Electronic Supplementary Information for

## Construction of efficient artificial light-harvesting system based on

## hyperbranched polyethyleneimine and improvement of photocatalytic

## performance

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### Experimental

### **Materials**

Unless specifically mentioned, the chemicals used are commercially available.

### **Synthesis**



Scheme S1. The synthetic route of the TPE-BSBO.

**Synthesis of TPE-2OH** : TPE-2OH was synthesized according to the literature report (Fig. S1).<sup>[S1]</sup> <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 9.33 (d, *J* = 11.3 Hz, 2H), 7.16 - 7.03 (m, 6H), 6.98 - 6.91 (m, 4H), 6.76 - 6.68 (m, 4H), 6.55 - 6.46 (m, 4H).

Synthesis of TPE-BSBO: TPE-2OH (182 mg, 0.5 mmol) was dissolved in 30 mL anhydrous ethanol under nitrogen. The sodium ethanol (68 mg, 1.0 mmol) was then dissolved in 5 mL of anhydrous ethanol and slowly added to the mixture. After stirring at room temperature for 30 min, 1,4-butane sultone (136 mg, 1.0 mmol) was dissolved in 5 mL anhydrous ethanol and slowly added into the mixed solution. Stir at room temperature for 24 h. At the end of the reaction, the solid residue was extracted and filtered, and then washed three times with anhydrous ethanol to obtain a white solid (204 mg, 75%) (Fig. S2 and S3). <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  7.19 – 7.04 (m, 3H), 7.03 – 6.91 (m, 1H), 6.90 – 6.75 (m, 1H), 6.75 – 6.63 (m, 1H), 3.92 – 3.76 (m, 10H), 2.48 – 2.38 (m, 1H), 1.78 – 1.67 (m, 4H). <sup>13</sup>C NMR (101 MHz, DMSO)  $\delta$  157.6, 144.3, 139.7, 136.0, 132.4, 131.3, 128.3, 126.8, 114.1, 67.6, 51.5, 28.6, 22.4.

### Characterizations

Bruker Avance 400 NMR instrument was used for testing <sup>1</sup>H NMR of synthetic compounds. Shimadzu UV-2450 spectrophotometer was used for obtaining UV-vis

absorption spectra. F-380A fluorescence spectrophotometer was used for obtaining fluorescence emission spectra. Malvern Zetasizer Nano ZS90 was used for testing zeta potential. Hamamatsu absolute quantum yield measuring instrument Quantaurus-QY was used to obtain fluorescence quantum yields.

### 1. Detection of <sup>1</sup>O<sub>2</sub> production in solution.

Compound 9,10-anthracenediyl-bis(methylene)-dimalonic acid (ABDA) was used as an indicator for detection of  ${}^{1}O_{2}$  in solution (Fig. S8). 20  $\mu$ M of photocatalyst was dissolved in 3 mL solution containing 0.2 mM of ABDA. The mixture was then placed in a cuvette and irradiated with a UV light (365-367 nm, 10 W). The absorption change of the sample at 378 nm was recorded by the UV-vis absorption spectrophotometer.

# 2. The generation of $O_2^-$ detected by *N*,*N*,*N'*,*N'*-tetramethyl-phenylenediamine (TMPD).

The mechanism of N,N,N',N'-tetramethyl-phenylenediamine (TMPD) as the scavenger monitors  $O_2^-$  in the solution. The 5 mM TMPD solution in DMSO was added to the aqueous solution to form a 0.1 mM solution. 20  $\mu$ M TPE-BSBO@PEI+DBT, TPE-BSBO and TPE-BSBO@PEI were added into TMPD solution respectively for  $O_2^-$  generation measurement. The mixture was then placed in a cuvette and irradiated with a UV light (365-367 nm, 10 W). The generation of  $O_2^-$  was detected by monitoring the absorption at 563 nm and 612 nm through UV-vis absorption spectra.

