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Integrating Amino Groups within Conjugated Microporous Polymers by Versatile Thiol-yne Coupling for Light-driven Hydrogen Evolution

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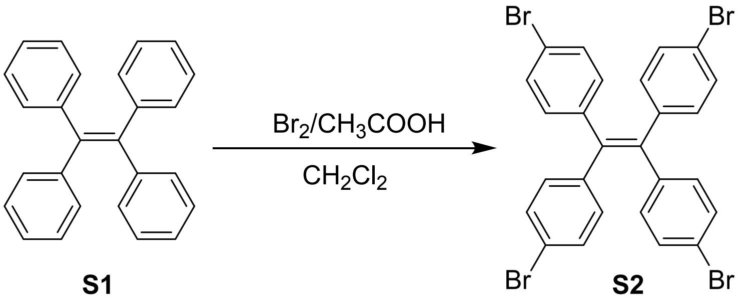
1. Experimental Section

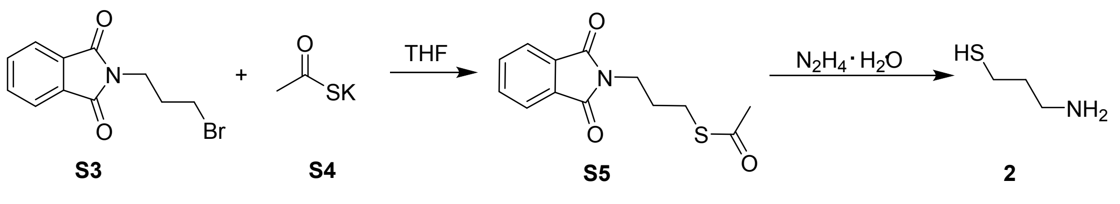
1.1 Characterization

^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker Advance (600 MHz) at ambient temperature. ^{1}H-NMR data are reported as follows: chemical shift in ppm downfield from tetramethylsilane (δ-scale), multiplicity (s =singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad), coupling constant (Hz), and integration. ^{13}C-NMR chemical shifts are reported in ppm downfield from tetramethylsilane (δ-scale).

1.2 Synthesis of monomers

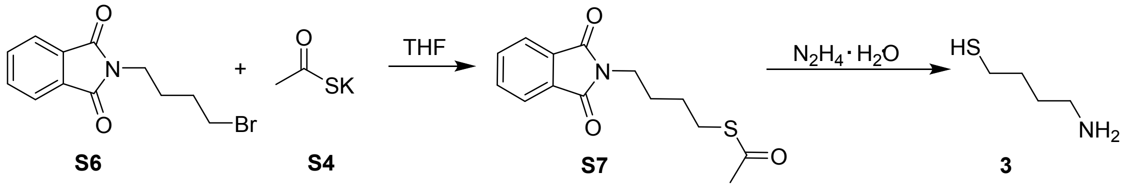


1,1,2,2-tetrakis(4-bromophenyl)ethane (S2): To the solution of tetraphenylethylene **1** (3.32 g, 10.0 mmol) in 10 mL glacial acetic acid and 20 mL dichloromethane was added Br_2 (4.0 mL, 80 mmol) dropwise at 0 °C. After being stirred at room temperature for 3 h, the mixture was poured into 100 mL ice water, and then it was extracted with CH_2Cl_2. The organic phase was dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by recrystallization with methanol and a white solid (6.15 g, 95%) was obtained. ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) 7.26 (d, J = 8.4 Hz, 8H), 6.84 (d, J = 8.4 Hz, 8H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 141.4, 139.5, 132.7, 131.3, 121.2.



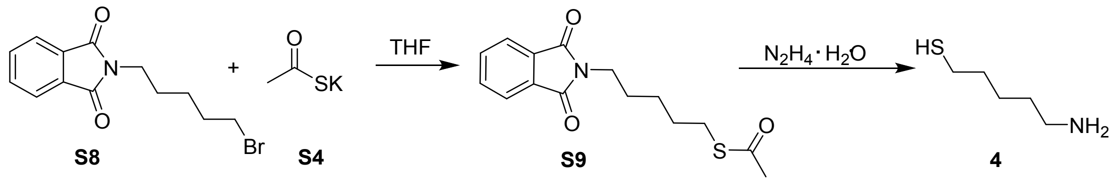
Compound S5. To the solution of **S3** (5.0 g, 18.7 mmol) in anhydrous THF (60 mL) was added potassium thioacetate (2.10 g, 18.7 mmol), and then the mixture was heated under reflux for 24 hours. After cooling to room temperature, H_2O (30 mL) was added, and aqueous solution was extracted with EtOAc. The combined organic phases were dried with Na_2SO_4, and the solvent was removed under reduced pressure to give the solid product (4.8 g, 96%), which was used direclty for the next step

Compound 2. Hydrazine hydrate (3 mL, 74.8 mmol) was added to a solution of **S5** (4.9 g, 18.7 mmol) in ethanol (150 mL), and the resulting mixture was stirred under reflux overnight. The solvent was removed under reduced pressure after cooling to room temperature. CH_2Cl_2 (20 mL) was added to the crude product and the organic layer was washed three times with water and concentrated under reduced pressure after drying with Na_2SO_4. The light yellow oil was obtained and used directly without further purification (528 mg, 31%). ^{1}H-NMR (600 MHz, DMSO-*d*6): δ (ppm) 7.49 (br, 3H), 2.77 (m, 2H), 2.61 (m, 2H), 1.45-1.62 (m, 2H).



