

Supporting Information

Zn(II) Tetraarylporphyrins Anchored to Nanocrystalline TiO₂, ZnO and ZrO₂ films through Rigid-Rod Linkers

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Table of contents:

- I.** Synthesis
 - Ia.** Synthesis of precursors **1a** and *p*-iodo-ZnTPP
 - Ib.** Synthesis of rigid-rod-Ipa porphyrins
- II.** FT-IR-ATR Spectra
- III.** Fluorescence emission spectra in Solution
- IV.** UV-Vis Absorption on TiO₂ and ZrO₂
- V.** Fluorescence emission on TiO₂ and plot of ‘emission quantum efficiency’ vs. porphyrin rods length on TiO₂
- VI.** Cyclic Voltammograms
- VII.** Complete Ref. 1b

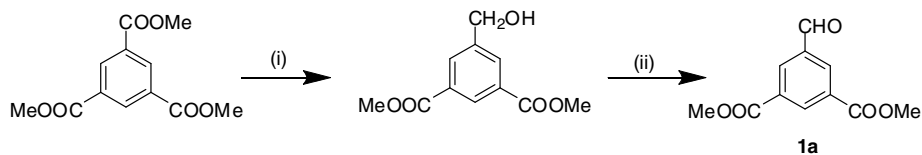
References

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I. Synthesis

General. All reactions involving air and moisture sensitive reagents were performed under a dry, oxygen-free, nitrogen atmosphere in oven-dried or flame-dried glassware. Reagents were purchased from Fisher-Acros or Sigma-Aldrich Chemical Company. Benzaldehyde, mesitylaldehyde, 1,4-diiodobenzene, bis(pinacolato)diboron, trimethylsilylacetylene, 2-methyl-3-butyn-2-ol, trimethyl-1,3,5-tricarboxybenzoate, 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), tetrakis(triphenylphosphine)palladium(0), dichlorobis(triphenylphosphine)palladium(II), tris(dibenzylideneacetone)dipalladium(0), cuprous(I) iodide, triphenylarsine, zinc(II) acetate, sodium hydroxide, sodium bicarbonate, sodium sulphate, potassium acetate, potassium carbonate and tetrabutylammonium fluoride, trimethyl-1,3,5-tricarboxybenzoate, sodium borohydride and manganese dioxide (activated, ~85 %, 5 μm) were all used as purchased without further purification. Pyrrole was freshly distilled over potassium hydroxide. Tetrahydrofuran (THF) was purchased anhydrous grade and then distilled under nitrogen atmosphere from sodium/benzophenone immediately prior to use. CH_2Cl_2 and hexane were both distilled over CaCl_2 prior to use. Triethylamine was distilled over CaH_2 before use. Ethyl acetate was purchased as HPLC grade and used as received. Thin-layer chromatography (TLC) was carried out using Whatman silica gel plates (Sorbent Technologies). NMR spectra were recorded on a Varian INOVA-500 spectrometer or a Varian INOVA-600 spectrometer under ambient probe temperature using CDCl_3 as solvent. Chemical shifts (δ) are given in parts per million (ppm) and reported to a precision of ± 0.01 ppm for proton and carbon. Proton coupling constants (J) are given in Hertz (Hz) and reported to a precision of ± 0.1 Hz. The spectra of all compounds were referenced to the residual solvent peak, i.e. CHCl_3 at 7.27 ppm and CH_3OH at 4.87 ppm, for the ^1H spectra and were referenced to CDCl_3 at 77.00 ppm for all ^{13}C spectra. Satisfactory ^{13}C spectra for all porphyrin acids could not be obtained due to their poor solubility. Dimethyl 5-iodobenzene-1,3-dicarboxylate **2a**¹ and linkers **4a**, **5a**, **6a**^{Error! Bookmark not defined.f,2} were synthesized by following published procedures.

