## Strongly Coupled Phenazine-Porphyrin Dyads: Light-Harvesting Molecular Assemblies with Broad Absorption Coverage

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## **Table of Contents**

Syntheses of Phenazines	S-3
Scheme S1. Synthesis of Po Scheme S2. Synthesis of Pm	S-3 S-5
Syntheses of Porphyrins	S-7
Scheme S3. Syntheses of 3 and S5 Scheme S4. Syntheses of S6, HZ-Ester, and HZ Scheme S5. Syntheses of 4 Scheme S6. Syntheses of AZ-Ester and AZ Scheme S7. Syntheses of PoZ-Ester and PoZ Scheme S8. Syntheses of PmZ-Ester and PmZ	S-7 S-8 S-9 S-10 S-12 S-13
Absorption Measurements	S-14
Absorption of HZ and emission spectra of Po, Pm, AZ, PmZ, and PoZ Extinction Coefficients Measurement Methods Table S2. Summary of absorption and emission properties.	S-14 S-14 S-14
DFT Calculation Results	S-15
Calculated Rotational Barriers of PmZ and PoZ Calculated Absorption Spectra Calculated NTOs for PoZ	S-15 S-15 S-16
Cyclic-Voltammograms	8-17
Cyclic-Voltammogram of HZ-Ester	S-17
Dye-Sensitized Solar Cells Fabrication Methods	
Supporting Information References	S-19

#### **Syntheses of Phenazines**

**General Methods:** <sup>1</sup>H spectra were recorded at 400 MHz with an Agilent NMR instrument, and chemical shifts are reported as ppm from the internal reference tetramethylsilane (TMS). Absorption spectra were recorded using a Shimadzu UV-2600 UV-visible spectrophotometer.

#### Scheme S1. Synthesis of Po



### 4-((Trimethylsilyl)ethynyl)benzothiadiazole (S1).

The synthesis of **S1** is a modified version of a reported procedure.<sup>1</sup> To a solution of 4bromobenzothiadiazole (500 mg, 2.33 mmol) dissolved in tetrahydrofuran (20.8 mL) was added Pd(PPh<sub>3</sub>)<sub>4</sub> (161.8 mg, 0.14 mmol), CuI (26.7 mg, 0.14 mmol), and triethylamine (16.6 mL). After stirring for 5 minutes, trimethylsilylacetylene (0.38 mL) was added and stirred for another 18 hours at 60 °C under nitrogen. The resulting dark brown mixture was extracted with dichloromethane and water. After several extractions, the combined organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure via rotary evaporation. Purification by column chromatography (SiO<sub>2</sub>, petroleum ether/dichloromethane = 1:1) afforded dark yellow liquid (385 mg, 71%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.76 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.32 (dd, *J* = 8.0 Hz, 1H), 0.15 (s, 9H); LC-MS (ESI) obsd 233.0 calcd 233.1 [(M+H)<sup>+</sup>, M = C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>SSi].



### 4-((Ethylsilyl)ethynyl)benzothiadiazole (S2).

The synthesis of **S2** is a modified version of reported procedures.<sup>1,2</sup> To a solution of **S1** (78 mg, 0.34 mmol) dissolved in a solvent mixture of tetrahydrofuran (4.4 mL) and methanol (4.4 mL) was added tetrabutylammonium fluoride in tetrahydrofuran (0.41 mL). After stirring under nitrogen for an hour at room temperature, the resulting mixture was extracted with ethyl acetate, NaHCO<sub>3</sub>, and brine. After several extractions, the combined organic layer was washed with brine once more, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure via rotary evaporation.

Purification by column chromatography (SiO<sub>2</sub>, tetrahydrofuran/hexanes = 1:5) afforded white solids (48.5 mg, 89%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.04 (dd, J = 0.8, 8.88 Hz, 1H), 7.80 (dd, J = 0.56, 6.94 Hz, 1H), 7.58 (dd, J = 1.88, 15.8 Hz, 1H), 3.59 (s, 1H); LC-MS (ESI) obsd 161.0 calcd 161.01 [(M+H)<sup>+</sup> M = C<sub>8</sub>H<sub>4</sub>N<sub>2</sub>S]



## **3-Ethynylbenzene-1,2-diamine (1).**

The synthesis of **1** is a modified version of a reported procedure.<sup>2</sup> To a flame-dried Schlenk flask containing a solution of **S2** (189 mg, 1.18 mmol) dissolved in tetrahydrofuran (32 mL) was added lithium aluminum hydride 1.0 M in diethyl ether (4.39 mL, 9.44 mmol) at 0 °C under nitrogen. The mixture was warmed to room temperature, stirred for 4 hours, and then added with dichloromethane for extraction. After several extractions, the combined organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure via rotary evaporation. Purification by column chromatography (SiO<sub>2</sub>, ethyl acetate/hexanes = 1:2) afforded UV-active, viscous yellow solids (50 mg, 32%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.91 (dd, *J* = 4.0, 7.6 Hz, 1H), 6.66 (dd, *J* = 1.6, 7.6 Hz, 1H), 6.60 (m, 1H), 3.64 (*broad* s, 4H), 3.35 (s, 1H). LC-MS (ESI) obsd 133.06 calcd 133.07 [(M+H)<sup>+</sup> M = C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>].