Compound S7. To the solution of **S6** (4.85 g, 17.2 mmol) in anhydrous THF (60 mL) was added potassium thioacetate (1.96 g, 17.2 mmol), and then the mixture was heated under reflux for 24 hours. After cooling to room temperature, H_2O (30 mL) was added, and aqueous solution was extracted with EtOAc. The combined organic phases were dried with Na_2SO_4, and the solvent was removed under reduced pressure to give the solid product (4.76 g, 99%), which was used direclty for the next step

Compound 3. Hydrazine hydrate (2.8 mL, 72.8 mmol) was added to a solution of **S7** (4.76 g, 17.2 mmol) in ethanol (140 mL), and the resulting mixture was stirred under reflux overnight. The solvent was removed under reduced pressure after cooling to room temperature. CH_2Cl_2 (20 mL) was added to the crude product and the organic layer was washed three times with water and concentrated under reduced pressure after drying with Na_2SO_4. The light yellow oil was obtained and used directly without further purification (632 mg, 35%). ^{1}H-NMR (600 MHz, DMSO-*d*6): δ (ppm) 8.14 (br, 3H), 2.83-2.70 (m, 4H), 1.73-1.63 (m, 4H).

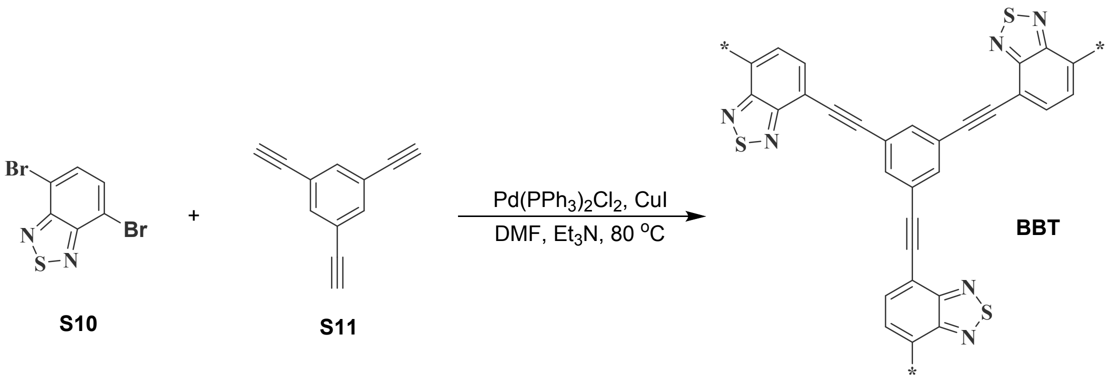


Compound S9. To the solution of **S6** (5.0 g, 16.9 mmol) in anhydrous THF (60 mL) was added potassium thioacetate (1.90 g, 16.9 mmol), and then the mixture was heated under reflux for 24 hours. After cooling to room temperature, H_2O (30 mL) was added, and aqueous solution was extracted with EtOAc. The combined organic phases were dried with Na_2SO_4, and the solvent was removed under reduced pressure to give the solid product (4.80 g, 98%), which was used direclty for the next step

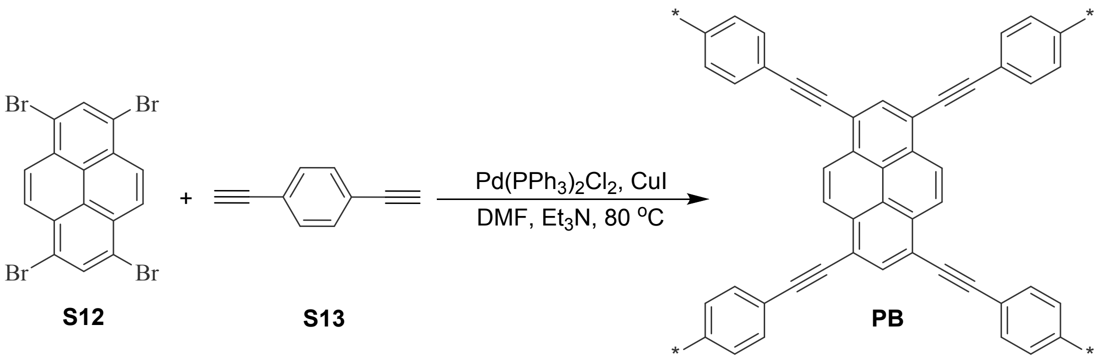
Compound 5. Hydrazine hydrate (2.6 mL, 67.6 mmol) was added to a solution of **S9** (4.9 g, 16.9 mmol) in ethanol (140 mL), and the resulting mixture was stirred under reflux overnight. The solvent was removed under reduced pressure after cooling to room temperature. CH_2Cl_2 (20 mL) was added to the crude product and the organic layer was washed three times with water and concentrated under reduced pressure after drying with Na_2SO_4. The light yellow oil was obtained and used directly without further purification (676 mg, 29%). ^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) 7.93 (br, 3H), 3.01-2.90 (m, 2H), 2.52-2.44 (m, 2H), 1.77-1.69 (m, 2H), 1.63-1.55 (m, 2H), 1.49-1.43 (m, 2H).

1.3 Synthesis of CMP

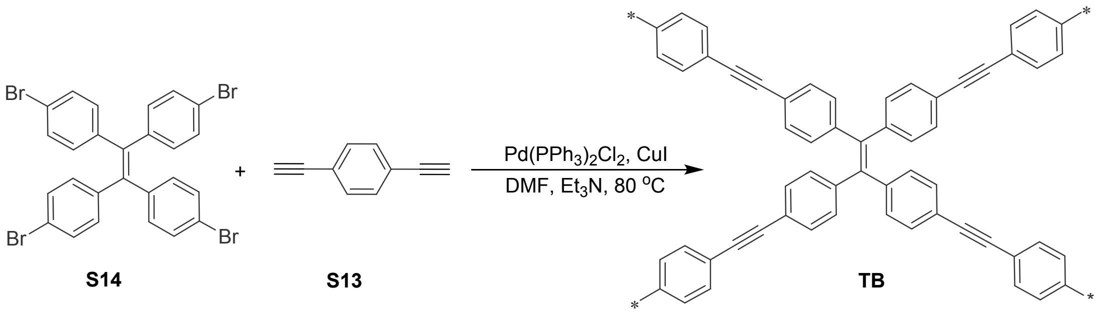
General procedure: The conjugated polymers were synthesized *via* Sonogashira–Hagihara cross-coupling polycondensation. In details, a dry 250 mL round-bottom flask was charged with two monomer reactants, $Pd(PPh_3)_2Cl_2$, CuI and mixed solvent (DMF/TEA), and then the resulting mixture degassed throughly with Ar. After being stirred under Ar at 80 ^oC for 24 hours, the precipitate was collected by filtration, and the solid was washed by Soxlhet extraction with methanol and CH_2Cl_2 for 48 hours. The final product was obtained by drying under vaccum at 60 ^oC overnight.



