Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Two consecutive postsynthetic modifications of benzothiadiazole-based conjugated polymer for enhanced photocatalytic H_2 evolution: the significance of sulfinyl group

*Xiaodong Zhao, [§] Bo Chen, [§] Wenbo Dong, Shengyao Wang, Yonggang Xiang * and Hao Chen**

[§] X.D. Zhao and B. Chen contributed equally to this work.

X.D. Zhao, B. Chen, W. B. Dong, S. Y. Wang, Prof. Y. G. Xiang, Prof. H. Chen
College of Science
Huazhong Agricultural University
Wuhan 430070, P. R. China
E-mail: hchenhao@mail.hzau.edu.cn, ygxiang@mail.hzau.edu.cn

Table of Contents

1. Materials and Methods

2. Synthetic procedures

3. Figures and Tables

4. References

1. Materials and Methods

General characterization

Liquid ^1H NMR and ^{13}C NMR spectra of all monomers were acquired at room temperature on Bruker Avance spectrometer (600 MHz for proton, 150 MHz for carbon) and were referenced to CDCl3 (7.26 and 77.16 ppm for ^1H and ^{13} C respectively). ^{13}C cross-polarization/magic angle spinning solid-state nuclear magnetic resonance (CP/MAS ssNMR) spectra were recorded on a Bruker AVANCE III 400 WB spectrometer operating at contact time of 2 ms (ramp 100) and a pulse delay of 3 s with a 4-mm double resonance probe. The Fourier transform infrared (FT-IR) measurements were performed on Nicolet FT-IR spectrometer. X-ray photoelectron spectroscopy (XPS) experiments were carried out on the Kratos XSAM800 spectrometer with the C 1s value was set at 284.6 eV for charge corrections. Elemental analysis was conducted with elemental analyzer (EA) on a Vario-EL Cube. The UV-vis diffuse reflectance spectra were obtained from Shimadzu UV-3100 spectrophotometer. Thermogravimetric analysis (TGA) was evaluated using NETZSCH TG209 under air environment over the temperature range from room temperature to 800 ^oC with a heating rate of 10 ^oC/min. Water contact angle measurements were taken on Dataphysics OCA15EC. The specific Brunauer-Emmett-Teller (BET) surface area and pore volumes were measured using by nitrogen adsorption and desorption isotherms on Micrometrics ASAP 2040. The Pd residue was determined by inductively coupled plasma-mass spectrometry (ICP-MS) on Agilent 7900. The steady-state photoluminescence (PL) measurements were carried out on Hitachi F-4600. The time-correlated single photon counting data were collected on Edinburgh Instruments F35 spectrofluorometer.

Electrochemical measurement

The electrochemical measurements were performed on the CHI660E workstation (Chenhua Instruments, China), and the standard three-electrode system includes platinum plate as the counter electrode, Ag/AgCl electrode as the reference electrode, and a working electrode. The working electrode was prepared as follows: 15 mg of each sample was thoroughly mixed with 200 μL isopropanol containing 5% Nafion, and the resulting suspension was carefully loaded on the ITO glass substrate (10 × 2.5 × 1.1 mm) and dried at 60 °C under vacuum for 1 h. 0.1 M Na_2SO_4 aqueous solution acted as the electrolyte for the photocurrent test while the aqueous solution of 0.1 M KCl and 0.005 M $K_3[Fe(CN)_6]$ was employed as the electrolyte for the electrochemical impedance spectroscopy (EIS) measurement. For cyclic voltammetry (CV) measurement, 0.1 M $TBAPF_6$ in CH_3CN solution was used as the electrolyte. The HOMO energy levels (E_{HOMO}) was calculated from onset oxidation potentials of CV curves according to the equation: E_{HOMO} =-(E^{ox} + 4.8 eV (v Ag/Ag$^+$) – $E^{\mathrm{ox}}{}_{\mathrm{Fc/Fc+}}$), and $E^{\mathrm{ox}}{}_{\mathrm{Fc/Fc+}}$ is the oxidation potential of ferrocene/ferrocenium (Fc/Fc$^+$) couple for the calibration. The Standard Hydrogen Electrode (SHE) could be derived from: E_{HOMO} (SHE) = – 4.5 eV - E_{HOMO}

Photocatalytic H_2 production procedure

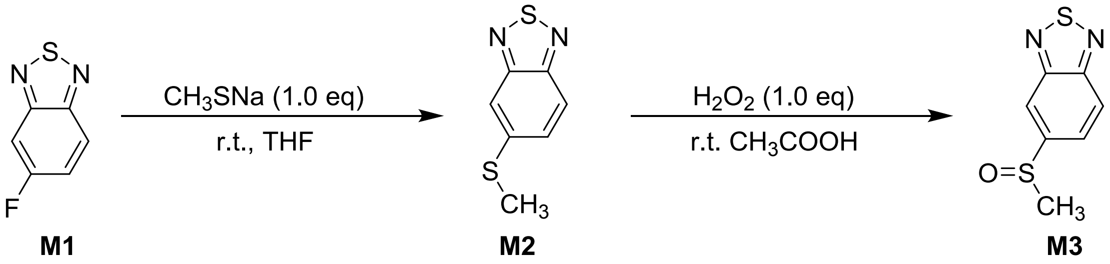
The photocatalytic hydrogen evolution experiments of all the conjugated polymers were performed in a Pyrex top-irradiation vessel with a closed gas circulation system, and 300 W Xe-lamp (PLS SXE300/300UV, Beijing Perfect Light Co., China) was used as the light source. First, the suspension of the as-prepared photocatalyst (20 mg) in a fresh aqueous solution (30 mL) containing 10 vol% triethanolamine (TEOA) was ultrasonically dispersed for ca. 10 min, and then the mixture was transferred to the reaction vessel equipped with circulating cooling water. After being vacuumed for 10 min to exclude the dissolved air by oil pump, the suspension was irradiated with the Xe lamp equipped with a UV cut-off (λ > 420 nm) filter. The hydrogen evolution rate was was calculated using a online gas chromatography (SP7820, 5 Å molecular sieve columns, Ar carrier, and TCD detector).

The apparent quantum yield (AQY) for hydrogen evolution was measured similar the process of Photocatalytic H_2 production except the replacement of cut-off (λ > 420 nm) filter by band-pass filter (λ = 420, 450 nm, etc.) in order to achieve monochromatic light. The AQY was calculated by the following formula:

$$\text{AQY (\%)} = \frac{2 \times \text{Number of evolved } H_2 \text{ molecules}}{\text{Number of incident photons}} \times 100\% = = \frac{2 \times C \times N_A}{S \times P \times t \times \lambda / (h \times c)} \times 100\%$$