# **3.** General procedure for the reaction of oxidative hydroxylation of arylboronic acid.

Arylboronic acid (0.10 mmol), and *N*,*N*-diisopropylethylamine (DIPEA) (88  $\mu$ L, 0.50 mmol) were dissolved in the freshly prepared TPE-BSBO@PEI+DBT assembly solution (0.5 mol%, 2.0 mL). The mixture was subsequently irradiated by UV light (365-367 nm, 10 W/cm<sup>2</sup>) at room temperature for 12 h. After that, it was extracted with dichloromethane, and the combined organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. Then the organic solvent was concentrated in vacuo and purified by flash column chromatography with petroleum ether/ethyl acetate to afford the corresponding products.

### 4. Energy-transfer efficiency calculation

The energy-transfer efficiency ( $\Phi_{ET}$ ) was calculated from excitation fluorescence spectra through the equation S1:  $\Phi_{ET} = 1 - I_{DA} / I_{D.}$  Where  $I_{DA}$  and  $I_{D}$  are the

fluorescence intensities of the emission of TPE-BSBO@PEI+DBT assemblies (donor and acceptor) and TPE-BSBO@PEI assemblies (donor) respectively when excited at 312 nm. The energy-transfer efficiency ( $\Phi_{ET}$ ) was calculated as 73.1% in aqueous environment (Fig. S7a), measured under the condition of [TPE-BSBO] = 2.0 × 10<sup>-5</sup> M, [PEI] = 2.5 × 10<sup>-7</sup> M, [DBT] = 8.0 × 10<sup>-7</sup> M.

### Antenna effect calculation

The antenna effect was calculated based on the excitation spectra using equation S2: Antenna effect =  $(I_{DA,312} - I_{D,312}) / I_{DA,470}$ . Where  $I_{D,312}$  and  $I_{DA,470}$  are the fluorescence intensities at 558 nm with the excitation of the donor at 312 nm and the direct excitation of the acceptor at 470 nm, respectively.  $I_{DA,312}$  is the fluorescence intensities at 558 nm of the TPE-BSBO@PEI+DBT, which was normalized with the TPE-BSBO@PEI assemblies at 525 nm. The antenna effect value was calculated as 6.1 in water (Fig. S7b), measured under the condition of [TPE-BSBO] =  $2.0 \times 10^{-5}$  M, [PEI] =  $2.5 \times 10^{-7}$ M, [DBT] =  $8.0 \times 10^{-7}$  M.



Fig. S1 <sup>1</sup>H NMR spectra of TPE-2OH in DMSO- $d_6$ .



Fig. S3 <sup>13</sup>C NMR spectra of TPE-BSBO in DMSO- $d_6$ .



Fig. S4 (a) Fluorescence emission spectra of TPE-BSBO aqueous solution after adding different concentrations of PEI; (b) Zeta potential of PEI; (c) Excitation and emission spectra of TPE-BSBO. Experimental conditions:  $[TPE-BSBO] = 2.0 \times 10^{-5} \text{ M}, [PEI] = 2.5 \times 10^{-7} \text{ M}.$ 



**Fig. S5** (a) UV-vis absorption spectra of TPE-BSBO and TPE-BSBO@PEI in the aqueous solution; (b) Fluorescence emission spectra of TPE-BSBO and TPE-BSBO@PEI in the aqueous solution. Inset: Photographs of TPE-BSBO (left) and TPE-BSBO@PEI (right) under UV light.



**Fig. S6** Zeta potentials of (a) TPE-BSBO, (b) TPE-BSBO@PEI (4000:3), and (c) TPE-BSBO@PEI (400:5) in the aqueous solution. Inset: Tyndall effects of TPE-BSBO, TPE-BSBO@PEI(4000:3) and TPE-BSBO@PEI (400:5).



Fig. S7 (a) Fluorescence emission spectra of TPE-BSBO@PEI and TPE-BSBO@PEI+DBT in water (b) Fluorescence spectra of TPE-BSBO@PEI+DBT in aqueous solution, blue line (acceptor emission,  $\lambda_{ex} = 470$  nm) ([TPE-BSBO] = 2.0 × 10<sup>-5</sup> M, [PEI] = 2.5 × 10<sup>-7</sup> M, [DBT] = 8.0 × 10<sup>-7</sup> M.; the black line represents the fluorescence spectrum of TPE-BSBO@PEI, which was normalized according to the fluorescence intensity at 525 nm of the red line.