BBT: 4,7-dibromobenzo[c][1,2,5]thiadiazole **S10** (558 mg, 1.5 mmol), 1,3,5-triethynylbenzene **S11** (150 mg, 1.00 mmol), $Pd(PPh_3)_2Cl_2$ (20 mg), CuI (3 mg), DMF (50 mL) and TEA (50 mL) were used. 348 mg product was obtained (Yield: 83%).



PB: 1,3,6,8-tetrabromopyrene **S12** (259 mg, 0.5 mmol), 1,4-diethynylbenzene **S13** (126 mg, 1.00 mmol), $Pd(PPh_3)_2Cl_2$ (20 mg), CuI (3 mg), DMF (50 mL) and TEA (50 mL) were used. 196 mg product was obtained (Yield: 88%).



TB: 1,1,2,2-tetrakis(4-bromophenyl)ethene **S14** (324 mg, 0.5 mmol), 1,4-diethynylbenzene **S13** (126 mg, 1.00 mmol), $Pd(PPh_3)_2Cl_2$ (20 mg), CuI (3 mg), DMF (50 mL) and TEA (50 mL) were used. 233 mg product was obtained (Yield: 81%).

2. Tables and Figures

Table S1. Elemental analysis found for unmodified CMPs and modified CMPs with 4 equivalence of cysteamine

sample	**C** (wt. %)	**H** (wt. %)	**N** (wt. %)	**S** (wt. %)
BBT	66.20	1.77	5.20	10.97
BBT-SC2NH2	61.60	2.07	6.21	12.11
PB	79.28	2.78	-	-
PB-SC2NH2	76.07	1.77	0.58	1.64
TB	79.41	3.64		
TB-SC2NH2	78.53	3.66	0.75	1.39

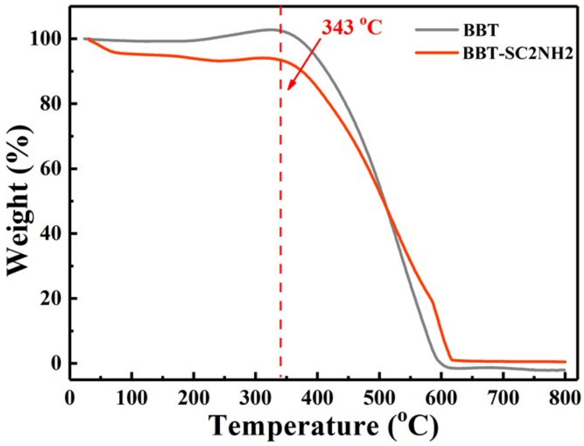


Fig. S1. Thermal gravimetric analysis of BBT and BBT-SC2NH2.

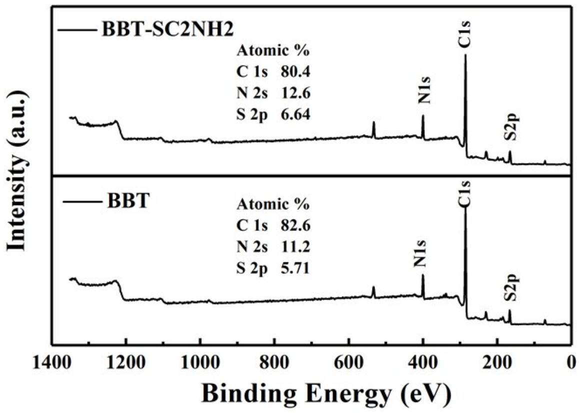


Fig. S2. XPS survey spectra of BBT and BBT-SC2NH2.

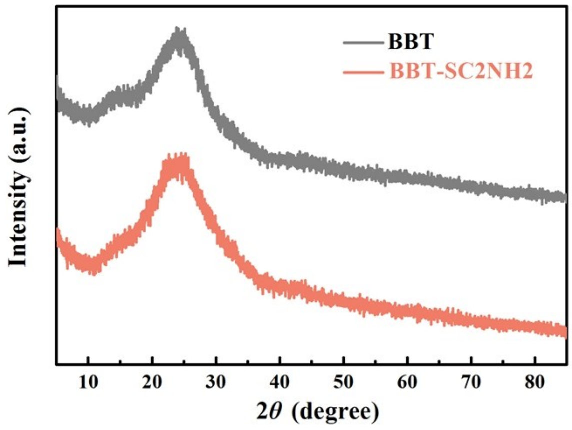


Fig. S3. PXRD patterns of BBT and BBT-SC2NH2.

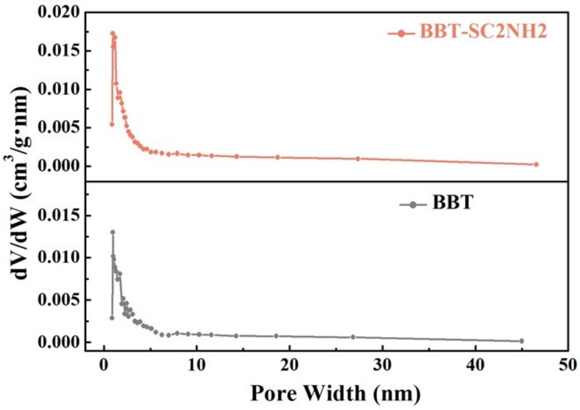


Fig. S4. Pore size distributions of BBT and BBT-SC2NH2.