2. Synthetic procedures

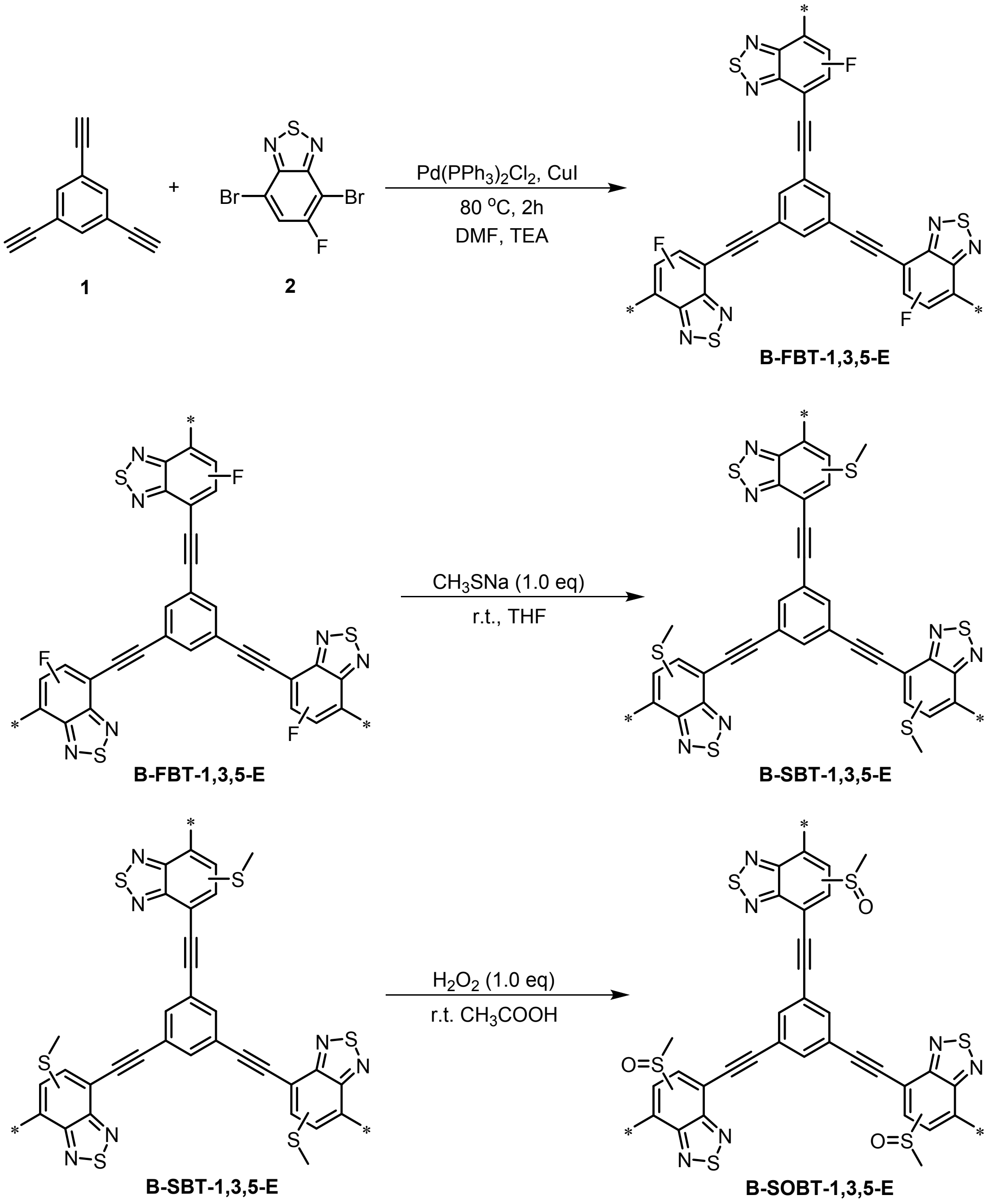
Synthesis of M2 and M3



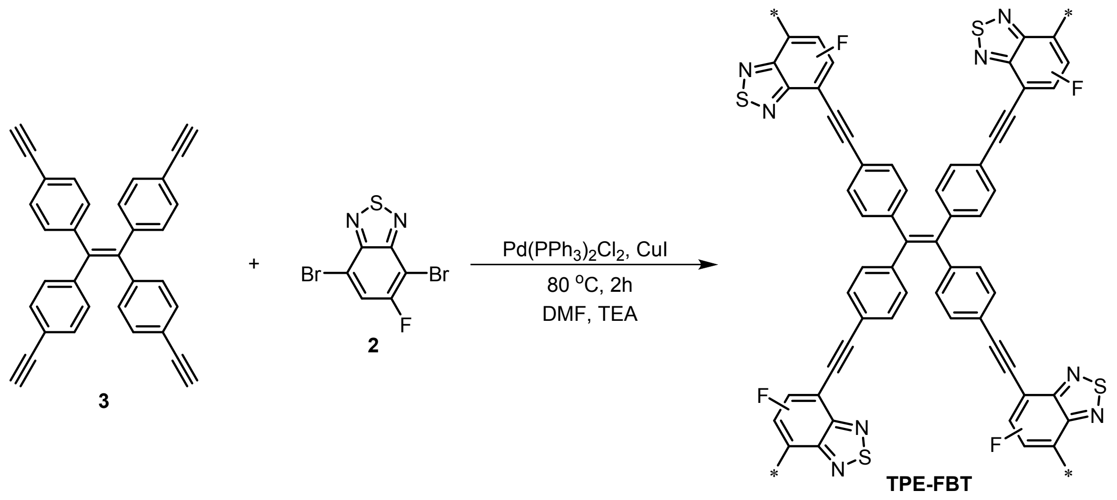
5-(methylthio)benzo[c][1,2,5]thiadiazole M2: A 250 mL round bottom flask was charge with 5-fluorobenzo[c][1,2,5]thiadiazole **M1** (1.54 g, 10.0 mmol) and THF (120 mL), and then a 20 wt.% aqueous solution of CH_3SNa (3.50 g, 10.0 mmol) was added. The mixture was stirred at room temperature for 24 h under argon atmosphere, and then the concentrated residue was purified by flash chromatography on silica gel using dichloromethane and petroleum ether (1:4) as eluent to afford the product **M2** (1.25 g 67% yield). ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.84 (d, J = 9.2 Hz, 1H), 7.60 (d, J = 1.3 Hz, 4H), 7.42 (dd, J = 9.2, 1.5 Hz, 1H), 2.59 (s, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 155.5, 153.2, 142.9, 130.1, 121.0, 113.9, 15.3.

5-(methylsulfinyl)benzo[c][1,2,5]thiadiazole M3: To the solution of **M1** (364 mg, 2.0 mmol) in CH_3COOH (10 mL) was added a 30 wt.% aqueous solution of H_2O_2 (227 mg, 2.0 mmol) slowly, and the resulting mixture was stirred at room temperature for 30 min. The reaction was quenched with water, diluted with EtOAc. The organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The crude product was purified by flash chromatography on silica gel using dichloromethane and petroleum ether (1:4) as eluent to afford the product **M3** (1.25 g 67% yield). ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.74 (d, J = 1.1 Hz, 1H), 8.22 (d, J = 9.1 Hz, 4H), 8.06 (dd, J = 9.1, 1.7 Hz, 1H), 3.17 (s, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 156.2, 153.6, 141.7, 125.8, 123.5, 123.3, 44.5.

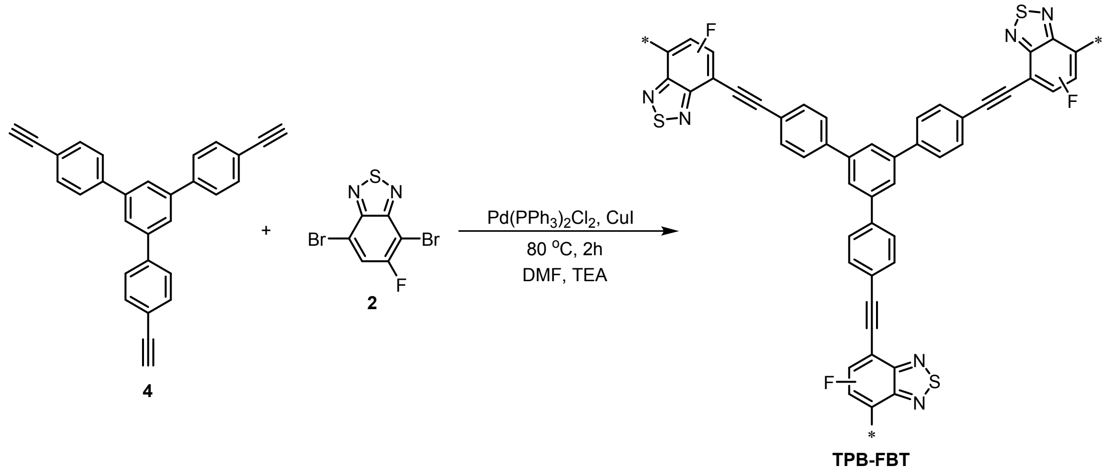
Synthetic procedures of B-FBT-1,3,5-E, B-SBT-1,3,5-E, B-SOBT-1,3,5-E



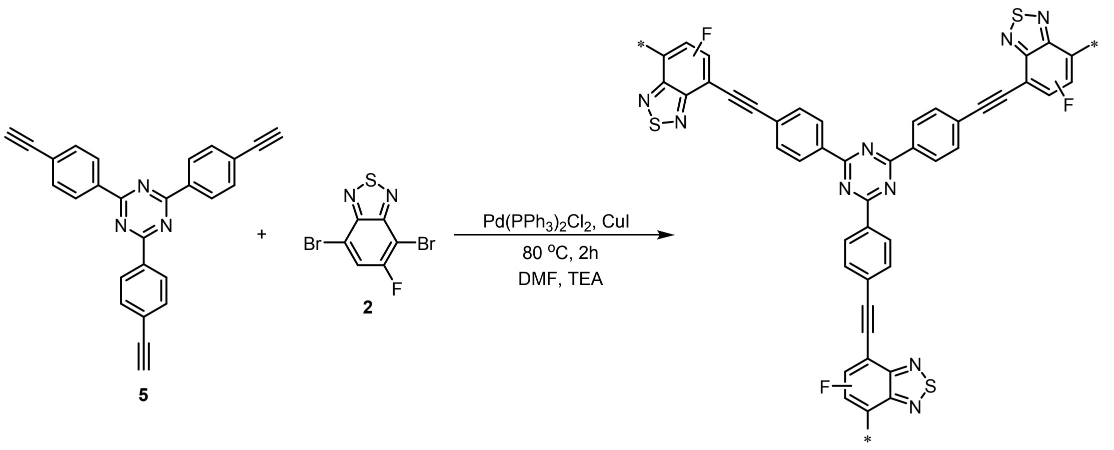
Synthesis of TPE-FBT, TPB-FBT and TPA-FBT: All of them were prepared following the procedure of B-FBT-1,3,5-E



TPE-FBT: 1,1,2,2-tetrakis(4-ethynylphenyl)ethene **3** (480 mg, 1.12 mmol), 4,7-dibromo-5-fluorobenzo[c][1,2,5]thiadiazole **2** (700 mg, 2.24 mmol), Pd $(PPh_3)_2Cl_2$ (20 mg, 0.03 mmol), CuI (5 mg, 0.03 mmol), DMF (75 mL) and TEA (75 mL). 706 mg product was obtained (Yield: 86%).



TPB-FBT: 2,4,6-tris(4-ethynylphenyl)-benzene **4** (400 mg, 1.06 mmol), 4,7-dibromo-5-fluorobenzo[c][1,2,5]thiadiazole **2** (495 mg, 1.59 mmol), Pd $(PPh_3)_2Cl_2$ (50 mg, 0.07 mmol), CuI (10 mg, 0.05 mmol), DMF (70 mL) and TEA (70 mL). 530 mg product was obtained (Yield: 83%).



TPA-FBT

TPA-FBT: 2,4,6-tris(4-ethynylphenyl)-1,3,5-triazine **5** (400 mg, 1.05 mmol), 4,7-dibromo-5-fluorobenzo[c][1,2,5]thiadiazole **2** (491 mg, 1.57 mmol), Pd $(PPh_3)_2Cl_2$ (50 mg, 0.07 mmol), CuI (10 mg, 0.05 mmol), DMF (125 mL) and TEA (125 mL). 566 mg product was obtained (Yield: 89%).

Synthesis of TPE-SBT, TPB-SBT and TPA-SBT: All of them were prepared following the procedure of B-SBT-1,3,5-E

TPE-SBT: TPE-FBT (290 mg), THF (40 mL), CH_3SNa (280 mg). 303 mg product was obtained (Yield: 97%).

TPB-SBT: TPB-FBT (380 mg), THF (50 mL), CH_3SNa (331 mg). 395 mg product was obtained (Yield: 97%).

TPA-SBT: TPA-FBT (360 mg), THF (50 mL), CH_3SNa (312 mg). 379 mg product was obtained (Yield: 99%).

Synthesis of TPE-SOBT, TPB-SOBT and TPA-SOBT: All of them were prepared following the procedure of B-SOBT-1,3,5-E

TPE-SOBT: TPE-SBT (150 mg), CH_3COOH (50 mL), H_2O_2 (400 mg). 156 mg product was obtained (Yield: 98%).

TPB-SOBT: TPB-SBT (160 mg), CH_3COOH (25 mL), H_2O_2 (180 mg). 162 mg product was obtained (Yield: 98%).

TPA-SOBT: TPA-SBT (160 mg), CH_3COOH (25 mL), H_2O_2 (177 mg). 160 mg product was obtained (Yield: 96%).