**Fig. S8** The absorption spectra of ABDA after irradiation by UV light for a different time in the presence of (a) ABDA in H<sub>2</sub>O, (b) TPE-BSBO+ ABDA dispersed in H<sub>2</sub>O, (c) TPE-BSBO@PEI+ABDA dispersed in H<sub>2</sub>O, and TPE-BSBO@PEI+DBT+ ABDA dispersed in H<sub>2</sub>O. (e) The mechanism of 9,10-anthracenediyl-bis(methylene)-dimalonic acid (ABDA) as the <sup>1</sup>O<sub>2</sub> scavenger monitors singlet oxygen generation in the solution. [TPE-BSBO] =  $2.0 \times 10^{-5}$  M, [PEI] =  $2.5 \times 10^{-7}$  M, [DBT] =  $8.0 \times 10^{-7}$  M, [ABDA] = $2.0 \times 10^{-4}$  M.



Fig. S9 (a) Plots of  $\Delta$ Abs (A<sub>0</sub>–A) for ABDA at 378 nm upon UV light irradiation for different time intervals in the presence of TPE-BSBO, TPE-BSBO@PEI, TPE-BSBO@PEI+DBT or blank; (b) The enhancement of absorption at 563 nm and 612 nm of TMPD with TPE-BSBO, TPE-BSBO@PEI, TPE-BSBO@PEI+DBT or blank in water after irradiation of UV light with different times; (c) The mechanism diagram of TMPD as a probe to detect O<sub>2</sub><sup>--</sup>.



**Fig. S10** The photocatalytic yields of OHAA were obtained by adding 0.1 mmol KI, 0.1 mmol NaN<sub>3</sub> and 0.1 mmol DMPO under optimal conditions, respectively.

ОН			
Ĺ	OH UV light (365-367	nm, 10 W)	Y <sup>OH</sup>
DIPEA, Cat., H <sub>2</sub> O, air			
Entry	conditions	Cat. (mol%)	Yield <sup>b</sup> (%)
1	None	0.50	10
2	TPE-BSBO	0.50	50
3	PEI	0.50	30
4	DBT	0.50	42
5	TPE-BSBO@PEI	0.50	65
6	TPE-BSBO@PEI+DBT	0.25	61
7	TPE-BSBO@PEI+DBT	0.75	91
8	TPE-BSBO@PEI+DBT	0.50	90
9°	TPE-BSBO@PEI+DBT	0.50	61
10 <sup>d</sup>	TPE-BSBO@PEI+DBT	0.50	92
11 <sup>e</sup>	TPE-BSBO@PEI+DBT	0.50	NR

 Table S1 Yields of oxidative hydroxylation of 4-pyridineboric acid under different conditions.<sup>a</sup>

<sup>*a*</sup>Reaction conditions: 4-pyridineboronic acid (0.1 mmol, 0.012 g), N,Ndiisopropylethylamine (DIPEA) (88  $\mu$ L, 0.5 mmol), 10 W UV light (365-367 nm), room temperature, 12 h; <sup>*b*</sup>Isolated yields; <sup>*c*</sup>Irradiation time was 6 h; <sup>*d*</sup>Irradiation time was 24 h; <sup>*e*</sup>Without UV light.



Table S2 Substrates scope with respect to different arylboronic acid derivatives.<sup>*a,b,c*</sup>

<sup>a</sup>Reaction conditions: arylboric acid substrate (0.1 mmol), N,N-diisopropylethylamine (DIPEA) (88 μL, 0.5 mmol), TPE-BSBO@PEI+DBT aqueous solution (2.0 mL), 10 W UV light (365-367 nm), room temperature; <sup>b</sup>Isolated yields; <sup>c</sup>The irradiation time was 6 h.



**Fig. S11** A plausible mechanism for the oxidative hydroxylation of 4-pyridineboronic acid using the TPE-BSBO@PEI+DBT as a photocatalyst.