### 10-Ethynyldibenzophenazine (Po).

To a solution of **1** (45 mg, 0.34 mmol) dissolved in a solvent mixture of ethanol (5.4 mL) and dichloromethane (1 mL) was added phenanthrene-9,10-dione (70.8 mg, 0.34 mmol). After stirring for 18 hours at 75 °C, the reaction was cooled to room temperature and concentrated for purification. Column chromatography (SiO<sub>2</sub>, ethyl acetate/hexanes = 1:2) afforded pale white solids (67 mg, 65%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.48 (dd, *J* = 1.6, 8.0 Hz, 1H), 9.35 (dd, *J* = 1.2, 8.0 Hz, 1H), 8.54 (dd, *J* = 4.0, 6.0 Hz, 2H), 8.31 (dd, 1.2, 8.0 Hz, 1H), 8.07 (dd, *J* = 1.2, 7.2, 1H), 7.81-7.70 (m, 5H), 3.68 (s, 1H). HRMS (m/z 100%) obsd 305.10636 calcd 305.1000 [(M+H)<sup>+</sup> M = C<sub>22</sub>H<sub>12</sub>N<sub>2</sub>];  $\lambda_{abs}$  (CH<sub>3</sub>OH) 379, 399 nm.

### Scheme S2. Synthesis of Pm



#### 5-((Trimethylsilyl)ethynyl)benzothiadiazole (S3).

The synthesis **S3** is a modified version of a reported procedure.<sup>1</sup> To a solution of 5bromobenzothiadiazole (500 mg, 2.33 mmol) dissolved in tetrahydrofuran (20.8 mL) was added with Pd(PPh<sub>3</sub>)<sub>4</sub> (161.8 mg, 0.14 mmol), CuI (26.7 mg, 0.14 mmol), triethylamine (16.6 mL). After stirring for 5 minutes, trimethylsilylacetylene (0.38 mL) was added and stirred for another 18 hours at 60 °C under nitrogen. The resulting dark brown mixture was extracted with dichloromethane and water. After several extractions, the combined organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure via rotary evaporation. Purification by column chromatography (SiO<sub>2</sub>, petroleum ether/dichloromethane = 1:1) afforded dark yellow liquid (459 mg, 85%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.82 (s, 1H), 7.61 (dd, *J* = 8.0 Hz, 1H), 7.31 (dd, *J* = 4.0 Hz, 1H), 0.04 (s, 9H); LC-MS (ESI) 233.0 calcd 233.1 [(M+H)<sup>+</sup> M = C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>SSi].



#### 5-((Ethylsilyl)ethynyl)benzothiadiazole (S4).

The synthesis S4 is a modified version of reported procedures.<sup>1,2</sup> To a solution of S3 (458.6 mg, 1.98 mmol) dissolved in a solvent mixture of tetrahydrofuran (27.5 mL) and methanol (27.5 mL) was added tetrabutylammonium fluoride in tetrahydrofuran (2.38 mL). After stirring under nitrogen for an hour at room temperature, the resulting mixture was extracted with NaHCO<sub>3</sub>, brine, and ethyl acetate. After several extractions, the combined organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure via rotary evaporation. Purification by column chromatography (SiO<sub>2</sub>, tetrahydrofuran/hexanes = 1:7) afforded white solids (284 mg, 90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.05 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.50 (dd, *J* = 1.6, 8.0 Hz, 1H), 3.22 (s, 1H); LC-MS (ESI) obsd 161.0 calcd 161.01 [(M+H)<sup>+</sup> M = C<sub>8</sub>H<sub>4</sub>N<sub>2</sub>S].



### 4-Ethynylbenzene-1,2-diamine (2).

The synthesis of **2** is a modified version of a reported procedure.<sup>2</sup> To a flame-dried Schlenk flask containing a solution of **S4** (274 mg, 1.71 mmol) dissolved in tetrahydrofuran (46.6 mL) was added lithium aluminum hydride 1.0 M in diethyl ether (6.36 mL, 13.7 mmol) at 0 °C under nitrogen. The mixture was warmed to room temperature, stirred for 4 hours, and then added with dichloromethane for extraction. After several extractions, the combined organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure via rotary evaporation. Purification by column chromatography (SiO<sub>2</sub>, ethyl acetate/hexanes = 1:2) afforded UV-active, viscous yellow solids (191 mg, 84%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.88 (dd, *J* = 2.0, 4.0 Hz, 1H), 6.81 (d, *J* = 1.6 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 3.41 (*broad* s, 4H), 2.94 (s, 1H). LC-MS (ESI) obsd 134.06 calcd 134.07 [(M+H)<sup>+</sup> M = C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>].