3. Figures and Tables

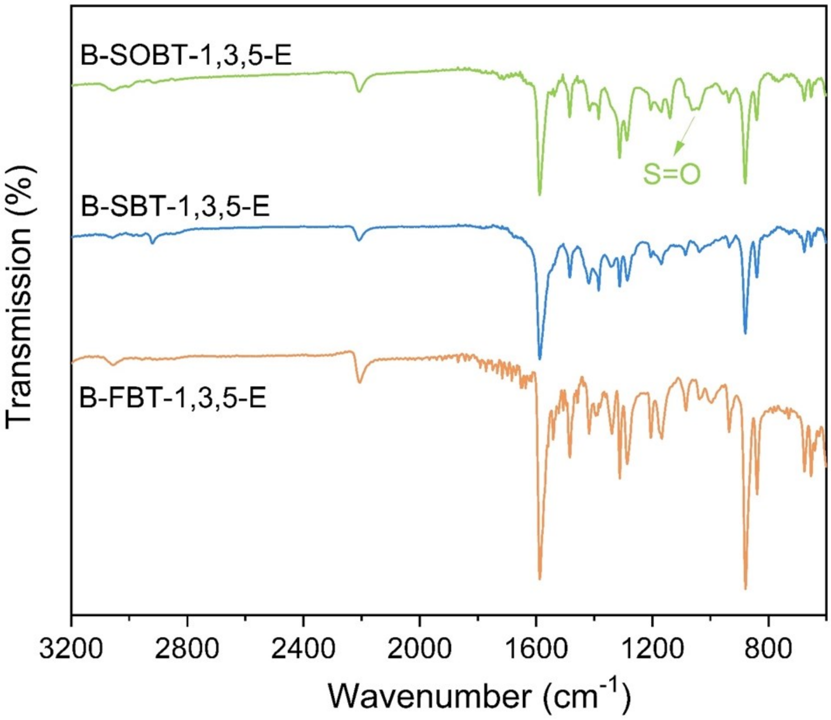


Fig. S1 XSP survey spectra of B-FBT-1,3,5-E, B-SBT-1,3,5-E, B-SOBT-1,3,5-E.

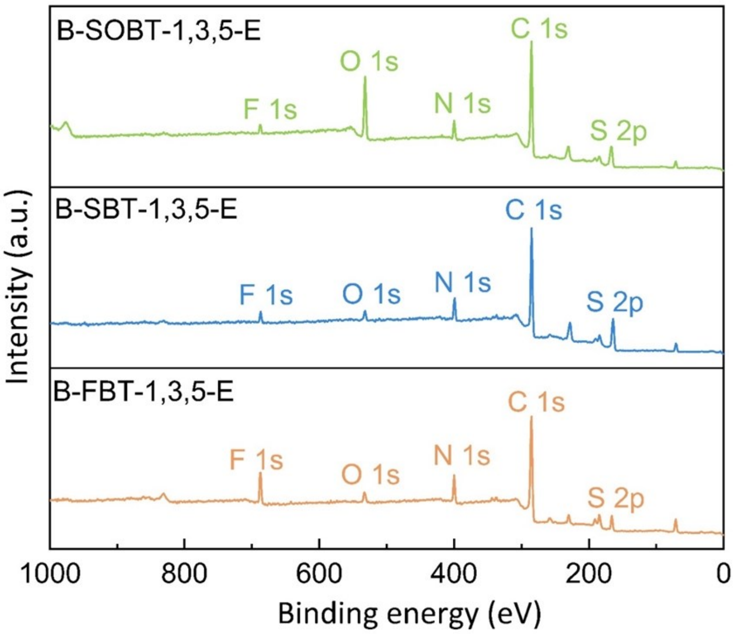


Fig. S2 XSP survey spectra of B-FBT-1,3,5-E, B-SBT-1,3,5-E, B-SOBT-1,3,5-E.

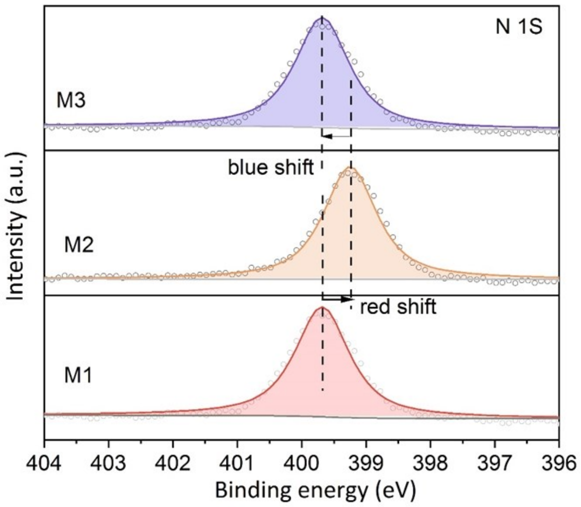


Fig. S3 High-resolution N 1s XPS spectra of **M1**, **M2** and **M3**.

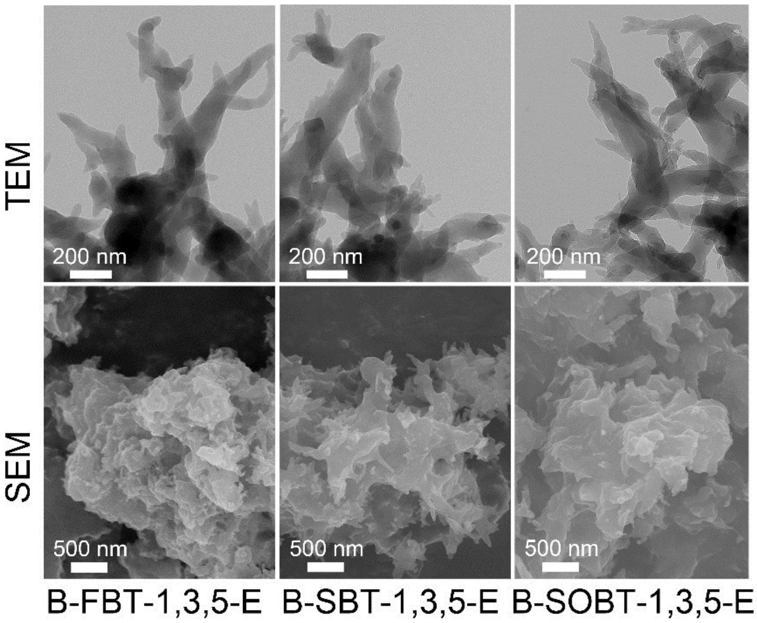


Fig. S4 TEM and SEM images of B-FBT-1,3,5-E, B-SBT-1,3,5-E, B-SOBT-1,3,5-E.

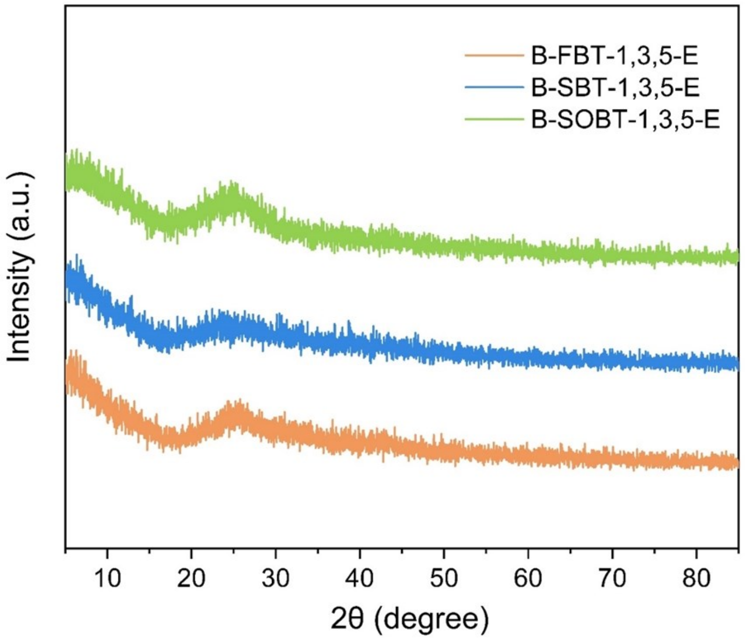


Fig. S5 PXRD patterns of B-FBT-1,3,5-E, B-SBT-1,3,5-E, B-SOBT-1,3,5-E.

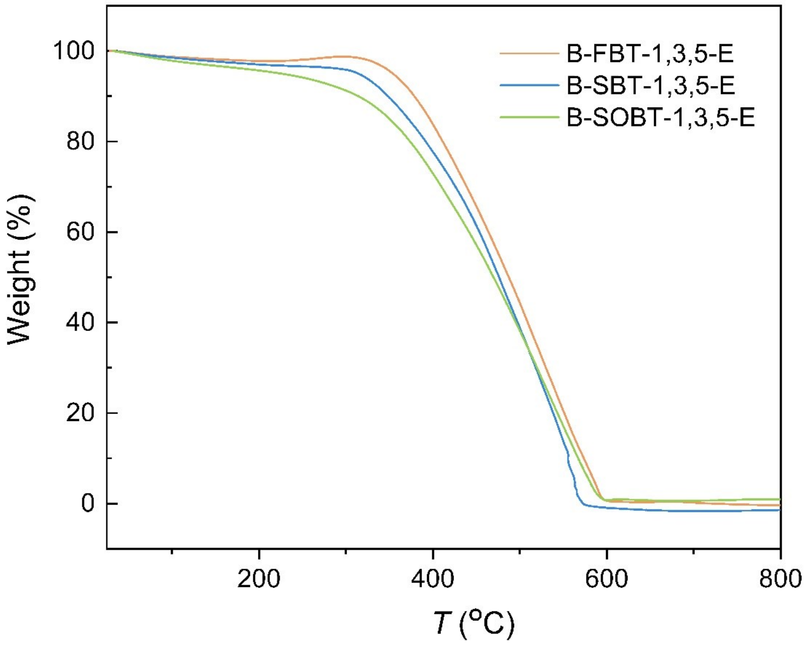


Fig. S6 Thermal gravimetric analysis of B-FBT-1,3,5-E, B-SBT-1,3,5-E, B-SOBT-1,3,5-E under air atomsphere.

