Electronic Supplementary Information (ESI †)

Donor-Acceptor Semiconducting Polymers as Superior Photocatalysts in Homogeneous Phase and Recycled via Antisolvent Precipitation Strategy

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1. Experimental Section

1.1. Materials and Methods.

All the chemicals and reagents were purchased from commercial sources and used directly as raw materials without further treatment. Solvents were dried as per the literature procedure prior to use according to the requirements. Thin layer chromatography (TLC) on silica gel GF₂₅₄ was used for the determination of R_f values, and the visualization was performed by irradiation with a UV lamp at 254 nm. Column chromatography was performed on Merck silica gel (100-200 mesh) with eluent, as mentioned. ¹H (500 MHz) and ¹³C (125 MHz) NMR spectra were recorded in a Bruker advance-500 NMR spectrometer in a deuterated solvent at ambient temperature (300 K). Chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) as the internal standard (CDCl₃ δ 7.26 ppm for ¹H, 77.0 ppm for ¹³C, and DMSO-d6 δ 2.50 ppm). Gel permeation chromatography (GPC) analysis was performed on an Agilent 1260 Infinity II system equipped with a MIXED-C column using polystyrene as the internal standard and chlorobenzene as eluent at 35 °C. Fourier transform infrared spectra (FTIR, 4000-600 cm⁻ ¹) were performed on a Nicolet 6700 FT-IR spectrometer (Thermo Fischer). The wave numbers of recorded IR signals are reported in cm⁻¹. Thermogravimetric analyses (TGA) were performed on a Pyris Diamond TG DTA (PerkinElmer) instrument. The ground states of the molecules were optimized using the DFT/B3LYP method with the 6-31++G* basis set in Gaussian. Here, one repeating unit was taken as a basic model structure to simulate the entire polymer skeleton. For easy calculation, the branched alkyl chains were replaced by small ethyl groups. XPS measurements were carried out using the PHI 5000 Versa Probe II, ULVAC-PHI, Inc. instrument. The as-synthesized polymers were characterized by ¹H NMR and ¹³C NMR. UV-visible absorption spectra were recorded on a Shimadzu UV-2550 UV-vis spectrophotometer. The samples were prepared by adding 1 mg of photocatalyst to a 1 mL 0.1 M air-saturated tetrahydrofuran solution of 5,5-dimethyl-1pyrroline-N-oxide (DMPO) and 2,2,6,6-tetramethyl-4-piperidinone (TEMP) as spin trappers for detection of superoxide anion radicals and singlet oxygen, respectively. The solution was irradiated in the presence of 20 W white LED for 5 min prior to the measurement.

1.2. Electrochemical Measurements

Cyclic voltammetry (CV) measurements were carried out using a CH instrument with a threeelectrode cell. A polymer film-coated glassy carbon electrode was used as a working electrode, platinum wire as a counter electrode, and Ag/Ag⁺ in acetonitrile (+0.49 V vs NHE)¹ as a reference electrode. A scan rate of 0.1 V/s was used. A 0.1 (M) tetrabutylammonium hexafluorophosphate solution in acetonitrile was used as the supporting electrolyte. 2 mg of the polymers was dissolved in 1 mL chloroform and the pre-polished glassy carbon electrode was coated with 20 μ L solution. The electrode was dried for 5 mL at room temperature prior to the CV experiment. The electrode potential values are given with respect to E_{Ag/AgCl} = 0.197 vs. NHE.² The LUMO energy levels of the polymers were determined using the empirical equation E_{LUMO} = (E_{onset/red}+0.49-0.197)V (vs Ag/AgCl).³ EIS is determined over 10²-10⁶ Hz frequency range with an AC amplitude of 10 mV at the open circuit voltage under room-light illumination by using 0.5 M Na₂SO₄ aqueous solution as a supporting electrolyte.