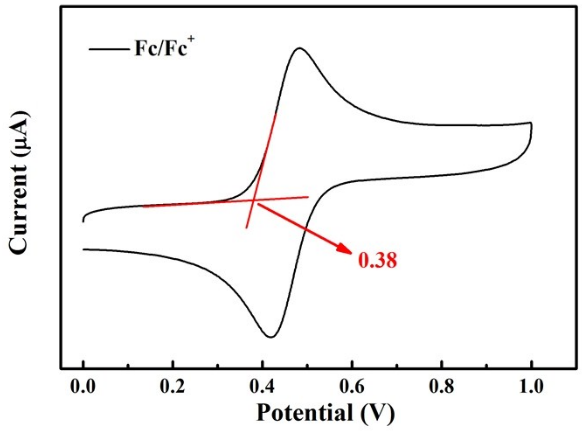


Fig. S5. Cyclic voltammograms of the internal reference ferrocene/ferrocenium (Fc/Fc^+) couple.

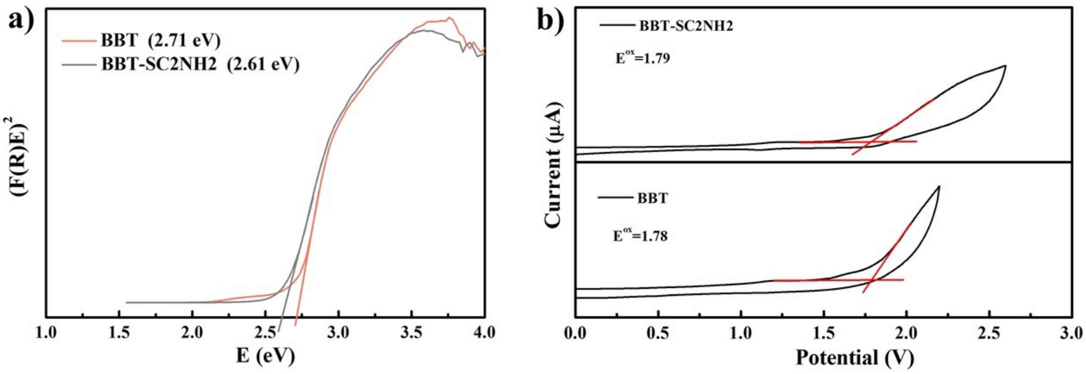


Fig. S6. Kubelka−Munk plots and cyclic voltammetry in the oxidation cycle of BBT and BBT-SC2NH2.

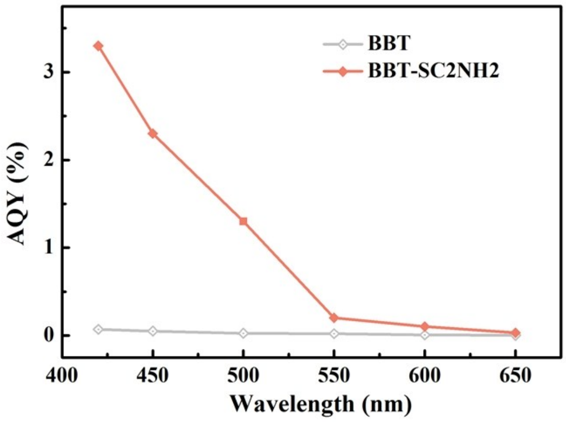


Fig. S7. AQY comparison of BBT and BBT-SC2NH2 under various monochromatic incident light.

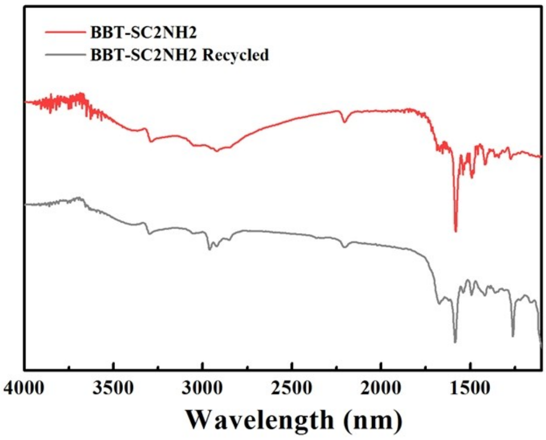


Fig. S8. FTIR spectra of BBT-SC2NH2 before and after photocatalytic reaction.

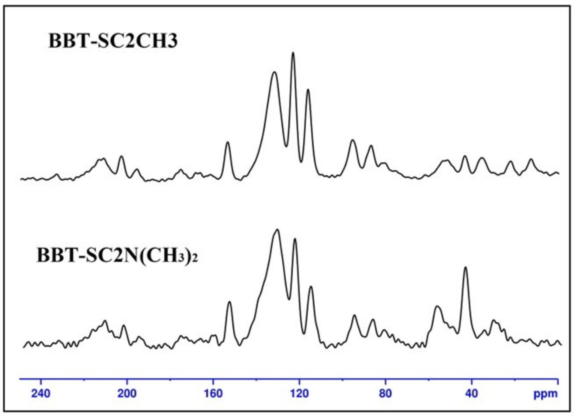


Fig. S9. Solid state ^{13}C CP/MAS NMR spectra of BBT-SC2CH3 and BBT-SC2N(CH_3)$_2$.

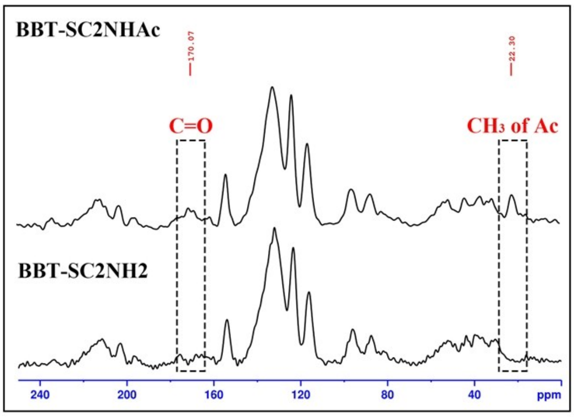


Fig. S10. Solid state ^{13}C CP/MAS NMR spectra of BBT-SC2NH2 and BBT-SC2NHAc.