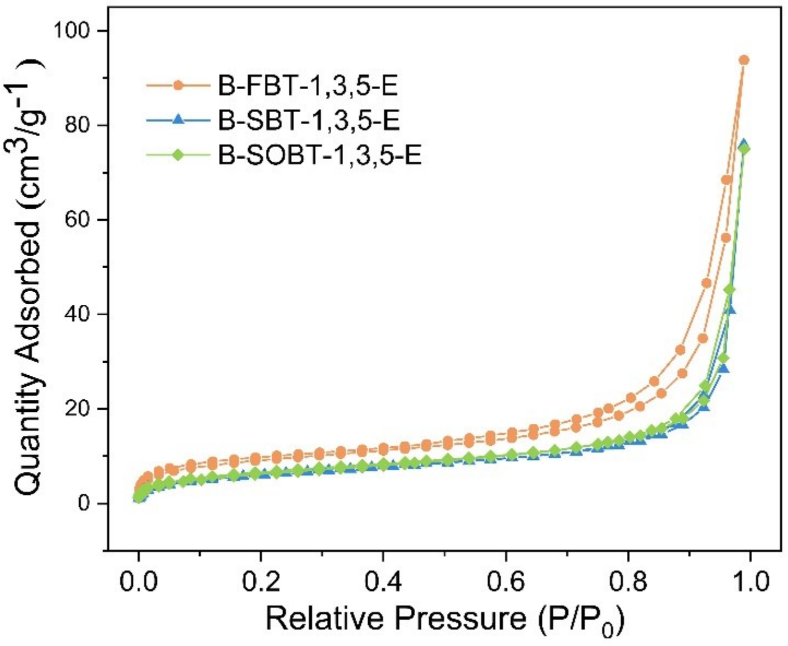


Fig. S7 Nitrogen adsorption and desorption isotherm curves of B-FBT-1,3,5-E, B-SBT-1,3,5-E, B-SOBT-1,3,5-E.

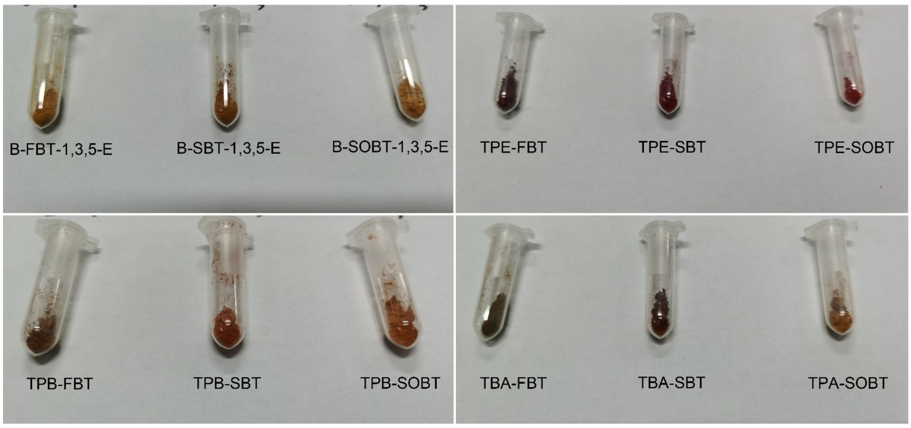


Fig. S8 Solid colors comparison before and after the PSM

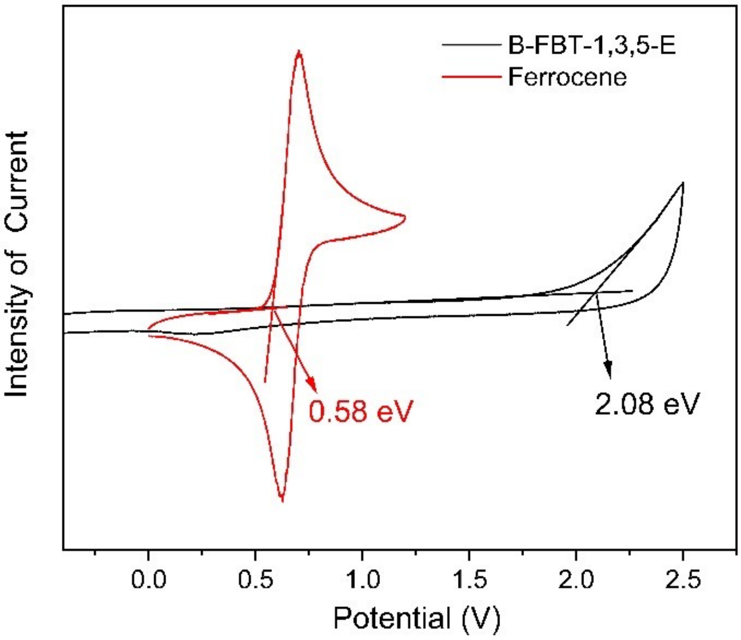


Fig. S9 Cyclic voltammetry measurements of Fc/Fc$^+$ and B-FBT-1,3,5-E.

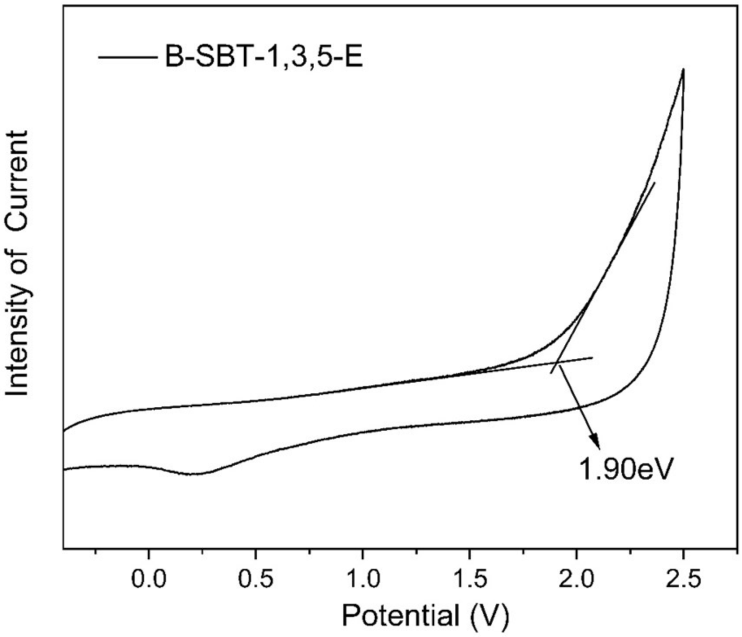


Fig. S10 Cyclic voltammetry measurements of B-SBT-1,3,5-E.

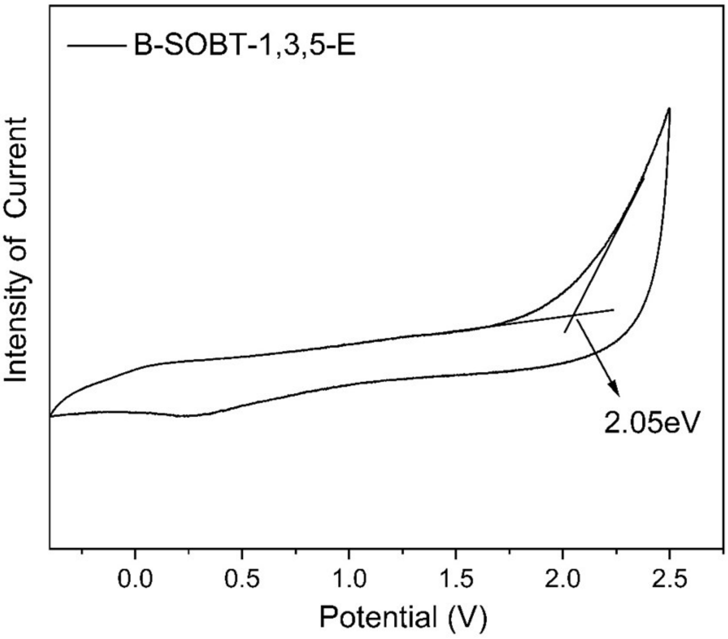


Fig. S11 Cyclic voltammetry measurements of B-SOBT-1,3,5-E.

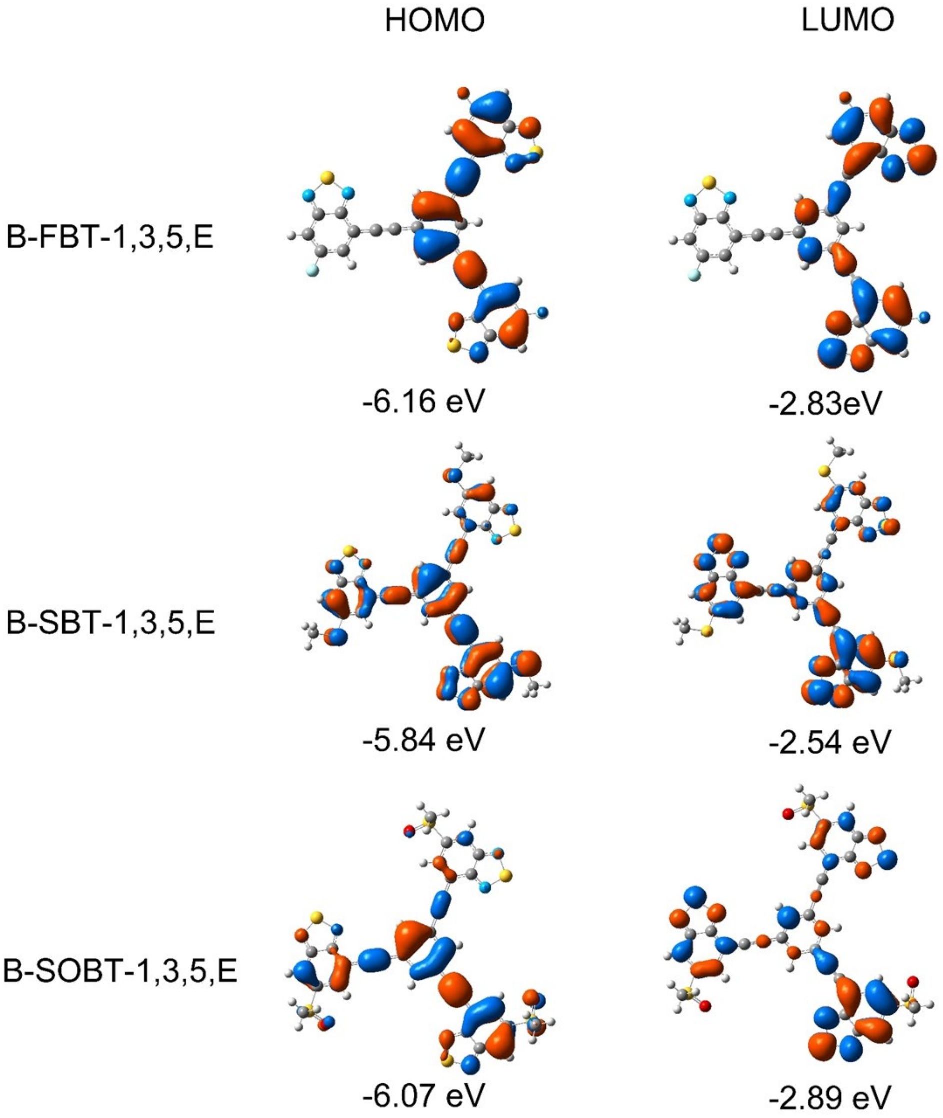


Fig. S12 Frontier molecular orbital (FMO) wave function distribution and energy levels for the oligomers of repeat units of benzene and substituted BT at the optimized geometries. Calculations were carried out at the DFT//b3lyp/6-31g (d, p) level.