2. Synthetic procedures

Synthetic procedure of PBDT-AQ polymer:

In a two-neck round-bottom flask, BDT-(SnBu₃)₂ (0.285 g, 0.19 mmol), AQ-Br₂ (0.070 g, 0.19 mmol), and Pd(PPh₃)₄ (0.011 g, 0.0095 mmol) were added. Then, dry toluene (6 mL) was added to the reaction mixture under an inert condition. After that, the reaction mixture was degassed with argon for 30 min. The reaction mixture was refluxed at 110 °C for 72 h. After cooling to room temperature, 50 mL water was added to the mixture, and the organic layer was extracted with chloroform. Then, the solvent was removed under reduced pressure. A black precipitate was obtained by adding methanol and collected by filtration. The product was purified by washing with methanol, acetone, and ethyl acetate in a Soxhlet extractor for 24 h each. Finally, the precipitate was extracted using hot chloroform. After removing the solvent, a deep red solid was collected (0.120 g, 55%). ¹H NMR (500 MHz, CDCl₃, ppm): δ 8.33 (m, br), 8.09 (m, br), 7.81 (m, br), 7.62 (m, br), 7.36 (m, br), 7.26 (m, br), 7.01 (m, br), 2.95 (m, br), 1.66 (m, br), 1.24 (m, br), 0.82 (m, br). Elemental Anal. Calcd for C₇₂H₉₆O₂S₄ (%, Calculated by repeated unit): C, 77.09; H, 8.63; O, 2.85; S, 11.43. Found (%):C 77.82, H 8.97, S 12.06. *M*_w = 11.4 kDa; *M*_w/*M*_n (PDI) = 1.81. *T*_d = 392 °C for 5% wt. loss under nitrogen.

Synthetic procedure of PBDT-AM polymer:

In a two-neck round-bottom flask, BDT-(SnBu₃)₂ (0.275 g, 0.18 mmol), AM-Br₂ (0.084 g, 0.18 mmol), and Pd(PPh₃)₄ (0.0106 g, 0.0092 mmol) were added. Dry toluene (5 mL) was added to the reaction mixture under an inert condition. Then, the reaction mixture was degassed with argon for 30 min. The reaction mixture was refluxed at 110 °C for 72 h. After cooling to room temperature, 50 mL water was added to the mixture, and the organic layer was extracted with chloroform. Then, the solvent was removed under reduced pressure. A black precipitate was obtained by adding methanol and collected by filtration. The product was purified by washing with methanol, acetone, and ethyl acetate in a Soxhlet extractor for 24 h each. Finally, the precipitate was extracted with hot chloroform in a Soxhlet extractor for 24 h. After removing the solvent, a black solid was collected (0.135g, 60%). ¹H NMR (500 MHz, CDCl₃, ppm): δ 8.53 (m, br), 8.07 (m, br), 7.92 (m, br), 7.64 (m, br), 7.35 (m, br), 7.26 (m, br), 6.93 (m, br), 2.89 (m, br), 1.75 (m, br), 1.24 (m, br), 0.83 (m, br). Elemental Anal. Calcd for C₇₈H₉₆N₄S₄ (%, Calculated by repeated unit): C, 76.92; H, 7.95; N, 4.60; S, 10.53. Found (%):C 76. 67, H 7.78, N 2.83, S 10.36. *M*_w = 20.7 kDa; *M*_w/*M*_n (PDI) = 2.72. *T*_d = 332 °C for 5% wt. loss under nitrogen.

General procedure for the hydroxylation of phenylboronic acids to phenols:

Arylboronic acid (0.2 mmol) and the as-synthesized polymer (1 mol%) were taken in a Pyrex tube, and 3 mL of DCM was added to dissolve the reactant and polymer, making a homogeneous reaction mixture. The solution was purged with oxygen for 5 minutes in the dark. Then triethylamine (0.3 mmol) was added to the reaction mixture and stirred at room temperature under 20 W white LED (400 mW/cm²). After that, the solvent was evaporated under reduced pressure, and methanol was added to the crude mixture, resulting in the precipitation of the polymer. The polymer was then separated by filtration. The filtrate was

evaporated, and the product was purified by column chromatography on a silica gel column using chloroform as the eluent. The ¹H NMR spectra of the resulting phenols are provided in Fig. S11-S17.