### 11-Ethynyldibenzophenazine (Pm).

To a solution of **2** (96.5 mg, 0.73 mmol) dissolved in a solvent mixture of ethanol (11.6 mL) and dichloromethane (2.3 mL) was added phenanthrene-9,10-dione (152 mg, 0.73 mmol). After stirring for 18 hours at 75 °C, the reaction was cooled to room temperature and dried for purification. Column chromatography (SiO<sub>2</sub>, ethyl acetate/hexanes = 1:2) afforded pale white solids (153 mg, 69%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.34 (d, *J* = 8.0 Hz, 2H), 8.53 (d, *J* = 8.0 Hz, 2H), 8.45 (d, *J* = 1.6 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 7.85 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.808-7.707 (m, 4H), 3.34 (s, 1H); HRMS (m/z 100%) obsd 305.10715 calcd 305.1000 [(M+H)<sup>+</sup> M = C<sub>22</sub>H<sub>12</sub>N<sub>2</sub>];  $\lambda_{abs}$  (CH<sub>3</sub>OH) 383, 405 nm.

## **Syntheses of Porphyrins**

**General Methods:** <sup>1</sup>H spectra were recorded at 400 MHz with an Agilent NMR instrument, and chemical shifts are reported as ppm from the internal reference tetramethylsilane (TMS). Absorption spectra were recorded using a Shimadzu UV-2600 UV-visible spectrophotometer.

## Scheme S3. Syntheses of 3 and S5



## 5,15-Dimesitylporphyrin (3).

The synthesis of **3** is a modified version of a reported procedure.<sup>3</sup> To a flame-dried Schlenk flask containing a solvent mixture of anhydrous dichloromethane (100 mL) and ethanol (0.75 mL) was added dipyrromethene (146 mg, 1 mmol) and mesitaldehyde (0.148 mL, 1 mmol) at room temperature. After stirring for 10 minutes, BF<sub>3</sub>OEt<sub>2</sub> (0.04 mL) was added and the flask was shielded from light with aluminum foil. The mixture was stirred under nitrogen at room temperature for 2 hours. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 0.18 g, 0.8 mmol) was added and the mixture was stirred for 30 minutes. The mixture was quenched with triethylamine (1.5 mL) and the solvent was removed partially via rotary evaporation for column chromatography  $(SiO_2)$ dichloromethane/hexanes = 1:1) to afford dark purple solids (71 mg, 24%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.21 (s, 2H), 9.32 (d, J = 4.0 Hz, 4H), 8.88 (d, J = 4.0 Hz, 4H), 7.32 (s, 4H), 2.65 (s, 6H), 1.84 (s, 12H), -3.06 (s, 2H).

## 10-bromo-5,15-dimesitylporphyrin (S5).

The synthesis of **S5** is a modified version of a reported procedure.<sup>4</sup> To a solution of porphyrin **3** (71.9 mg, 0.24 mmol) dissolved in a solvent mixture of dichloromethane (55.2 mL) and methanol (6.1 mL) was added *N*-bromosuccinimide (NBS, 46 mg, 0.26 mmol) at room temperature. After stirring for 5 minutes, the mixture was quenched with NaHCO<sub>3</sub> (20 mg), and then diluted with water (60 mL). The organic phase was separated, and the aqueous phase was extracted with dichloromethane (2 x 40 mL). The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure via rotary evaporation. Purification by column chromatography (SiO<sub>2</sub> toluene/hexanes = 4:1) afforded compound **S5** (90 mg, 60%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.07 (s, 1H), 9.66 (d, *J* = 4.0 Hz, 2H), 9.22 (d, *J* = 4.0 Hz, 2H), 8.78 (d, *J* = 4.0 Hz, 4H), 7.30 (s, 4H), 2.64 (s, 6H), 1.83 (s, 12 H), -2.85 (s, 2H).

### Scheme S4. Syntheses of S6, HZ-Ester, and HZ



### 5-(4-Methylcarboxyphenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (S6).

The synthesis of **S6** is a modified version of a reported procedure.<sup>5</sup> To a flame-dried Schlenk flask containing a solution of porphyrin **S5** (41 mg, 0.066 mmol) dissolved in anhydrous tetrahydrofuran (14.52 mL) was added methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (120.57 mg, 0.46 mmol), K<sub>3</sub>PO<sub>4</sub> (265.34 mg, 1.25 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (7.6 mg, 10% mol). After stirring at 67 °C under nitrogen for 18 hours, the mixture was cooled to room temperature and extracted with dichloromethane (3 x 20 mL). The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated. Purification by gradient column chromatography (SiO<sub>2</sub>, dichloromethane/hexanes = 3:7 to 5:5 to 6:4) afforded purple solids (40 mg, 90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.13 (s, 1H), 9.28 (d, *J* = 4.0 Hz, 2H), 8.84 (d, *J* = 4.0 Hz, 2H), 8.75 (s, 3H), 7.30 (s, 4H), 4.10 (s, 3H), 2.64 (s, 6H), 1.84 (s, 12H), -2.90 (s, 2H).