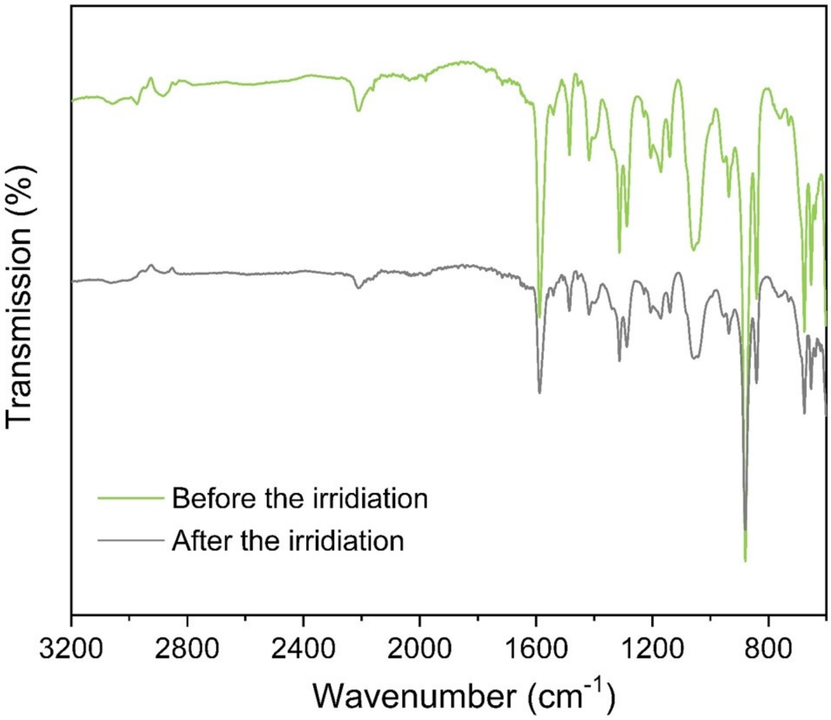


Fig. S13 FTIR comparison before and after the photocatalytic reaction

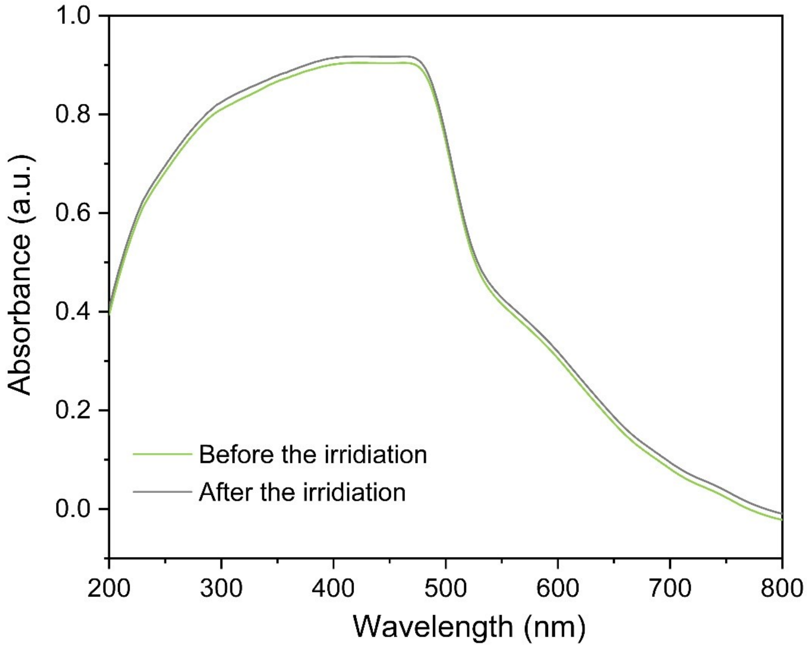


Fig. S14 DRS comparison before and after the photocatalytic reaction

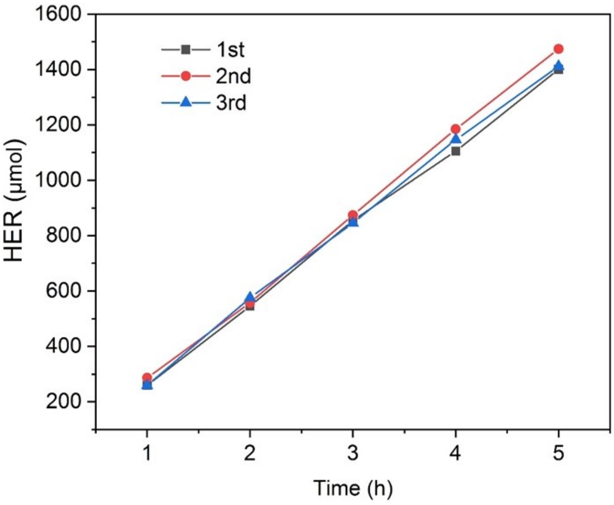


Fig. S15 Batch-to-batch Photocatalytic H_2 evolution rate of B-SOBT-1,3,5-E

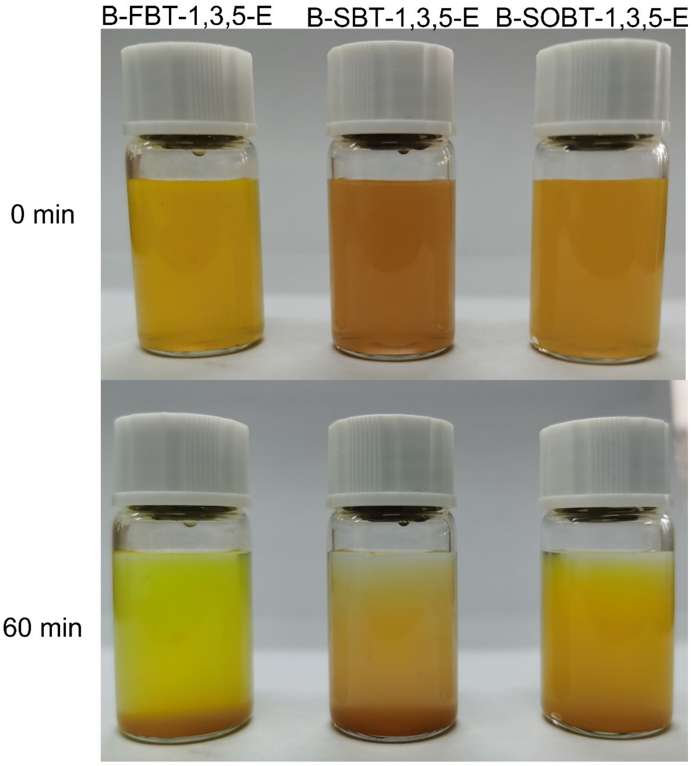


Fig. S16 Dispersion measurements of B-FBT-1,3,5-E, B-SBT-1,3,5-E, B-SOBT-1,3,5-E. in TEOA/H2O after standing for 10 min

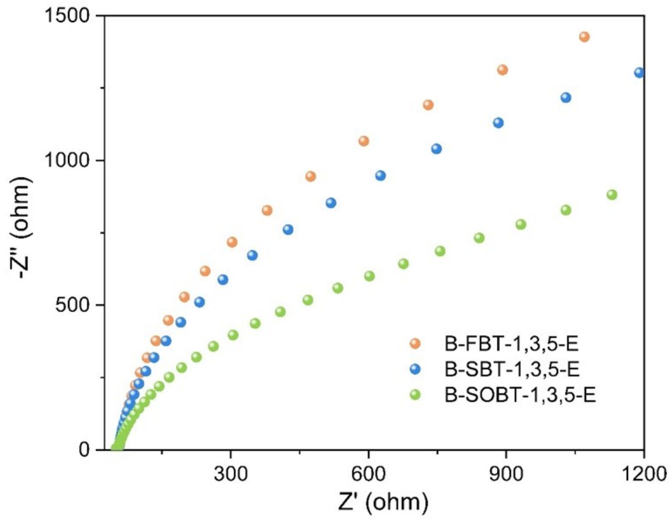


Fig. S17 electrochemical impedance spectroscopy plots of B-FBT-1,3,5-E, B-SBT-1,3,5-E, B-SOBT-1,3,5-E.

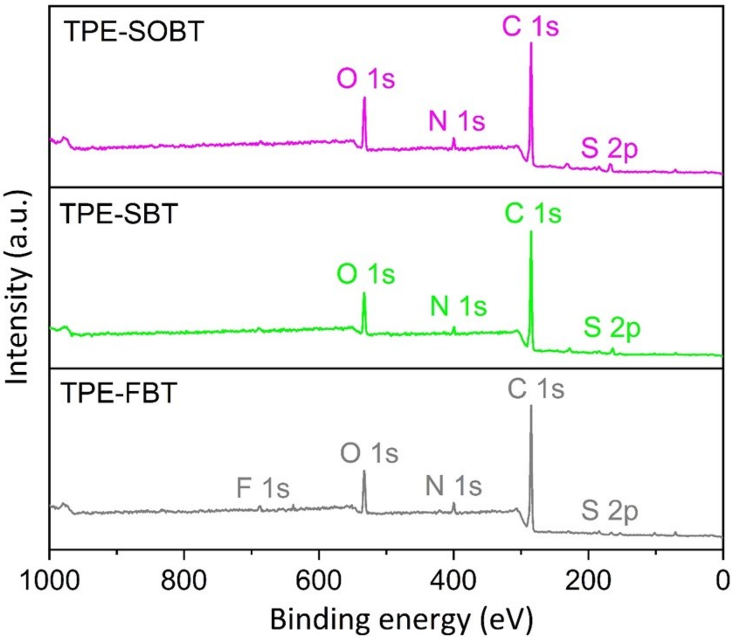


Fig. S18 XSP survey spectra of TPE-FBT, TPE-SBT, TPE-SOBT.