General procedure for the photo-oxidation of phenyl methyl sulfides to sulfoxides:

Phenyl methyl sulfides (0.2 mmol) and the as-synthesized polymer (1 mol%) were taken in a Pyrex tube, and 3 mL of THF:H₂O (10:1) was added to dissolve the reactant and polymer, making a homogeneous reaction mixture. The solution was purged with oxygen for 5 minutes in the dark. Then, the mixture was stirred at room temperature under 20 W white LED (400 mW/cm²). After that, the solvent was evaporated under reduced pressure, and methanol was added to the crude mixture, resulting in the precipitation of the polymer. The polymer was then separated by filtration. The filtrate was evaporated, and the product was purified by column chromatography on a silica gel column using chloroform as the eluent. The ¹H NMR spectra of the resulting sulfoxides are provided in Fig. S18-S24.

3. Characterization:



Fig. S1. ¹H NMR of PBDT-AQ in CDCl₃ solvent.



Fig. S2. ¹H NMR of PBDT-AM in CDCl₃ solvent.



Fig. S3. FT-IR spectra of PBDT-AQ and PBDT-AM.



Fig. S4. XPS deconvoluted spectra of a) O 1s, b) S 2p of **PBDT-AQ**, and d) C 1s, e) N 1s, and f) S 2p of **PBDT-AM**.

Table S1. Photophysical and electrochemical properties of the polymers.

| Polymer | M_{n}^{a} (Da) | Mw (Da) | PDI | <i>T</i> d ^{<i>b</i>} (°C) | λ_{\max}^c (nm) | $E_{g}^{d}(\mathbf{eV})$ | HOMO (eV) | LUMO ^e (eV) |
|---------|------------------|------------|------|--|-------------------------|--------------------------|--------------|---------------------------|
| PBDT-AQ | 6300 | 11400 | 1.81 | 392 | 323, 400 | 2.06 | -5.37 | -3.31 |
| PBDT-AM | 7600 | 20700 | 2.72 | 332 | 340, 410 | 1.92 | -5.21 | -3.29 |

^{*a*}Calculated from the GPC study. ^{*b*}Decomposition temperature (T_d) was evaluated from TGA under nitrogen atmosphere with scan rate 10 °C/min. ^{*c*}Estimated from UV-vis absorption spectra. ^{*d*}Calculated by using equation $E_g = 1240/\lambda_{onset}$ from UV-vis spectra. ^{*d*}HOMO and LUMO energy levels are estimated from CV in acetonitrile solvent with 0.1 M TBAPF₆ as the supporting electrolyte, drop-casted from chloroform solution.



Fig. S5. a) TGA curves under N_2 atmosphere and b) cyclic voltammograms of **PBDT-AQ** and **PBDT-AM**.



Fig. S6. HOMO-LUMO distribution of PBDT-AQ and PBDT-AM by DFT calculations.

Table S2. Photocatalytic activity comparison in homogeneous and heterogeneous phases of oxidative hydroxylation of phenylboronic acid to phenol.



Reaction conditions: 1 mol % catalyst, 0.2 mmol phenylboronic acid, solvent (2 mL), 20 W white LED, O₂, Room temperature (RT).

| Entry | Catalyst | Solvent | Time (h) | Isolated Yield (%) |
|-------|----------|---|----------|--------------------|
| 1 | PBDT-AQ | CH ₃ CN (Heterogeneous) | 16 | 81 |
| 2 | PBDT-AQ | CH ₂ Cl ₂ (Homogeneous) | 8 | 90 |
| 3 | PBDT-AM | CH ₃ CN (Heterogeneous) | 48 | 55 |
| 4 | PBDT-AM | CH ₂ Cl ₂ (Homogeneous) | 16 | 50 |

Table S3. Photocatalytic activity comparison in homogeneous and heterogeneous phases of photo-oxidation of phenyl methyl sulfide to sulfoxide.