## 5-(4-Methoxycarboxylphenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrinatozinc (II) (HZ-Ester).

The synthesis of **HZ-Ester** is a modified version of a reported procedure.<sup>6</sup> To a solution of **S6** (80 mg, 0.12 mmol) dissolved in a solvent mixture of chloroform (180 mL) and methanol (30 mL) was added Zn(OAc)<sub>2</sub> dihydrate (395.1 mg, 1.8 mmol). The mixture was refluxed for 18 hours and cooled down to room temperature. After several extractions with dichloromethane, water, and brine, the organic layer was dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated. Purification by column chromatography (SiO<sub>2</sub>, dichloromethane/hexanes = 1:3) afforded pink solids (81 mg, 91%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.17 (s, 1H), 9.34 (d, *J* = 4.0 Hz, 2H), 8.92 (d, *J* = 4.0 Hz, 2H), 8.84 (d, *J* = 4.0 Hz, 4H), 8.31 (d, 4H), 7.29 (s, 4H), 3.99 (s, 3H), 2.64 (s, 6H), 1.82 (s, 12H); MALDI-MS obsd 742.31, calcd 742.23 [M<sup>+</sup>, M = C<sub>46</sub>H<sub>38</sub>N<sub>4</sub>O<sub>2</sub>Zn].

## 5-(4-Carboxylphenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrinatozinc (II) (HZ).

To a solution of **HZ-Ester** (20 mg, 0.027 mmol) dissolved in a solvent mixture of tetrahydrofuran (1.4 mL) and ethanol (0.7 mL) was added 1.4 mL of 2.0 M KOH solution. After stirring for 18 hours at room temperature under nitrogen, the mixture was acidified with 1.0 M HCl solution and extracted with dichloromethane, NaHCO<sub>3</sub>, and brine. The solution was concentrated under reduced pressure via rotatory evaporation and purified using gradient column chromatography (SiO<sub>2</sub>, ethyl acetate/hexanes = 1:1 to 4:1) to afford pink solids (16 mg, 82%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.09 (s, 1H), 9.26 (d, *J* = 4.0 Hz, 2H), 8.84 (d, *J* = 4.0 Hz, 2H), 8.78 (q, *J* = 4.0 Hz, 4H), 8.40 (d, *J* = 8.0 Hz, 2H), 8.28 (d, *J* = 8.0 Hz, 2H), 7.22 (s, 4H), 2.55 (s, 6H), 1.75 (s, 12H); MALDI-MS obsd 728.87, calcd 728.21 [M<sup>+</sup>, M = C<sub>45</sub>H<sub>36</sub>N<sub>4</sub>O<sub>2</sub>Zn];  $\lambda_{abs}$  (CH<sub>3</sub>OH) 416, 551, 587 nm.



## 5-Bromo-15-(4-methylcarboxyphenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (S8).

The synthesis of **S8** is a modified version of a reported procedure.<sup>5</sup> To a solution of **S6** (45.8 mg, 0.067 mmol) dissolved in dichloromethane (14 mL) was added *N*-bromosuccinimide (13 mg, 0.074 mmol). After stirring for 0.5 hours, the mixture was quenched with NaHCO<sub>3</sub> (6 mg) and was extracted with dichloromethane (3 x 15 mL). The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure via rotary evaporation. Purification by column chromatography (SiO<sub>2</sub>, dichloromethane/hexanes = 1:1) afforded compound **S8** (47 mg, 92%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.60 (d, *J* = 8.0 Hz, 2H), 8.75 (d, *J* = 4.0 Hz, 2H), 8.67 (dd, *J* = 4.0, 12.0, 4H), 8.41 (d, *J* = 8.0 Hz, 2H), 8.27 (d, *J* = 8.0 Hz, 2H), 7.28 (s, 4H), 4.09 (s, 3H), 2.63 (s, 6H), 1.83 (s, 12H), -2.58 (s, 2H); MALDI-MS obsd 758.34, calcd 758.23 [M<sup>+</sup>, M = C<sub>46</sub>H<sub>39</sub>BrN<sub>4</sub>O<sub>2</sub>].

## 5-Bromo-15-(4-methylcarboxyphenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrinatozinc(II) (4).

To a solution of **S8** (50 mg, 0.066 mmol) dissolved in a solvent mixture of dichloromethane (13.2 mL) and methanol (1.32 mL) was added pure Zn(OAc)<sub>2</sub> (242 mg, 1.32 mmol). After stirring for 2 hours at room temperature, the resulting mixture was extracted three times with water. The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure by rotary evaporation. Purification by gradient column chromatography (SiO<sub>2</sub>, dichloromethane/hexanes = 1:1 to 3:1) afforded pink solids (49 mg, 91%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.70 (d, *J* = 4.0 Hz, 2H), 8.82 (d, *J* = 4.0 Hz, 2H), 8.74 (dd, *J* = 4.0, 12.0, 4H), 8.33 (d, *J* = 8.0 Hz, 2H), 8.26 (d, *J* = 8.0 Hz, 2H), 7.28 (s, 4H), 4.02 (s, 3H), 2.63 (s, 6H), 1.82 (s, 12H); MALDI-MS obsd 820.22, calcd 820.14 [M<sup>+</sup>, M = C<sub>46</sub>H<sub>37</sub>N<sub>4</sub>O<sub>2</sub>Zn].