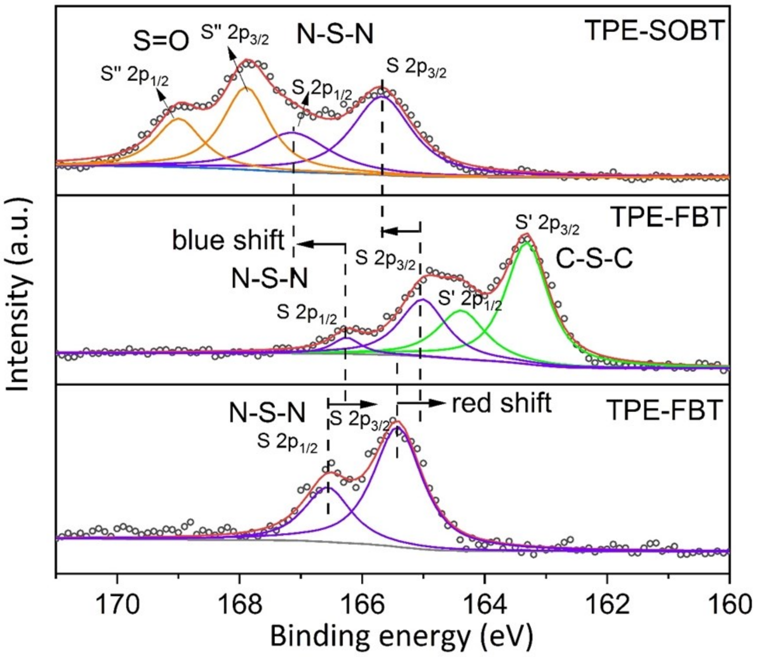


Fig. S19 High-resolution S 2p XPS spectra of TPE-FBT, TPE-SBT, TPE-SOBT.

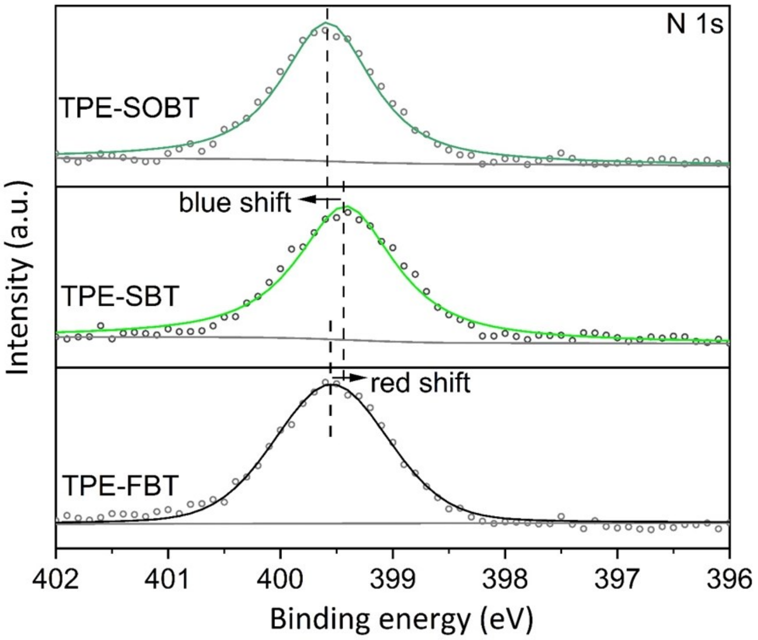


Fig. S20 High-resolution S 2p XPS spectra of TPE-FBT, TPE-SBT, TPE-SOBT.

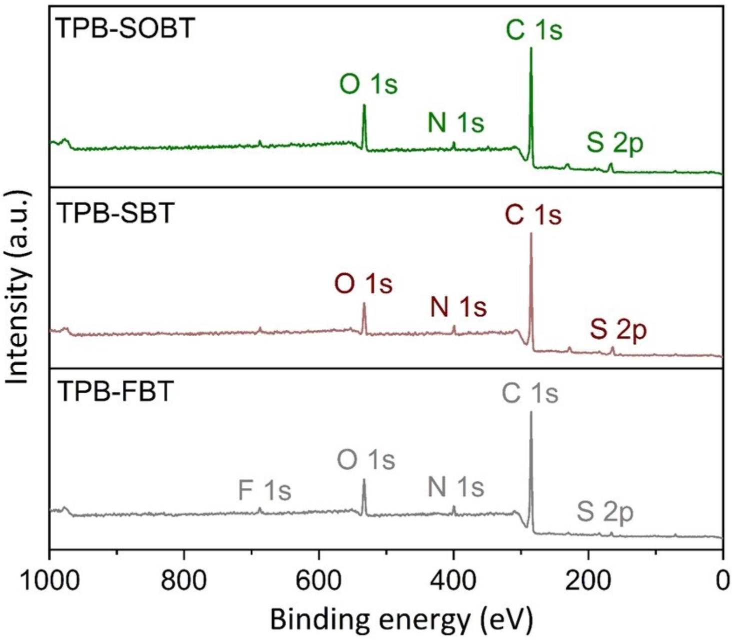


Fig. S21 XSP survey spectra of TPB-FBT, TPB-SBT, TPB-SOBT.

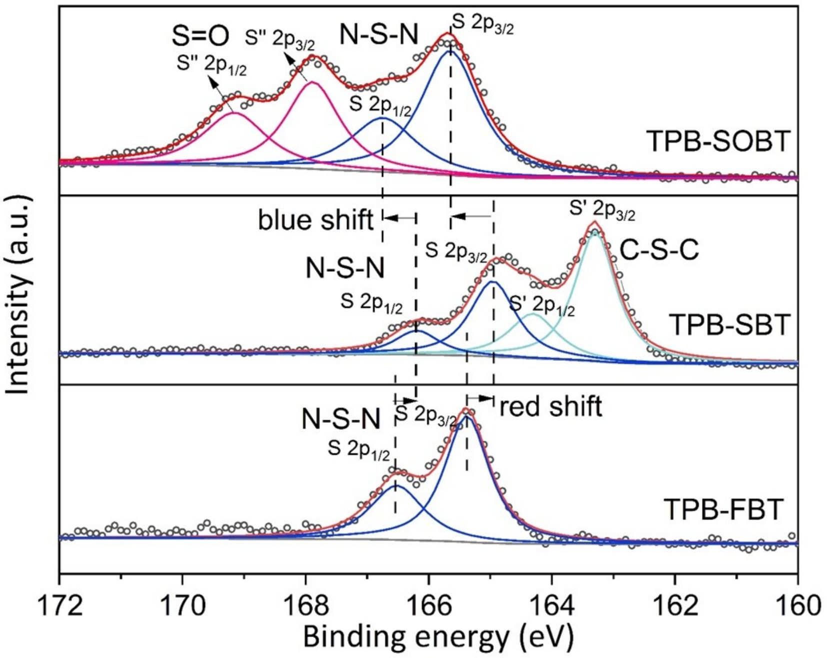


Fig. S22 High-resolution S 2p XPS spectra of TPB-FBT, TPB-SBT, TPB-SOBT.

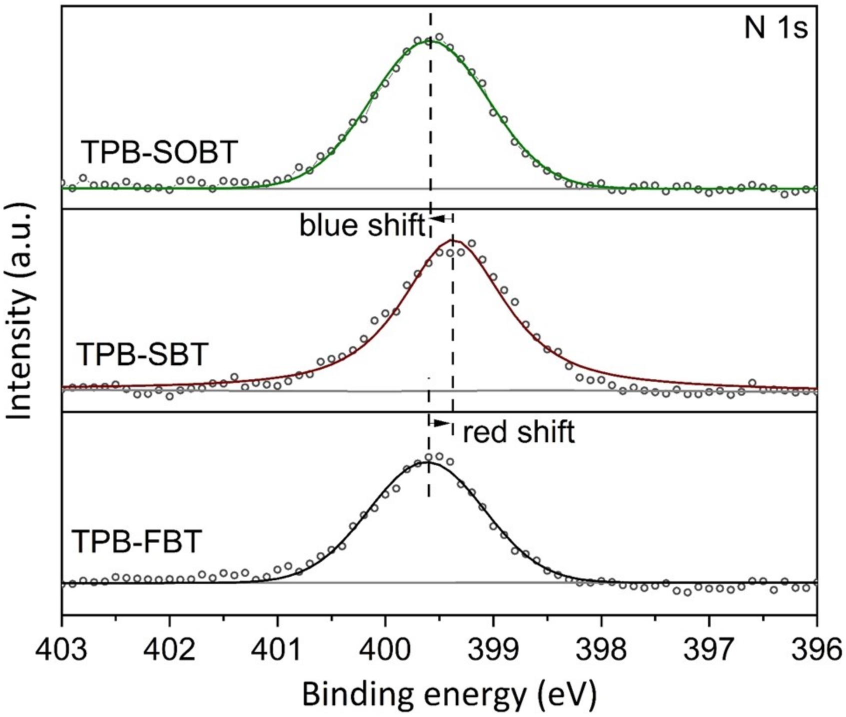


Fig. S23 High-resolution N 1s XPS spectra of TPB-FBT, TPB-SBT, TPB-SOBT.