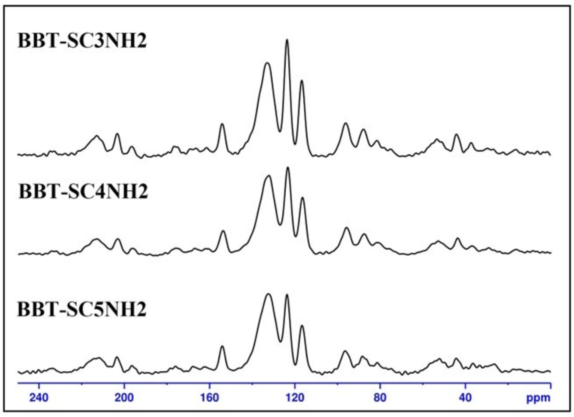


Fig. S11. Solid state ^{13}C CP/MAS NMR spectra of BBT-SC3NH2, BBT-SC4NH2 and BBT-SC5NH2.

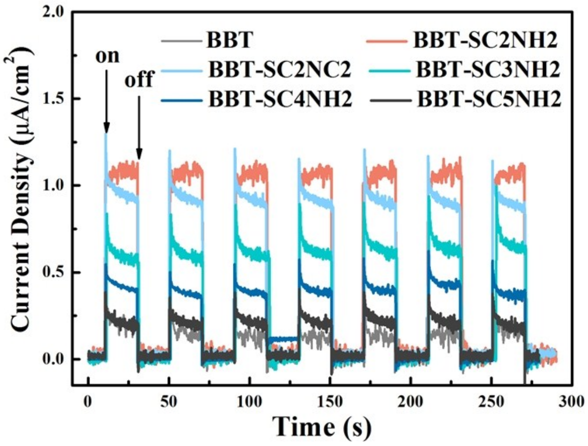


Fig. S12. Comparison of photocurrent curves versus time.

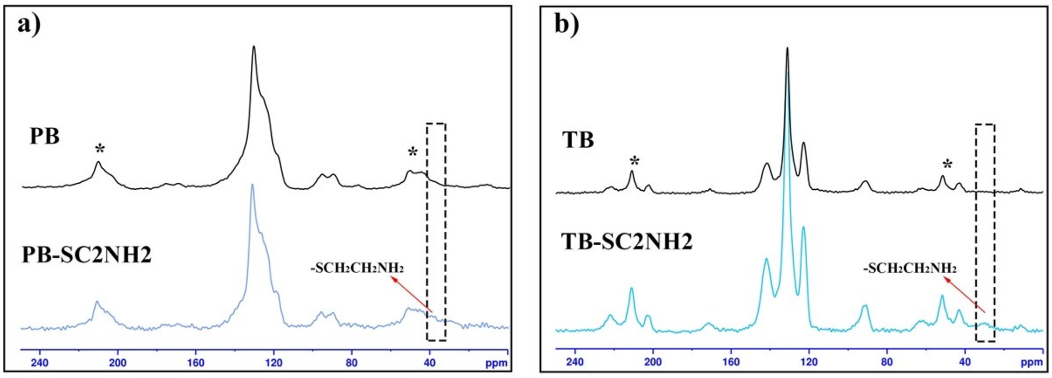


Fig. S13. Solid state ^{13}C CP/MAS NMR spectra of PB and TB before and after thiol-yne reaction, * indicates the spinning side bands.

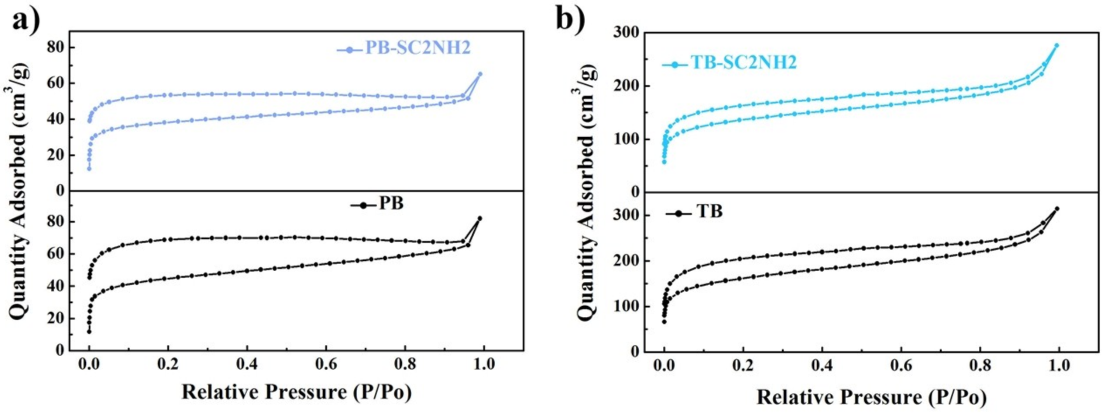


Fig. S14. Nitrogen adsorption and desorption isotherm curves of PB and TB before and after thiol-yne reaction.

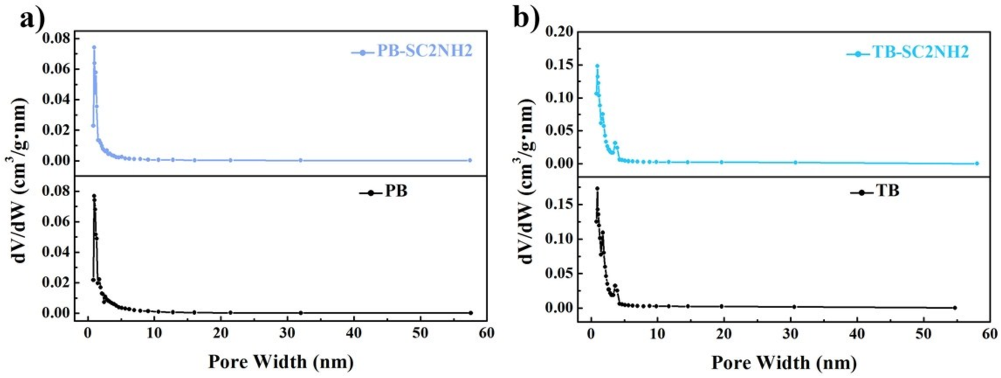


Fig. S15. Pore size distributions of PB and TB before and after thiol-yne reaction.

