65	50.00	1.085422

Table S3. PHP Performance of **TzDTDO** and the other reported CMPs.

Photocatalyst	cocatalyst	PHP (mmol g ⁻¹ h ⁻¹)	Irradiation light	AQY%	Reference
TzDTDO	3 wt% Pt	45.1	AM1.5	7.74(10 mg@420 nm)	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
TtaTfa	3 wt% Pt	20.7	>420 nm	1.43@450 nm	3
PyTP-2	No	33.07	>420 nm	14.8@500 nm	4
PBDTTS-1SO	3 wt% Pt	97.1	>420 nm	18@500 nm	5
BTT-CPP	No	37.86	UV-vis	3.3@365 nm	6
BSO ₂ -EDOT	No	158	>420 nm	13.6@550 nm	7
PDBTSSO-T	3 wt% Pt	147	UV-vis	No	8
TP-BTDO-2	No	108.59	>420 nm	30.48@520 nm	9
CTF NSs	No	25.7	>420 nm	No	10
PyBS-3	3 wt% Pt	43	>420 nm	29.2@420 nm	11
PyTz-COF	3 wt% Pt	2.07	AM1.5	No	12
BTH-3	No	15.1	>420 nm	1.256@500nm	13
CMPBDP@T-10	1 wt% Pt	40	UV-vis	No	14
Py-Tt	No	45.8	UV-vis	No	15
triazine-Ph-CPP	No	16.28	UV-vis	61.5@365 nm	16
PDBTSSO	3 wt% Pt	44.2	>420 nm	No	17
PyDTDO-3	No	16.32	>420 nm	3.93@550 nm	18
PyDF	3 wt% Pt	18.93	UV-vis	4.5@400 nm	19
CP-St	No	105.4	>420 nm	11.4@550 nm	20
FS-COF	3 wt% Pt	10.1	AM1.5G	7.8@420 nm	21
ter-CTF-0.7	3 wt% Pt	19.3	>420 nm	22.8@420 nm	22

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