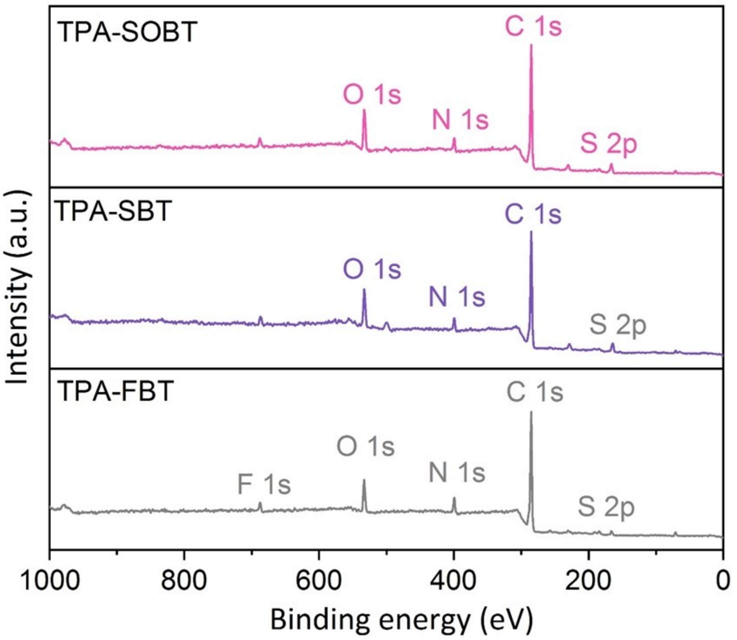


Fig. S24 XSP survey spectra of TPA-FBT, TPA-SBT, TPA-SOBT.

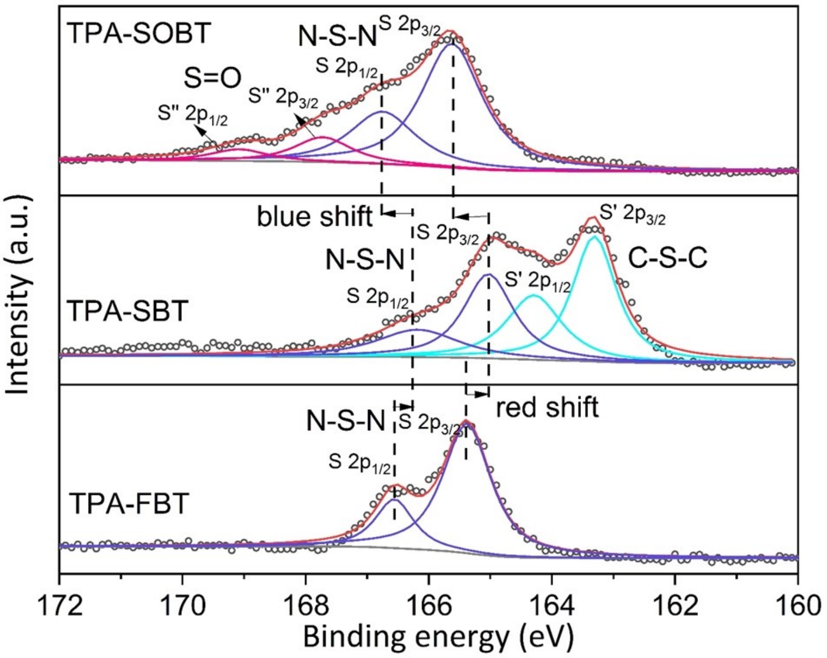


Fig. S25 High-resolution S 2p XPS spectra of TPA-FBT, TPA-SBT, TPA-SOBT.

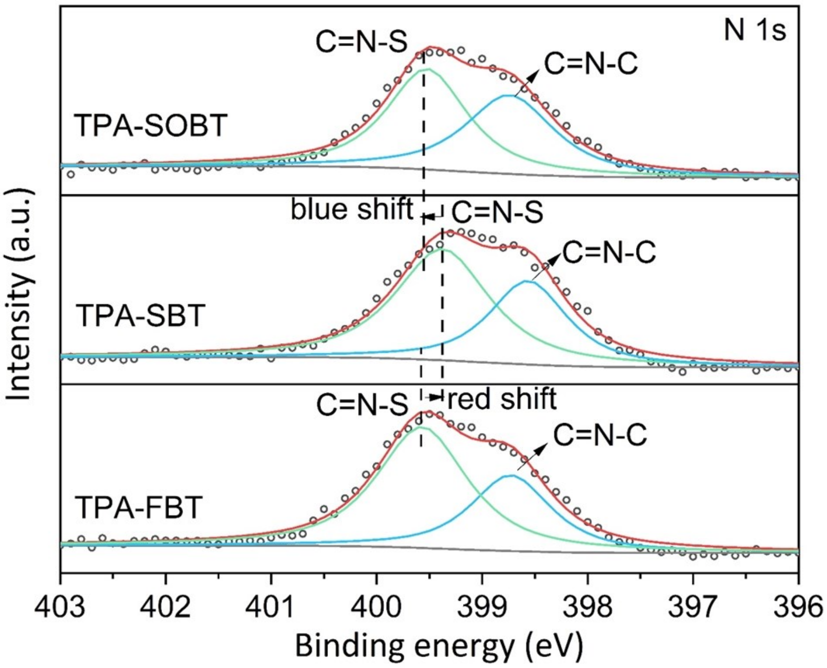


Fig. S26 High-resolution N 1s XPS spectra of TPA-FBT, TPA-SBT, TPA-SOBT.

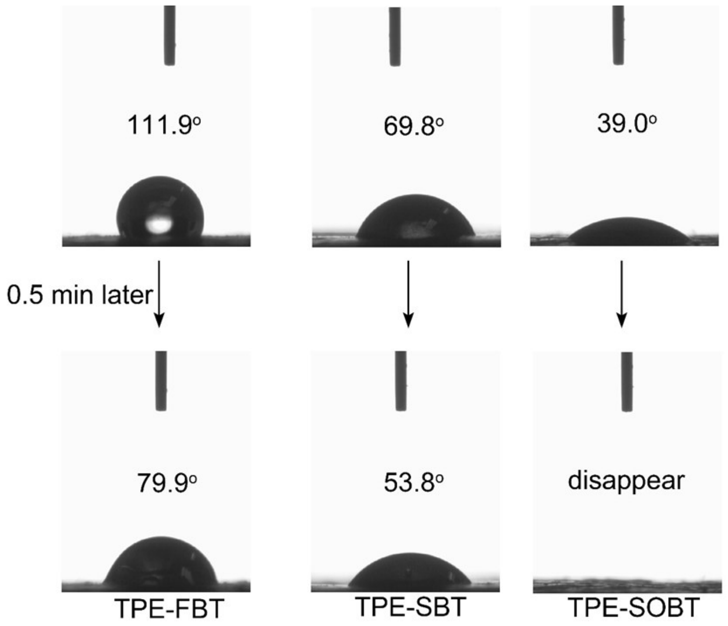


Fig. S27 water contact angle changes over 3 min of TPE-FBT, TPE-SBT, TPE -SOBT.

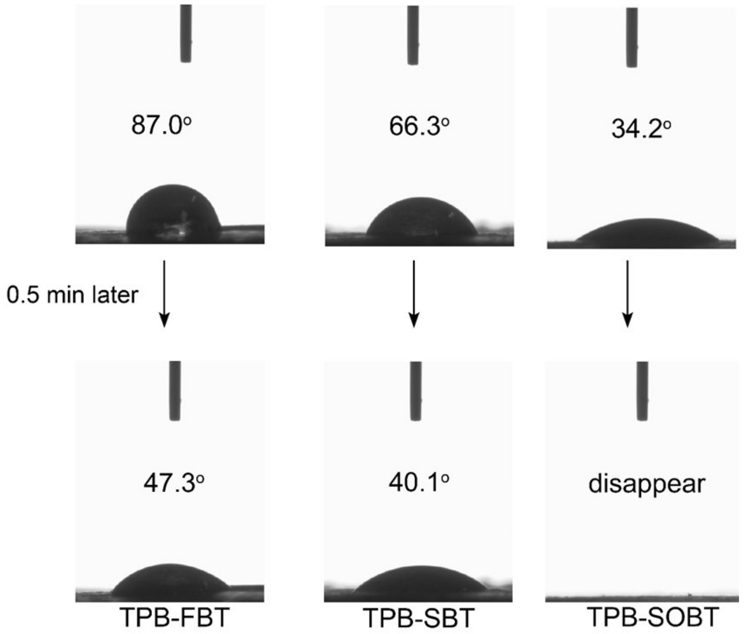


Fig. S28 water contact angle changes over 3 min of TPB-FBT, TPB-SBT, TPB -SOBT.

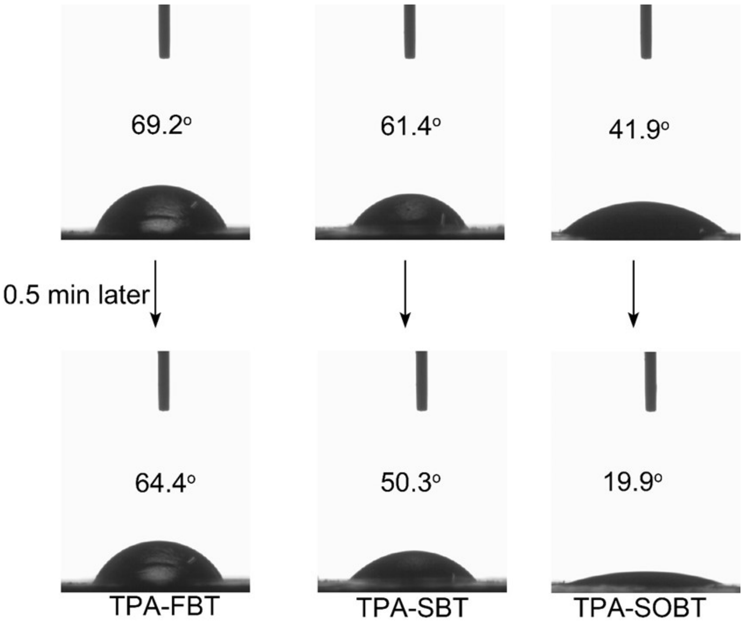


Fig. S29 water contact angle changes over 3 min of TPA-FBT, TPA-SBT, TPA -SOBT.