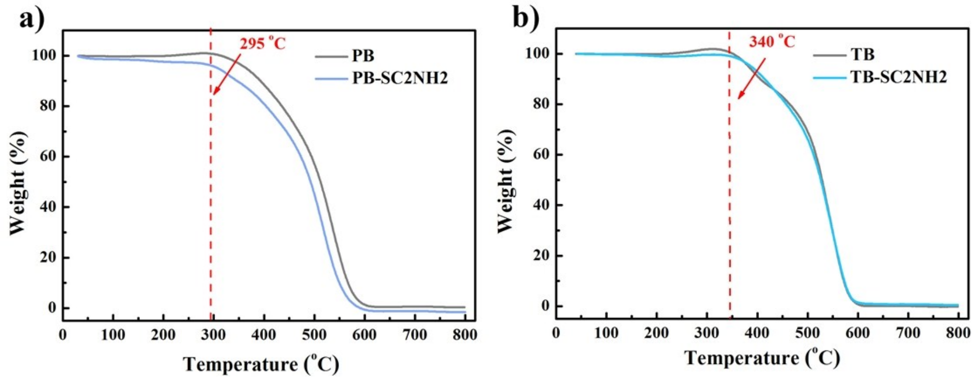


Fig. S16. Thermal gravimetric analysis of PB and TB before and after thiol-yne reaction.

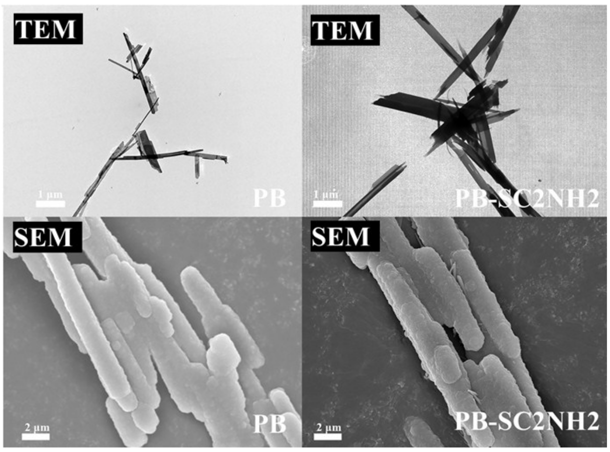


Fig. S17. TEM and SEM images comparison of PB and PB-SC2NH2.

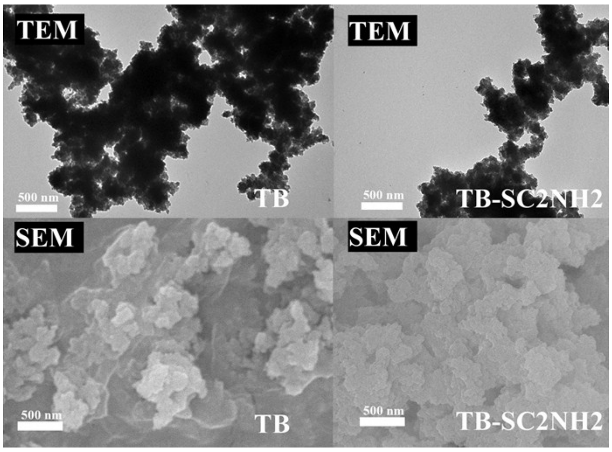


Fig. S18. TEM and SEM images comparison of TB and TB-SC2NH2.

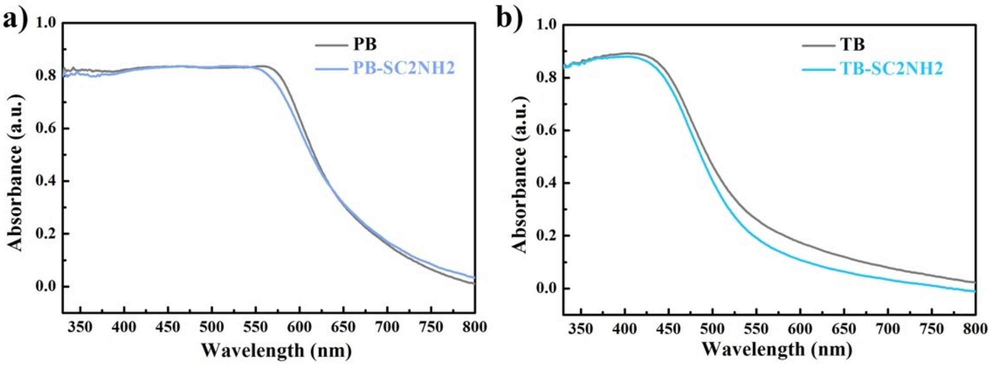


Fig. S19. UV–vis diffuse reflectance spectra of PB and TB before and after thiol-yne reaction.

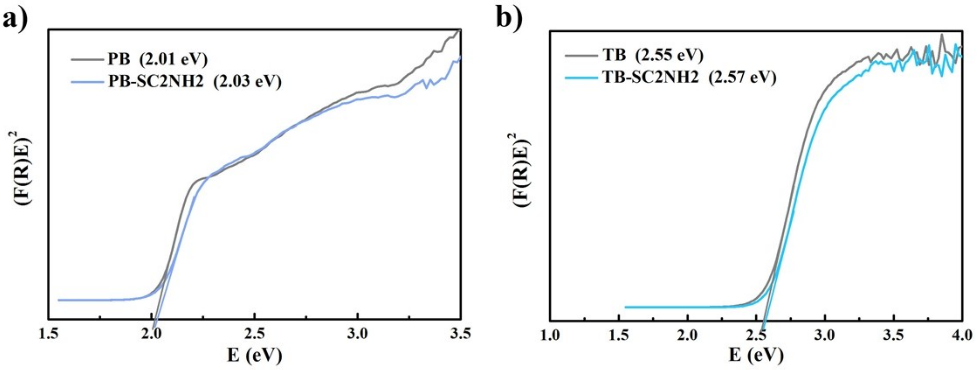


Fig. S20. Kubelka−Munk plots of PB and TB before and after thiol-yne reaction.