Scheme S6. Syntheses of AZ-Ester and AZ



## 5-((Trimethylsilyl)ethynyl)-15-(4-carboxylphenyl)-10,20-bis(2,4,6-trimethylphenyl) porphyrinatozinc (89).

To a flame-dried Schlenk flask containing a solution of 4 (21 mg, 0.026 mmol) dissolved in anhydrous tetrahydrofuran (0.9 mL) was added Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (4.5 mg, 25% mol), CuI (1.2 mg, 25% mol), and triethylamine (0.3 mL). After stirring for 10 minutes, the mixture was cooled to -7 °C, and trimethylsilylacetylene (17  $\mu$ L, 0.52 mmol) was added. The mixture was warmed to room temperature and stirred for 12 hours. Dichloromethane was added to the resulting mixture and washed three times with water. The organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure by rotary evaporation. Purification by column chromatography (SiO<sub>2</sub>, dichloromethane/hexanes = 1:1) afforded purple solids (21 mg, 96%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.71 (d, *J* = 4.0 Hz, 2H), 8.83 (d, *J* = 4.0 Hz, 2H), 8.74 (d, *J* = 4.0 Hz, 2H), 8.71 (d, *J* = 4.0 Hz, 2H), 8.26 (d, *J* = 4.0 Hz, 2H), 7.28 (s, 4H), 4.03 (s, 3H), 2.63 (s, 6H), 1.82 (s, 12H), 0.59 (s, 9H); MALDI-MS obsd 838.41, calcd 838.27 [M<sup>+</sup>, M = C<sub>51</sub>H<sub>46</sub>N<sub>4</sub>O<sub>2</sub>SiZn].

## 5-Ethynyl-15-(4-methylcarboxyphenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrinatozinc (AZ-Ester).

To a solution of **S9** (20 mg, 0.024 mmol) dissolved in dichloromethane (9.4 mL) was added tetrabutylammonium fluoride in tetrahydrofuran (0.1 mL). The reaction was stirred and tracked by Thin Layer Chromatography. The resulting mixture was concentrated under reduced pressure via rotary evaporation for purification, and purification by column chromatography afforded purple solids (12.5 mg, 68% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.72 (d, *J* = 4.0 Hz, 2H), 8.84 (d, *J* = 4.0 Hz, 2H), 8.76 (d, *J* = 4.0 Hz, 2H), 8.72 (d, *J* = 4.0 Hz, 2H), 8.36 (d, *J* = 8.0 Hz, 2H), 8.27 (d, *J* = 8.0 Hz, 2H), 7.29 (s, 4H), 4.14 (s, 1H), 4.05 (s, 3H), 2.63 (s, 6H), 1.82 (s, 12H); MALDI-MS obsd 766.30, calcd 766.23 [M<sup>+</sup>, M = C<sub>48</sub>H<sub>38</sub>N<sub>4</sub>O<sub>2</sub>Zn].

**5-Ethynyl-15-(4-carboxyphenyl)-10,20-bis(2,4,6-trimethylphenyl) porphyrinatozinc (AZ).** To a solution of **AZ-Ester** (21 mg, 0.025 mmol) dissolved in a solvent mixture of tetrahydrofuran (1.29 mL) and ethanol (0.65 mL) was added 2.0 M KOH solution (1.29 mL). After stirring for 18 hours at room temperature under nitrogen, the resulting mixture was added with dichloromethane, 1.0 M citric acid solution and water for extraction. After several extractions with water, the combined organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure via rotary evaporation. Purification by gradient column chromatography (SiO<sub>2</sub>, 100% dichloromethane to dichloromethane/ethyl acetate = 4/1) afforded purple solids (13 mg, 69%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.65 (d, *J* = 4.0 Hz, 2H), 8.77 (d, *J* = 4.0 Hz, 2H), 8.71 (d, *J* = 4.0 Hz, 2H), 8.67 (d, *J* = 4.0 Hz, 2H), 8.40 (d, *J* = 8.0 Hz, 2H), 8.25 (d, *J* = 8.0 Hz, 2H), 7.22 (s, 4H), 4.07 (s, 1H), 2.57 (s, 6H), 1.76 (s, 12H); MALDI-MS obsd 752.32, calcd 752.21 [M<sup>+</sup>, M = C<sub>47</sub>H<sub>36</sub>N<sub>4</sub>O<sub>2</sub>Zn];  $\lambda_{abs}$  (CH<sub>3</sub>OH) 428, 566, 611 nm.