## **Characterization Data for Products 2a-2n**

2a. 4-Hydroxypyridine

OH

90% yield; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.76 - 7.69 (m, 2H), 6.25 6.16 (m, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 176.2, 139.7, 116.3. HRMS (ESI):
Calcd for C<sub>4</sub>H<sub>6</sub>NO [M+H]<sup>+</sup>: 96.0444; found: 96.0441.

**2b.** Phenol

ОН

84% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.27 - 7.21 (m, 2H), 6.93 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.89 - 6.77 (m, 2H), 5.23 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  155.3, 129.7, 120.8, 115.3. HRMS (ESI): Calcd for C<sub>6</sub>H<sub>7</sub>O [M+H]<sup>+</sup>: 95.0497; found: 95.0493.

2c. 4-Fluorophenol

OH

F 92% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.98 - 6.88 (m, 2H), 6.82 - 6.73 (m, 2H), 5.28 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  158.6, 156.2, 151.21 (d, J = 2.2 Hz), 116.43 - 116.17 (m), 116.0. HRMS (ESI): Calcd for C<sub>6</sub>H<sub>6</sub>FO [M+H]<sup>+</sup>: 113.0403; found: 113.0400.

2d. 4-Chlorophenol

OH

Cl 93% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.21 – 7.16 (m, 1H), 6.79 – 6.73 (m, 1H), 5.36 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  153.9, 129.5, 125.7, 116.6. HRMS (ESI): Calcd for C<sub>6</sub>H<sub>6</sub>ClO [M+H]<sup>+</sup>: 129.0107; found: 129.0106.

2e. 4-Bromophenol

Br

87% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 - 7.28 (m, 2H), 6.76 - 6.66 (m, 2H), 5.25 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  154.6, 132.4, 117.2, 112.8. HRMS (ESI): Calcd for C<sub>6</sub>H<sub>6</sub>BrO [M+H]<sup>+</sup>: 172.9602; found: 172.9601.

**2f.** p-Nitrophenol

O2N OH

91% yield; <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  11.10 (s, 1H), 8.11 (d, J = 9.2 Hz, 2H), 6.93 (d, J = 9.2 Hz, 2H). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ )  $\delta$  164.5, 140.2, 126.7, 116.3. HRMS (ESI): Calcd for C<sub>6</sub>H<sub>6</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 140.0343; found: 140.0341.

**2g.** p-Hydroxybenzaldehyde

OHC 96

OHC 96% yield; <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  10.63 (s, 1H), 9.79 (s, 1H), 7.78 - 7.73 (m, 2H), 6.95 - 6.90 (m, 2H). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ )  $\delta$  191.5, 163.8, 132.6, 128.9, 116.3. HRMS (ESI): Calcd for C<sub>7</sub>H<sub>7</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 123.0441; found: 123.0440.

2h. 3-Hydroxybenzaldehyde

OHC  $\rightarrow$  0HC  $\rightarrow$  86% yield; 1H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.95 (s, 1H), 7.47 - 7.38 (m, 3H), 7.16 (ddd, J = 7.1, 2.6, 1.9 Hz, 1H), 6.26 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  192.7, 156.5, 137.7, 130.4, 123.5, 122.2, 114.7. HRMS (ESI): Calcd for C<sub>7</sub>H<sub>7</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 123.0441; found: 123.0441.

2i. 3-Cyanopheno

NC-

90% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.35 (t, J = 7.9 Hz, 1H), 7.23 (d, J = 7.7, 1.3 Hz, 1H), 7.19 – 7.13 (m, 1H), 7.13 – 6.75 (m, 1H), 6.99 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 156.5, 130.7, 124.4, 121.1, 118.8, 112.3. HRMS (ESI): Calcd for C<sub>7</sub>H<sub>6</sub>NO [M+H]<sup>+</sup>: 123.0441; found: 123.0439.

2j. 2-Cyanopheno

# CN OH

70% yield;<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 11.09 (s, 1H), 7.59 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.49 (ddd, *J* = 8.9, 7.4, 1.7 Hz, 1H), 7.01 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.92 (td, *J* = 7.5, 1.0 Hz, 1H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 160.2, 134.8, 133.3, 119.6, 117.1, 116.2, 98.9. HRMS (ESI): Calcd for C<sub>7</sub>H<sub>6</sub>NO [M+H]<sup>+</sup>: 123.0441; found: 123.0440.