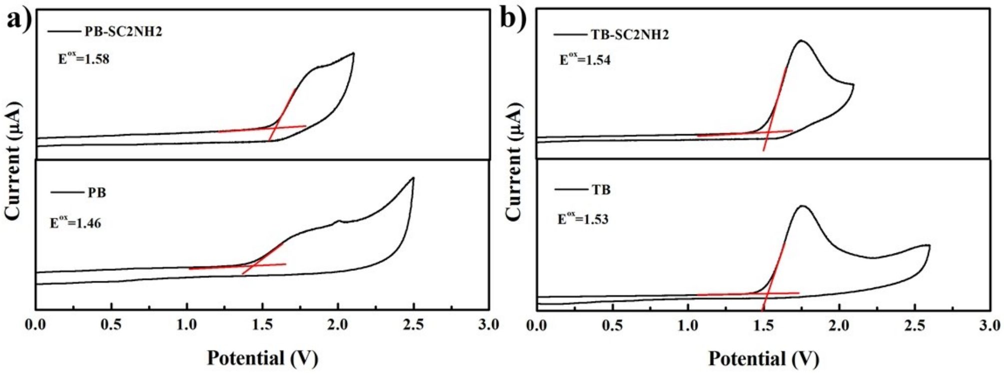


Fig. S21. Cyclic voltammetry in the oxidation cycle of PB and TB before and after thiol-yne reaction.

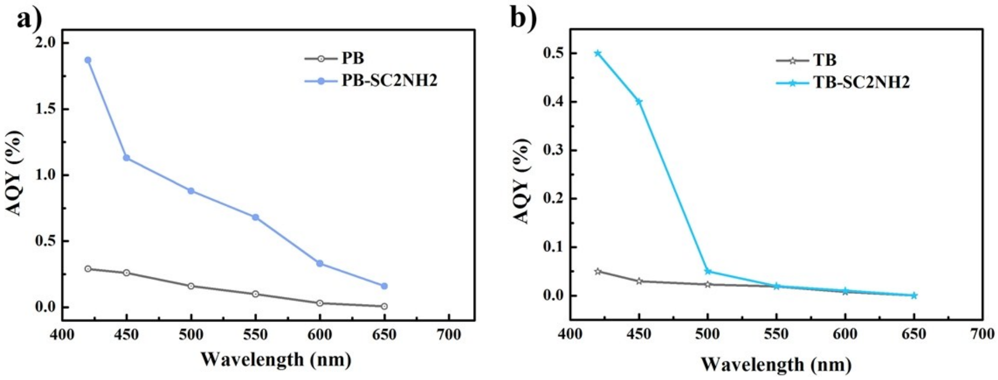


Fig. S22. AQY comparison of PB and TB before and after thiol-yne reaction under various monochromatic incident light.

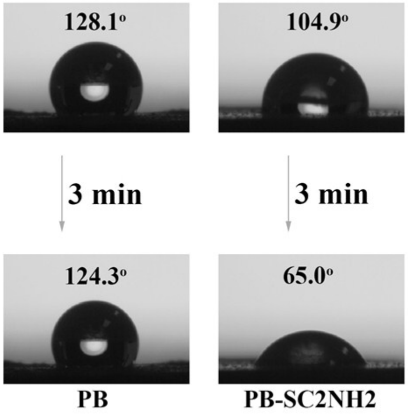


Fig. S23. Water contact angle measurements of PB and PB-SC2NH2 over 3 min.

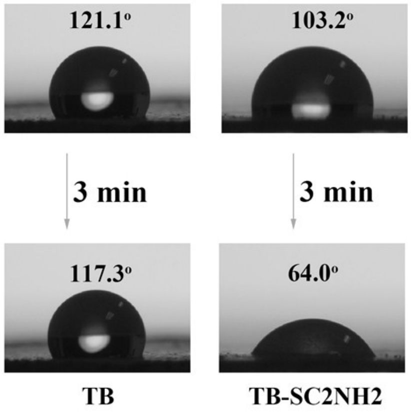


Fig. S24. Water contact angle measurements of TB and TB-SC2NH2 over 3 min.

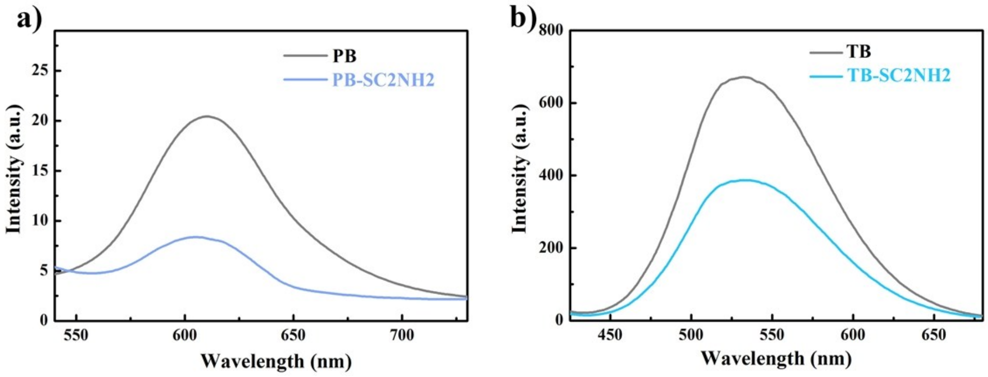


Fig. S25. Photoluminescence spectra of PB (excited at 435 nm) and TB (excited at 415 nm) before and after thiol-yne reaction.