#### Scheme S7. Syntheses of PoZ-Ester and PoZ



## 5-(10-Ethynyldibenzophenazine)-15-(4-methylcarboxyphenyl)-10,20-bis(2,4,6-trimethylphenyl) porphyrinatozinc (PoZ-Ester).

To a solution of **4** (23.7 mg, 0.029 mmol) and 10-Ethynyldibenzophenazine (**Po**) (26.5 mg, 0.087 mmol) dissolved in anhydrous tetrahydrofuran (2.4 mL) was added Pd<sub>2</sub>(dba)<sub>3</sub> (8 mg, 30% mol), CuI (0.28 mg, 5% mol), P(*o*-tol)<sub>3</sub> (21 mg, 0.07 mmol), and triethylamine (0.48 mL). After stirring for 18 hours at 60 °C under nitrogen, the mixture was extracted with dichloromethane. Purification by dry-loading gradient column chromatography (SiO<sub>2</sub>, unstabilized tetrahydrofuran/hexanes = 1/19 to 1/9 to 3/17) afforded green solids that fluoresces in red (22mg, 73%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.28 (d, *J* = 4.0 Hz, 2H), 10.05 (dd, *J* = 4.0, 8.0 Hz, 1H), 9.50 (dd, *J* = 4.0, 8.0 Hz, 1H), 8.93 (d, *J* = 4.0 Hz, 2H), 8.77 (d, *J* = 4.0 Hz, 2H), 8.74 (d, *J* = 4.0 Hz, 2H), 8.63 (d, *J* = 8.0 Hz, 2H), 8.59 (dd, *J* = 4.0, 8.0 Hz, 1H), 8.47-8.41 (m, 3H), 8.32-8.29 (m, 2H), 8.04 (dd, *J* = 4.0, 4.0 Hz, 1H), 7.85-7.78 (m, 3H) 7.63 (t, *J* = 4.0 Hz, 1H), 7.32 (s, 4H), 4.10 (s, 3H), 2.66 (s, 6H), 1.90 (s, 12H); MALDI-MS obsd 1044.46, calcd 1044.31 [M<sup>+</sup>, M = C<sub>68</sub>H<sub>48</sub>N<sub>6</sub>O<sub>2</sub>Zn];  $\lambda_{abs}$  (CH<sub>3</sub>OH) 489, 578, 636 nm.

# 5-(10-Ethynyldibenzophenazine)-15-(4-carboxyphenyl)-10,20-bis(2,4,6-trimethylphenyl) porphyrinatozinc (PoZ).

To a solution of **PoZ-Ester** (34.6 mg, 0.033 mmol) dissolved in a solvent mixture of tetrahydrofuran (1.70 mL) and ethanol (0.85 mL) was added 1.70 mL of 2.0M KOH solution. After stirring under nitrogen for 18 hours at room temperature, the mixture was acidified with saturated solution of NH<sub>4</sub>Cl and extracted with dichloromethane, NaHCO<sub>3</sub> and brine. The resulting mixture was concentrated under reduced pressure via rotatory evaporation and purified using gradient column chromatography (SiO<sub>2</sub>, dichloromethane/methanol = 9:1) to afford green solids (20 mg, 59%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.26 (d, *J* = 4.0 Hz, 2H), 10.08 (d, *J* = 8.0 Hz, 1H), 9.51 (dd, *J* = 8.0 Hz, 1H), 8.90 (d, *J* = 8.0 Hz, 2H), 8.76 (d, *J* = 4.0 Hz, 2H), 8.72 (d, *J* = 4.0 Hz, 2H), 8.65 (d, *J* = 8.0 Hz, 2H), 8.59 (d, *J* = 8.0 Hz, 1H), 8.49-8.44 (m, 3H), 8.34 (d, *J* = 8.0 Hz, 2H), 8.04 (t, *J* = 8.0 Hz, 1H), 7.88-7.79 (m, 3H), 7.66 (t, *J* = 4.0 Hz, 1H), 7.33 (s, 4H), 2.67 (s, 6H), 1.91 (s, 12H); MALDI-MS obsd 1030.76, calcd 1030.30 [M<sup>+</sup>, M = C<sub>67</sub>H<sub>46</sub>N<sub>6</sub>O<sub>2</sub>Zn];  $\lambda_{abs}$  (CH<sub>3</sub>OH) 436, 579, 636 nm.

#### Scheme S8. Syntheses of PmZ-Ester and PmZ



## 5-(11-Ethynyldibenzophenazine)-15-(4-methylcarboxyphenyl)-10,20-bis(2,4,6-trimethylphenyl) porphyrinatozinc (PmZ-Ester).