2k. p-Cresol



<sup>H3C</sup> 85% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.02 – 6.96 (m, 1H), 6.73 (s, 1H), 6.38 – 5.79 (m, 1H), 2.24 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.8, 130.1, 115.2, 20.4. HRMS (ESI): Calcd for C<sub>7</sub>H<sub>9</sub>O [M+H]<sup>+</sup>: 109.0653; found: 109.0650.

# 2l. 4-Aminophenol

H<sub>2</sub>N  $(400 \text{ MHz}, \text{DMSO-}d_6) \delta 8.34 (s, 1H), 6.49 - 6.36 (m, 4H), 4.38 (s, 2H). {}^{13}\text{C NMR} (101 \text{ MHz}, \text{DMSO-}d_6) \delta 148.6,$ 

141.1, 116.0, 115.7. HRMS (ESI): Calcd for C<sub>6</sub>H<sub>8</sub>NO [M+H]<sup>+</sup>: 110.0606; found: 110.0604.

# 2m. 4-Methoxyphenol



80% yield; <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.90 (s, 1H), 6.80 - 6.60 (m, 4H), 3.65 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ )  $\delta$ 

152.5, 151.5, 116.1, 115.0, 55.7. HRMS (ESI): Calcd for C<sub>7</sub>H<sub>9</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 125.0603; found: 125.0603.

2n. p-tert-Butylphenol

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**20.** Pyrimidin-5-ol

OH

87% yield; <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  10.52 (s, 1H), 8.66 (s, 1H), 8.33 (s, 2H). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ )  $\delta$  152.5, 150.3, 144.7. HRMS (ESI): Calcd for C<sub>4</sub>H<sub>5</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 97.0402; found: 97.0401. Spectra of prepared Products 2a-2n



Fig. S13 <sup>13</sup>C NMR spectra of 4-Hydroxypyridine in DMSO- $d_6$ .



Fig. S15 <sup>13</sup>C NMR spectra of Phenol in CDCl<sub>3</sub>.



Fig. S17 <sup>13</sup>C NMR spectra of 4-Fluorophenol in CDCl<sub>3</sub>.



Fig. S19 <sup>13</sup>C NMR spectra of 4-Chlorophenol in CDCl<sub>3</sub>.



Fig. S21 <sup>13</sup>C NMR spectra of 4-Bromophenol in CDCl<sub>3</sub>.



Fig. S23 <sup>13</sup>C NMR spectra of p-Nitrophenol in DMSO- $d_6$ .



Fig. S25 <sup>13</sup>C NMR spectra of p-Hydroxybenzaldehyde in DMSO- $d_6$ .



Fig. S27 <sup>13</sup>C NMR spectra of 3-Hydroxybenzaldehyde in CDCl<sub>3</sub>.

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Fig. S29 <sup>13</sup>C NMR spectra of 3-Cyanophenol in CDCl<sub>3</sub>.



Fig. S31 <sup>13</sup>C NMR spectra of 2-Cyanopheno in DMSO- $d_6$ .



Fig. S33 <sup>13</sup>C NMR spectra of p-Cresol in CDCl<sub>3</sub>.



Fig. S35 <sup>13</sup>C NMR spectra of 4-Aminophenol in DMSO-*d*<sub>6</sub>.



Fig. S37 <sup>13</sup>C NMR spectra of 4-Methoxyphenol in DMSO- $d_6$ .



Fig. S39 <sup>13</sup>C NMR spectra of p-tert-Butylphenol in DMSO- $d_6$ .



Fig. S41 <sup>13</sup>C NMR spectra of Pyrimidin-5-ol in DMSO-*d*<sub>6</sub>.

[S1] L.-B. Xing, Y. Wang, X.-L. Li, N. Han, C.-Q. Ma, H. Liu, S. Yu, R. Wang, S. Zhuo, Adv. Opt. Mater., 2023, 11, 2201710.