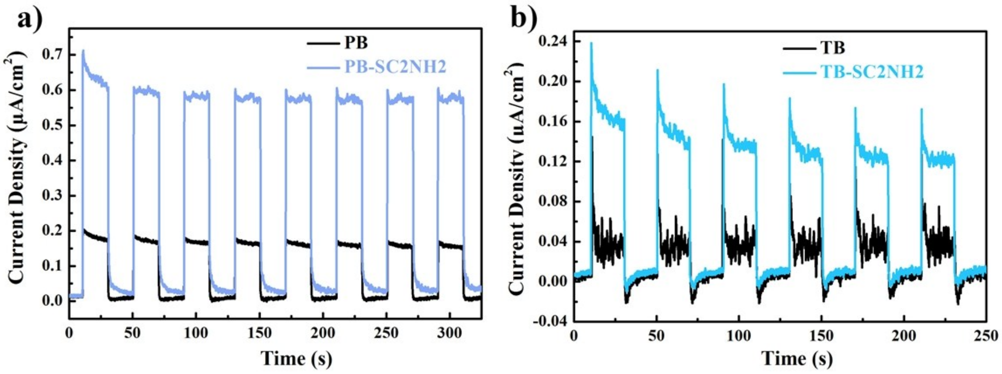


Fig. S26. Photocurrent curves versus time of PB and TB before and after thiol-yne reaction.

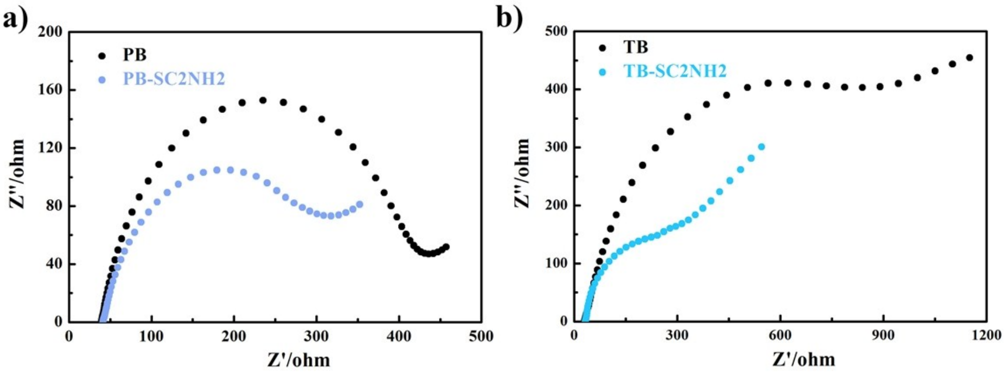


Fig. S27. Electrochemical impedance spectroscopy plots of PB and TB before and after thiol-yne reaction.

Table S2 Reported photocatalytic H_2 evolution performance of conjugated polymer-based photocatalysts.

Catalysts	Cocatalyst	Sacrificial regent	HER(mmol h^{-1} g^{-1})	AQY (%)	References
CP-CMP10	Pd residue	20 vol% diethylamine	0.18	4.2 (420 nm)	*J. Am. Chem. Soc.*, **2015**, 137: 3265-3270
PCP4e	2.0 wt% Pt	H_2O/MeOH/TEA	0.17	1.8 (420 nm)	*J. Am. Chem. Soc.*, **2016**, 138: 7681-7686
B-BT-1,4	3.0 wt% Pt	10 vol% TEOA/ H_2O	2.32	4.01 (420 nm)	*Angew. Chem. Int. Ed.*, **2016**, *55: 9202*-9206
P7	Pd residue	H_2O/MeOH/TEA	3.68	2.25 (420 nm)	*Angew. Chem. Int. Ed.*, **2016**, 55: 1824-1828
PFBT Pdots	Pd residue	0.2 M ascorbic acid	8.3	0.5 (445 nm)	*Angew. Chem. Int. Ed.*, **2016**, 55: 12306 –12310
PrCMP-3	Pd residue	20 vol% TEOA/ H_2O	0.12	-	*Macromol. Chem. Phys.*, **2017**, 218: 1700049
P8-i	Pd residue	H_2O /MeOH/TEA	0.12	0.56 (420 nm)	*Adv. Energy Mater.*, **2017**, 7: 1700479
PFODTBT Pdots	Pd residue	0.2 M ascorbic acid	50.0	0.6 (550 nm)	*Energy Environ. Sci.*, **2017**: 1372-1376
OB-POP-3	3.0 wt% Pt	20 vol% TEOA/ H_2O	0.91	2.0 (420 nm)	*Adv. Funct. Mater.*, **2017**, 27: 1703146
PyBT-2	3.0 wt% Pt	20 vol% TEOA	1.06	-	*Appl. Catal. B:*

	& Pd residue				*Environ.*, **2018**, 228: 1-9
P12	Pd residue	H_2O/MeOH/TEA	0.42	1.4 (420 nm)	*J. Mater. Chem. A*, **2018**, 6: 11994-12003
PMTPA225	3.0 wt% Pt	20 vol% TEOA/ H_2O	0.58	1.1 (432 nm)	*Green Chem.*, **2018**, 20: 664-670
P10	Pd residue	H_2O/MeOH/TEOA	3.2	11.6 (420 nm)	*Nat. Commun.*, **2018**, 9: 4968
PFTFQ-PtPy15	Pd residue	diethylamine	12.7	10.2 (420 nm)	*ACS Catal.*, **2018**, 8: 7766−7772
B-FOBT-1,4-E	Pd residue	10 vol% TEOA	13.3	5.7 (420 nm)	*ACS Energy Lett.* **2018**, 3, 2544−2549
Py-SO	Pd residue	Et_3N	11.2	3.28 (420 nm)	*Small*, **2018**, 14: 1801839
TP-BDDA	3.0 wt% Pt	10 vol% TEOA/ H_2O	0.32	-	*J. Am. Chem. Soc.*, **2018**, 140: 1423-1427
FS-COF+ WS5F	3.0 wt% Pt	0.1 M ascorbic acid	16.3	7.3 (420 nm)	*Nat. Chem.*, **2018**, 10: 1180
$F_{0.5}$CMP	Pd residue	Na_2S /Na_2SO_4	0.66	5.8 (400 nm)	*Chem. Eur. J.*, **2019**, 25: 1-9
S-CMP3	Pd residue	H_2O/MeOH/TEOA	3.1	13.2 (420 nm)	*Chem. Mater.*, **2019**, 31: 305-313
BBT-SC2NH2	Pd residue	10 vol% TEOA/ H_2O	8.2	3.3 (420 nm)	***This work***

The values are calculated according to the reported data in literatures