To a solution of **4** (35 mg, 0.04 mmol) and 11-Ethynyldibenzophenazine (**Pm**) (37 mg, 0.12 mmol) dissolved in anhydrous tetrahydrofuran (3.3 mL) was added Pd<sub>2</sub>(dba)<sub>3</sub> (11 mg, 30% mol), CuI (0.38 mg, 5% mol), P(*o*-tol)<sub>3</sub> (29 mg, 0.1 mmol), and triethylamine (0.66 mL). After stirring under nitrogen for 18 hours at 60 °C, the mixture was extracted with dichloromethane. Purification by dry-loading gradient column chromatography (SiO<sub>2</sub>, unstabilized tetrahydrofuran/hexanes = 1/19 to 1/9 to 3/17) afforded green solids that fluoresces in red (35.6 mg, 85%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.88 (d, *J* = 4.0 Hz, 2H), 9.50 (qd, *J* = 8.0 Hz, 2H), 8.97 (s, 1H), 8.90 (d, *J* = 4.0 Hz, 2H), 8.75 (d, *J* = 4.0 Hz, 2H), 8.71 (d, *J* = 4.0 Hz, 2H), 8.62 (d, *J* = 8.0 Hz, 2H), 8.49 (d, *J* = 8.0 Hz, 1H), 8.43-8.39 (m, 3H), 8.29-8.27 (m, 3H), 7.88-7.78 (m, 3H), 7.32 (s, 4H), 4.10 (s, 3H), 2.66 (s, 6H), 1.87 (s, 12H); MALDI-MS obsd 1044.32, calcd 1044.31 [M<sup>+</sup>, M = C<sub>68</sub>H<sub>48</sub>N<sub>6</sub>O<sub>2</sub>Zn];  $\lambda_{abs}$  (CH<sub>3</sub>OH) 447, 575, 636 nm.

# 5-(11-ethynyldibenzophenazine)-15-(4-carboxyphenyl)-10,20-bis(2,4,6-trimethylphenyl) porphyrinatozinc (PmZ).

To a solution of **PmZ-Ester**. (27 mg, 0.026 mmol) dissolved in tetrahydrofuran (1.34 mL) and ethanol (0.67 mL) was added 2.0M KOH solution (1.34 mL). After stirring under nitrogen for 18 hours at room temperature, the mixture was acidified with saturated solution of NH<sub>4</sub>Cl and extracted with dichloromethane, NaHCO<sub>3</sub> and brine. The resulting mixture was concentrated under reduced pressure via rotatory evaporation and purified by gradient column chromatography (SiO<sub>2</sub>, unstabilized tetrahydrofuran/hexanes = 1:2) to afford green solids (13 mg, 50%). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD):  $\delta$  9.83 (d, *J* = 8.0 Hz, 2H), 9.47 (dd, *J* = 8.0, 12.0 Hz, 2H), 8.90 (s, 1H), 8.80 (d, *J* = 8.0 Hz, 2H), 8.72 (d, *J* = 8.0 Hz, 4H), 8.58 (d, *J* = 4.0 Hz, 2H), 8.49 (d, *J* = 4.0 Hz, 2H), 8.33 (d, *J* = 8.0 Hz, 2H), 8.19 (d, *J* = 8.0 Hz, 2H), 7.84 (q, *J* = 8.0 Hz, 4H), 7.33 (s, 4H), 2.64 (s, 6H), 1.90 (s, 12H); MALDI-MS obsd 1030.71, calcd 1030.30 [M<sup>+</sup>, M = C<sub>67</sub>H<sub>46</sub>N<sub>6</sub>O<sub>2</sub>Zn];  $\lambda_{abs}$  (CH<sub>3</sub>OH) 434, 446, 576, 636 nm.

#### Absorption Measurements

#### Absorption of HZ and emission spectra of Po, Pm, AZ, PmZ, and PoZ



Figure S1. Absorption of HZ (left) and emission spectra of Po, Pm, AZ, PmZ, and PoZ (right).

#### **Extinction Coefficients Measurement Methods**

Stock solutions of samples were prepared with volumetric flasks through the dissolution of weighted samples in HPLC grade methanol. An aliquot of the stock solutions was then diluted according to the factors in **Table S1** with methanol to around 3 mL. Absorption spectra of the resulting diluted solutions were measured at room temperature with a two-sided glass cuvette ( $1 \text{ cm} \times 1 \text{ cm}$ ) without deaeration, affording absorbance in the range of 0.6 to 1.3. The extinction coefficient of each compound at the peak wavelength was then calculated based on the Beer's Law.

Compound	Mass (mg)	Initial concentration (M)	Dilution factor	Final concentration (M)	$A_{\mathrm{peak}}$	$\mathcal{E}_{peak} \ (\mathrm{M}^{-1}\mathrm{cm}^{-1})$
HZ	1.0	$1.4 \times 10^{-3}$	628	$2.2 \times 10^{-6}$	1.20	$5.4 \times 10^{5}$
AZ	1.2	$1.6 \times 10^{-3}$	276	$5.8 \times 10^{-6}$	1.04	$1.8 \times 10^{5}$
PmZ	1.1	$4.3 \times 10^{-5}$	4.78	$9.0 \times 10^{-6}$	0.833	$9.2 \times 10^{4}$
PoZ	1.0	$9.7 \times 10^{-5}$	14.5	$6.7 \times 10^{-6}$	1.06	$1.6 \times 10^{5}$
Pm	1.1	$7.2 \times 10^{-4}$	10.4	$6.9 \times 10^{-5}$	0.753	$1.1 \times 10^4$
Ро	1.1	$7.2 \times 10^{-4}$	4.45	$1.6 \times 10^{-4}$	0.655	$4.0 \times 10^{3}$

 Table S1.
 Measurements of Extinction Coefficients in Methanol.