Reaction conditions: 1 mol% catalyst, 0.2 mmol phenyl methyl sulfide, solvent (2 mL) and H_2O (0.2 mL), 20 W white LED, O_2 , Room temperature (RT).

| Entry | Catalyst Solvent | | Time (h) | Isolated Yield (%) |
|-------|------------------|---|----------|--------------------|
| 1 | PBDT-AQ | CH ₃ OH (Heterogeneous) | 48 | 89 |
| 2 | PBDT-AQ | THF/H ₂ O (10:1) (Homogeneous) | 9 | 90 |
| 3 | PBDT-AM | CH ₃ OH (Heterogeneous) | 48 | 53 |
| 4 | PBDT-AM | THF/H ₂ O (10:1) (Homogeneous) | 24 | 54 |

Table S4. Scavenger study for the oxidative hydroxylation of phenylboronic acid to phenol.

| Entry | Scavenger | Time (h) | Isolated Yield (%) |
|-------|-----------------------|----------|--------------------|
| 1 | p-Benzoquinone (p-BQ) | 8 | Trace |
| 2 | Isopropanol | 8 | 83 |
| 3 | Sodium Azide | 8 | 82 |
| 4 | Potassium Iodide | 8 | 70 |
| 5 | Cupric Chloride | 8 | 40 |

Reaction conditions: 1 mol % **PBDT-AQ**, 0.2 mmol phenylboronic acid, CH₂Cl₂ (2 mL), 20 W white LED, O₂, Room temperature (RT).



Fig. S7. EPR signals for DMPO-O₂⁻ adduct, without and with **PBDT-AQ** and **PBDT-AM** under visible light illumination.

Table S5. Control experiments for oxidative hydroxylation of phenylboronic acid to phenol.

| Entry | Reaction conditions | Solvent | Isolated Yield (%) |
|-------|----------------------------|---------------------------------|--------------------|
| 1 | No catalyst | CH ₂ Cl ₂ | No conversion |
| 2 | No oxygen | CH ₂ Cl ₂ | Trace |
| 3 | No triethylamine | CH ₂ Cl ₂ | Trace |
| 4 | No light | CH ₂ Cl ₂ | No conversion |
| 5 | In open air | CH ₂ Cl ₂ | 75% |

Reaction conditions: 1 mol % **PBDT-AQ**, 0.2 mmol phenylboronic acid, CH₂Cl₂ (2 mL), 20 W white LED, 8 h, Room temperature (RT).



Fig. S8. Proposed mechanistic pathway for the hydroxylation of phenylboronic acid.

| Table S6. | Catalytic J | performance | comparison | of polymer | catalyst, | PBDT-AQ | with | different |
|-------------|-------------|---------------|---------------|-------------|------------|---------|------|-----------|
| catalyst do | sages towa | urds photo-ox | idation of ph | nenyl methy | l sulfides | | | |

| Catalyst | Catalyst dosage (mol%) | Time | Solvent | Isolated Yield (%) |
|----------|------------------------|------|-----------------------------|--------------------|
| PBDT-AQ | 0.50 | 9h | THF/H ₂ O (10:1) | 85 |
| PBDT-AQ | 1.00 | 9h | THF/H ₂ O (10:1) | 90 |
| PBDT-AQ | 1.50 | 9h | THF/H ₂ O (10:1) | 93 |
| PBDT-AQ | 2.00 | 9h | THF/H ₂ O (10:1) | 95 |

Reaction conditions: 1 mol % **PBDT-AQ**, 0.2 mmol phenyl methyl sulfides, THF (2 mL) and H₂O (0.2 mL), 20 W white LED, O₂, rt, and isolated yields.

| Catalyst | Light source | Time | Solvent | Isolated Yield (%) |
|----------|--------------|------|-----------------------------|--------------------|
| PBDT-AQ | White | 9h | THF/H ₂ O (10:1) | 90 |
| PBDT-AQ | Blue | 9h | THF/H ₂ O (10:1) | 93 |
| PBDT-AQ | Green | 9h | THF/H ₂ O (10:1) | 20 |
| PBDT-AQ | Red | 9h | THF/H ₂ O (10:1) | Trace |

Reaction conditions: 1 mol% **PBDT-AQ**, 0.2 mmol phenyl methyl sulfides, THF (2 mL) and H_2O (0.2 mL), O_2 , rt, and isolated yields.