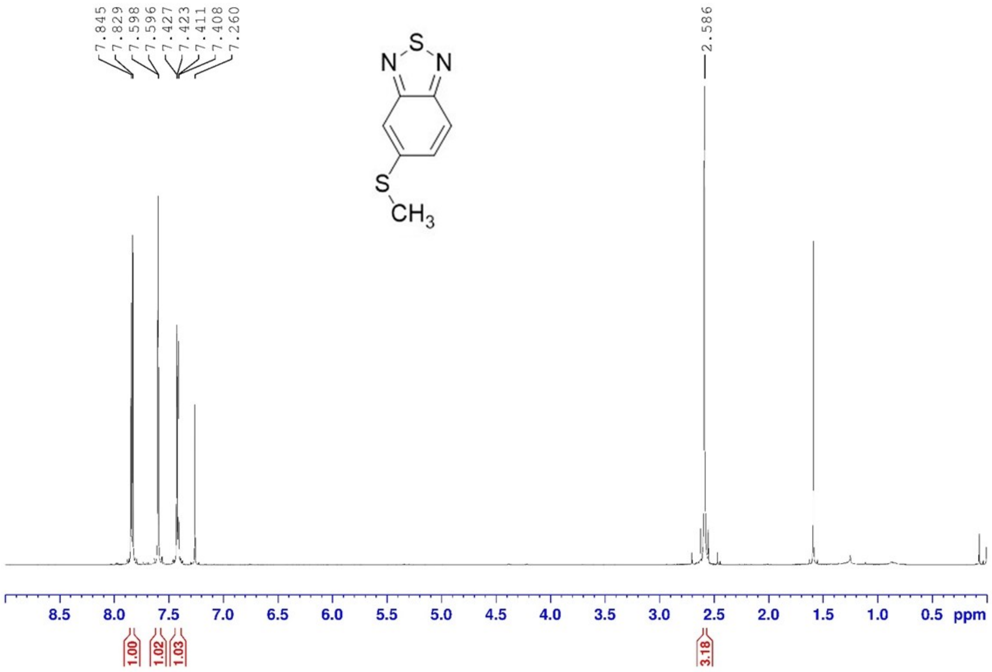


Figure S30. Liquid ^{1}H-NMR spectrum of **M2**.

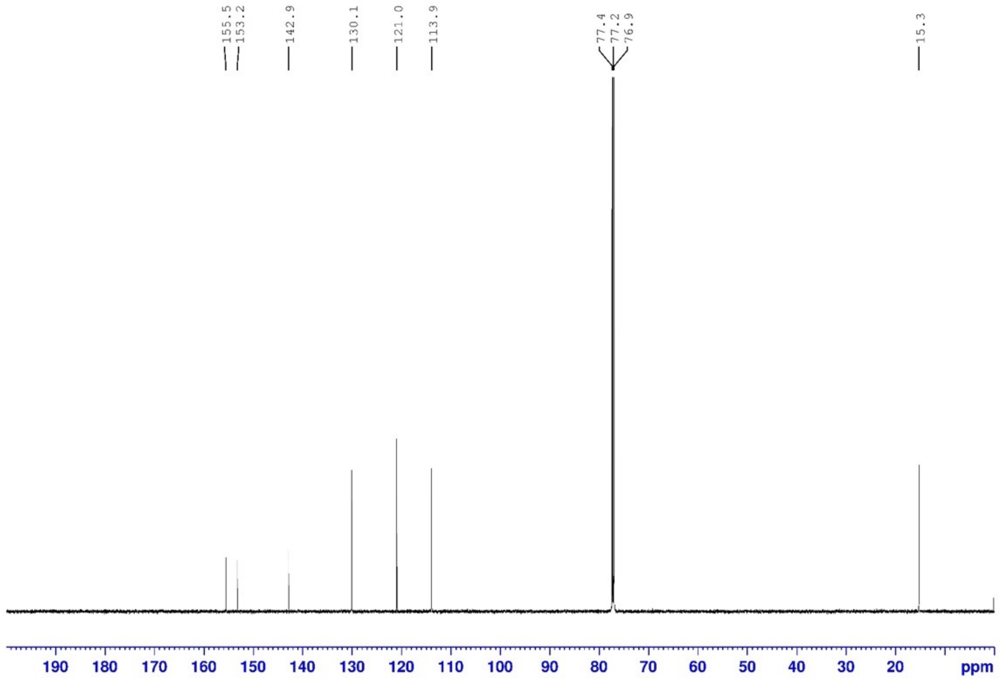


Figure S31. Liquid ^{13}C-NMR spectrum of **M2**.

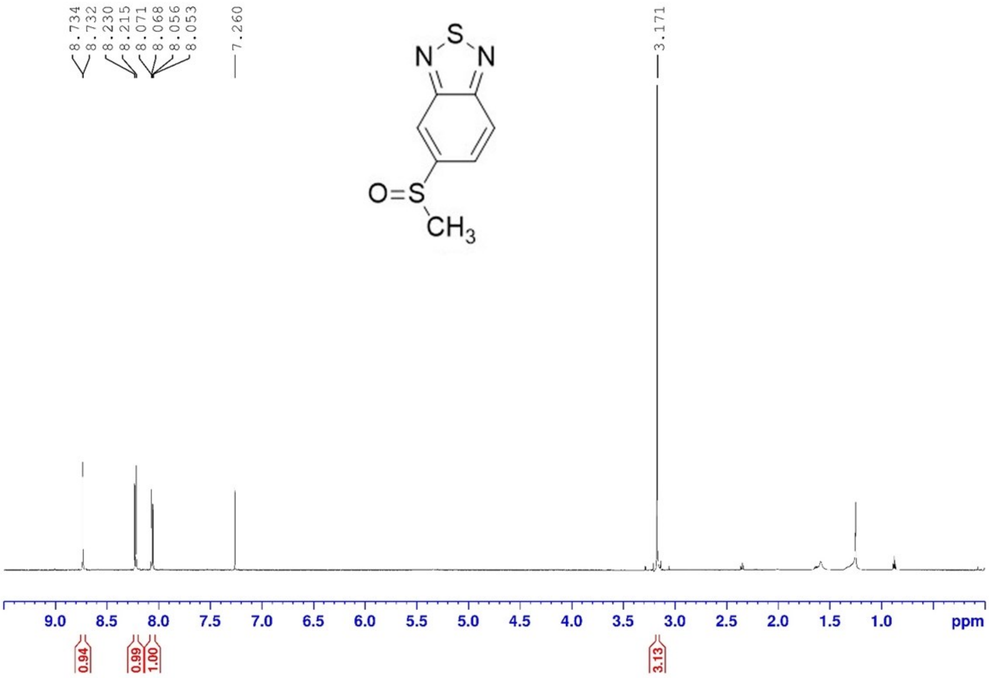


Figure S32. Liquid ^{1}H-NMR spectrum of **M3**.

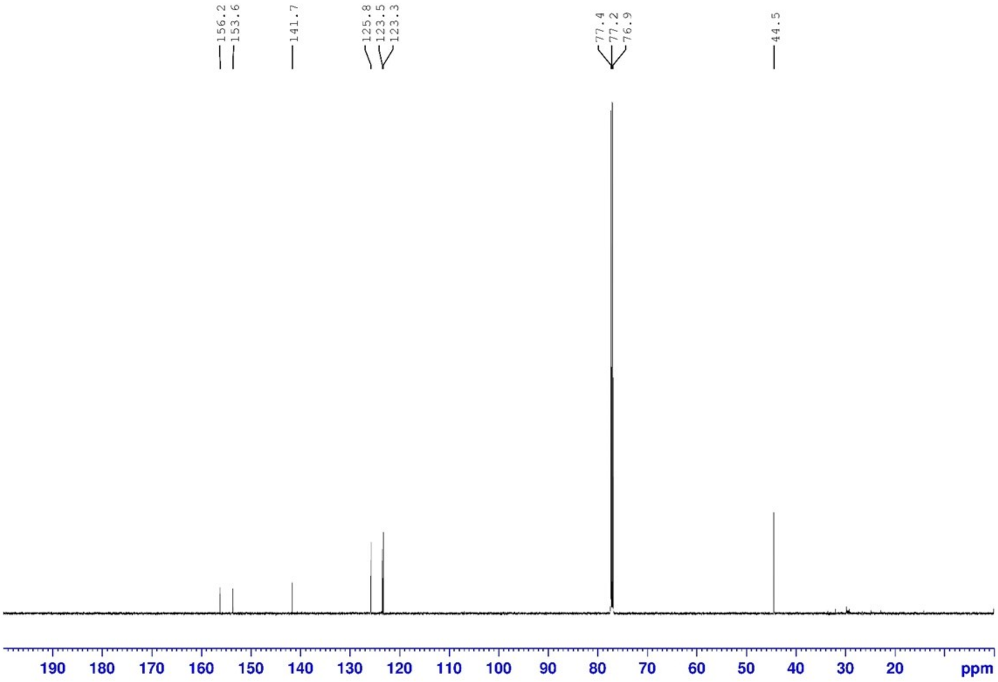


Figure S33. Liquid ^{13}C-NMR spectrum of **M3**.

Table S1 Element analysis and ICP-MS results for all the polymers

	Element analysis Theory (wt. %)			Element analysis Found (wt. %)			Metal content (wt. %)	
Polymers	C	H	N	C	H	N	Pd	Cu
B-FBT-1,3,5-E	67.19	1.21	11.19	63.09	1.12	10.09	0.35	0.005
B-SBT-1,3,5-E	64.73	2.17	10.06	60.09	0.69	9.64	0.33	0.004
B-SOBT-1,3,5-E	61.21	2.05	9.52	61.15	1.54	9.03	0.32	0.004
TPE-FBT	75.81	2.49	5.21	69.32	2.24	4.96	0.52	0.010
TPE-SBT	73.44	3.08	7.14	66.33	2.69	6.12	0.49	0.008
TPE-SOBT	69.21	2.90	6.73	62.08	2.39	6.05	0.46	0.007
TPB-FBT	77.60	2.76	6.96	70.31	2.58	6.12	0.58	0.011
TPB-SBT	75.32	3.28	6.51	68.25	2.86	5.98	0.55	0.009
TPB-SOBT	72.62	3.16	6.27	66.12	2.73	5.62	0.53	0.009
TPA-FBT	71.28	2.24	13.85	65.09	2.03	10.28	0.44	0.008
TPA-SBT	69.42	2.80	12.95	62.12	2.25	9.63	0.43	0.007
TPA-SOBT	66.95	2.70	12.49	59.18	2.30	9.24	0.40	0.006

Table S2 The contribution of conduction band electron (τ_1) and trapped electron (τ_2) lifetimes as well as the average lifetime.

Photocatalyts	τ_1 (ns)	A1 (%)	τ_2 (ns)	A2 (%)	τ_{ave} (ns)
B-FBT-1,3,5-E	1.07	707	4.02	8.97	1.11
B-SBT-1,3,5-E	1.07	1009.64	5.79	3.64	1.08
B-SOBT-1,3,5-E	1.19	241.16	4.04	11.09	1.31