Table S2. Summary of absorption and emission properties.

Dye	$\lambda_{max} (nm)^a$	$\epsilon (M^{-1} \cdot cm^{-1})^a$	$\lambda_{\mathrm{Ex}}  (\mathrm{nm})^b$	$\lambda_{Em} (nm)^c$
AZ	611	$1.8 \times 10^{5}$	419	607, 659
Ро	398	$0.040 \times 10^{5}$	380	430
Pm	404	$0.11 \times 10^{5}$	365	412, 433
PoZ	634	$1.6 \times 10^{5}$	420	642
PmZ	636	$0.92 \times 10^5$	420	642

<sup>*a*</sup>Absorption peaks ( $\lambda_{max}$ ) and molar extinction coefficients ( $\epsilon$ ) were measured in methanol solutions (~10<sup>-6</sup> M). <sup>*b*</sup>Excitation wavelengths used to measure the emission peaks. <sup>*c*</sup>Emission peaks ( $\lambda_{Em}$ ) were measured in toluene solutions.

### **DFT Calculation Results**

Calculated Rotational Barriers of PmZ and PoZ



Figure S2. Calculated rotational barrier of PmZ (black) and PoZ (blue).





Figure S3. Calculated absorption spectra of HZ (black) and AZ (blue).



Figure S4. Calculated conformationally-averaged absorption spectra of PoZ.



Figure S5. Calculated transition at 620 nm for PoZ in its minimum-energy conformation.



Figure S6. DFT-calculated minimum energy conformations of PoZ (left) and PmZ (right).

## **Cyclic-Voltammograms**

## Cyclic-Voltammogram of HZ-Ester



**Figure S7.** Cyclic voltammogram of **HZ-Ester** in 0.1 M TBAPF<sub>6</sub> in dichloromethane with a 50 mV/s scan rate.

#### **Dye-Sensitized Solar Cells Fabrication Methods**

The assembly of the dye-sensitized solar cells was based on a previously reported method.<sup>7</sup> Electrodes used for the TiO<sub>2</sub> thin film working electrodes and counter electrodes were transparent conductive fluorine:SnO<sub>2</sub> glass (FTO, 7  $\Omega$ /square, Hartford Glass). The FTO was pre-treated prior to the deposition of TiO<sub>2</sub> films by immersing in a solution of 40 mM titanium (IV)-chloride-THF complex at 75 °C for a period of 30 minutes. The treated films were sintered in a box furnace at 370 °C and 570 °C for periods of 5 minutes and 30 minutes, respectively.

Deposition of the TiO<sub>2</sub> films was done by doctor-blading the TiO<sub>2</sub> paste obtained from Solaronix (14411,T-SP, 15 – 20 nm TiO<sub>2</sub> nanoparticles) to produce a reproducible thickness of 15  $\mu$ m for a transparent TiO<sub>2</sub> layer, and the resulting films were annealed at 370 °C for a period of 10 minutes and at 470 °C for a period of 30 minutes. These films were subsequently treated with TiCl<sub>4</sub> by immersing in a solution of TiCl<sub>4</sub> at 75 °C for a period of 30 minutes, and then they were sintered in a box furnace at 370 °C and 570 °C for periods of 5 minutes and 30 minutes, respectively. The films were taken out of the box at 100 °C and sensitized in a staining jar of fresh 0.2 mM dyad/porphyrin in methanol (17 mL) for a period of 17.5 hours in the dark at room temperature. Each porphyrin/dyad film was prepared in quadruplets.

The counter electrodes were prepared on FTO glass (15  $\Omega$ /square, Hartford Glass) via a deposition of chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>) solution in ethanol, followed by a heat treatment to crystallize the platinum at 450 °C for 30 minutes. The complete dye-sensitized solar cells were prepared by sealing the working and counter electrodes together with a 60 µm thick hot-melt film spacer (Surlyn), which serves as both a sealant and spacer. The electrolyte was prepared from a combination of 1,2-dimethyl-3-propylimidazolium iodide (DMPII, TCI, 0.6 M), lithium iodide (anhydrous, 99.95%, Alfa Aesar, 0.1 M), iodine (pure, Acros Organics, 0.2 M), 4-tert-butylpyridine (TBP, Sigma-Aldrich, 0.5 M) and anhydrous acetonitrile as the solvent (Omni Solv, EMD Millipore). The electrolyte solution was inserted into the cell through a pre-drilled hole in the counter electrode via vacuum back-filling method. Prior to this step, the hole in the counter electrode was sealed with a glass cover-slip and hotmelt film. The active area of each cell was 0.25 cm<sup>2</sup>. The J-V curves were performed without a mask.

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