Table S8. Scavenger study for the photo-oxidation of phenyl methyl sulfide to sulfoxide.

| Entry | Scavenger | Time (h) | Isolated Yield (%) |
|-------|-----------------------|----------|--------------------|
| 1 | p-Benzoquinone (p-BQ) | 9 | 40 |
| 2 | Isopropanol | 9 | 78 |
| 3 | Sodium Azide | 9 | 60 |
| 4 | Potassium Iodide | 9 | 85 |
| 5 | Cupric Chloride | 9 | 80 |

Reaction conditions: 1 mol % PBDT-AQ, 0.2 mmol phenyl methyl sulfide, THF (2mL) and H_2O (0.2 mL), 20 W white LED, O_2 , Room temperature (RT).



Fig. S9. EPR signals for TEMPO, without and with **PBDT-AQ** and **PBDT-AM** under visible light illumination.

| Entry | Reaction condition | Solvent | Isolated Yield (%) |
|-------|---------------------------|-----------------------------|--------------------|
| 1 | No catalyst | THF/H ₂ O (10:1) | No conversion |
| 2 | No oxygen | THF/H ₂ O (10:1) | Trace |
| 3 | No light | THF/H ₂ O (10:1) | No conversion |
| 4 | In open air | THF/H ₂ O (10:1) | 70% |

Table S9. Control experiments for the photo-oxidation of phenyl methyl sulfide to sulfoxide.

Reaction conditions: 1 mol % **PBDT-AQ**, 0.2 mmol phenyl methyl sulfide, THF (2 mL) and H_2O (0.2 mL), 20 W white LED, Room temperature (RT).

Table S10. Recovery rate of polymer catalyst, PBDT-AQ for photo-oxidation of phenyl methyl sulfides.

| Cycle number | Catalyst recovery (%) |
|--------------|-----------------------|
| 1 | 100 |
| 2 | 98 |
| 3 | 96 |
| 4 | 94 |
| 5 | 91 |



Fig. S10. FT-IR spectra of **PBDT-AQ** and recovered **PBDT-AQ** after five cycles for the a) oxidative hydroxylation of phenylboronic acid to phenol and b) photo-oxidation of phenyl methyl sulfide to sulfoxide.

Table S11. GPC study of the recovered polymer.

| Polymer | $M_{ m w}({ m Da})$ | M _n (Da) | PDI |
|---------|---------------------|---------------------|------|
| PBDT-AQ | 10189 | 5617 | 1.81 |

¹H NMR spectra of the products:

¹H NMR of oxidative hydroxylation of para-substituted phenylboronic acids.



Fig. S11. ¹H NMR (DMSO-d6, 400 MHz) of 4-hydroxybenzoic acid.



Fig. S12. ¹H NMR (CDCl₃, 400 MHz) of 4-nitrophenol.



Fig. S13. ¹H NMR (CDCl₃, 400 MHz) of 4-hydroxybenzonitrile.



Fig. S14. ¹H NMR (CDCl₃, 400 MHz) of 4-bromophenol.



Fig. S15. 1 H NMR (CDCl₃, 400 MHz) of Phenol.



Fig. S16. ¹H NMR (CDCl₃, 400 MHz) of p-cresol.



Fig. S17. ¹H NMR (CDCl₃, 400 MHz) of 4-methoxyphenol.

¹H NMR of photo-oxidation of para-substituted phenyl methyl sulfides.



Fig. S18. ¹H NMR (CDCl₃, 400 MHz) of 1-methoxy-4-(methylsulfinyl)benzene.



Fig. S19. ¹H NMR (CDCl₃, 400 MHz) of 4-(methylsulfinyl)phenol.



Fig. S20. ¹H NMR (CDCl₃, 400 MHz) of 1-bromo-4-(methylsulfinyl)benzene.



Fig. S21. ¹H NMR (CDCl₃, 400 MHz) of (methylsulfinyl)benzene.



Fig. S22. ¹H NMR (CDCl₃, 400 MHz) of 1-fluoro-4-(methylsulfinyl)benzene.



Fig. S23. ¹H NMR (CDCl₃, 400 MHz) of 4-(methylsulfinyl)benzonitrile.



Fig. S24. ¹H NMR (CDCl₃, 400 MHz) of 1-(methylsulfinyl)-4-nitrobenzene.

5. References

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