Ia. Synthesis of precursors **1a** and *p*-iodo-ZnTPP

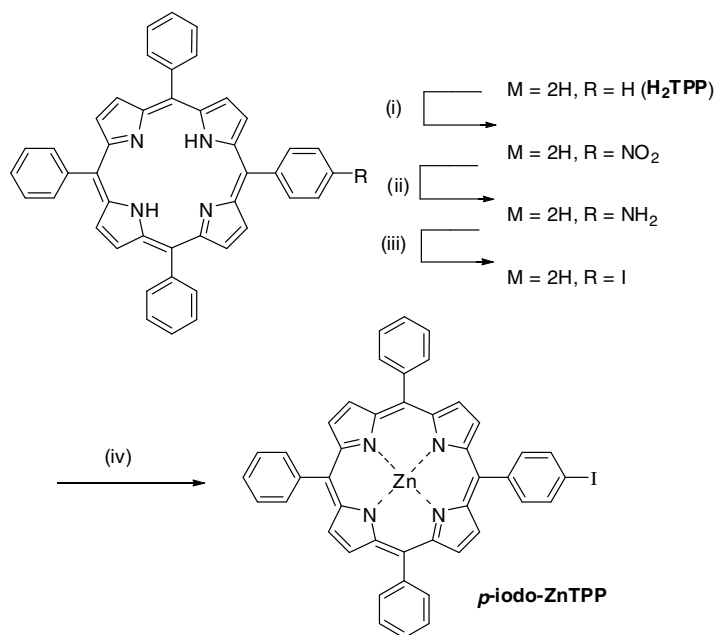


Scheme S-1. Preparation of aldehyde **1a**. *Reagents and conditions:* (i) THF / MeOH / NaBH₄/ r.t. / 30 min.; 57% yield (ii) CH₂Cl₂ / MnO₂ ; r.t. / 3 days; 94 % yield.

Dimethyl-5-(hydroxymethyl)isophthalate. Trimethyl-1,3,5-tricarboxybenzoate (5 g, 19.82 mmol) was placed, along with a stirring bar, in a two-neck 100 ml flask equipped with a reflux condenser and a 20 ml addition funnel. While maintaining a dry nitrogen atmosphere anhydrous THF (15 ml) was added to the reaction flask causing dissolution of the white solid. NaBH₄ (0.9 g, 23.79 mmol) was then added to this solution thus forming a suspension which was stirred continuously at room temperature. While stirring, a mixture of THF:MeOH (12.5ml:3.7ml) was added dropwise via the addition funnel. The reaction mixture was then refluxed for 30 min., during which time the reaction mixture changed from a transparent solution to a light yellow and back to transparent again. After cooling the reaction was quenched with 20 ml 1 N HCl (*note:* add slowly as evolution of H₂ gas occurs). The product was then extracted with EtOAc (3 x 25 ml). The organic phase was dried over Na₂SO₄ and the solvent removed *in vacuo* affording an off-white solid. The crude mixture was purified by silica gel column chromatography with EtOAc to afford 2.53 g (11.30 mmol, yield 57 %) of a white solid. Analytical data were in good agreement with the reported data.³ R_f = 0.46. ¹H NMR δ_H (CDCl₃): 8.62 (s, 1H), 8.25 (s, 2H), 4.83 (s, 2H), 3.96 (s, 6H) ppm.

Dimethyl-5-formylisophthalate (1a**).** Dimethyl-5-(hydroxymethyl)isophthalate (2.50 g, 11.15 mmol) was dissolved in 120 ml of dichloromethane and the solution purged with nitrogen for 10 min. Activated MnO₂ (4.85 g, 55.75 mmol) was then added and the reaction mixture was stirred vigorously at room temperature under nitrogen atmosphere. The progress of aldehyde formation was monitored using silica gel TLC (CH₂Cl₂). After three days the solution was filtered through Celite to remove MnO₂. The solvent was then removed *in vacuo*. The resulting yellow crude oil was purified by silica gel column chromatography (CH₂Cl₂) to afford 887 mg (5.40 mmol, 94 %) of a white solid.

Analytical data were in good agreement with the reported data.⁴ $R_f = 0.45$. ^1H NMR $\delta_{\text{H}}(\text{CDCl}_3)$: 10.14 (s, 1H), 8.93 (s, 1H), 8.73 (s, 2H), 4.01 (s, 6H) ppm.



Scheme S-2. Synthetic strategy followed for the preparation of Zn(II)-5-(4-iodophenyl)-10,15,20-triphenylporphyrin (*p*-iodo-ZnTPP). *Reagents and conditions:* (i) CH_2Cl_2 / 20 eq. fuming HNO_3 / 0°C / 2 h; 90 % yield (ii) conc. H_2SO_4 / 3 eq. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ / 70°C / 2 h; 85 % yield (iii) 20 % HCl / NaNO_3 / 2 eq. KI / -5°C / 1.5 h / 35 % yield. (iv) $\text{Zn}(\text{OAc})_2$ / CH_2Cl_2 / MeOH ; r.t. / 12 h; 95 % yield.

H_2 -5-(4-nitrophenyl)-10,15,20-triphenylporphyrin. Mononitration of H_2TPP was carried out by a modification of the procedure reported by Kruper et. al.⁵ In the published procedure fuming HNO_3 was added neat, whereas here it was added as a dichloromethane solution. This small change resulted in much improved yields. H_2TPP ⁶ (1 g, 1.62 mmol) was dissolved in 150 ml of dichloromethane in a two-necked round bottom flask fitted with a 10 ml addition funnel and a nitrogen inlet. The flask was placed in an ice bath and the solution was purged with nitrogen for 10 min. Dichloromethane (8.6 ml) was placed in the addition funnel followed by fuming nitric acid (1.4 ml, 32.4 mmol) and the resulting solution (total volume = 10 ml) was purged with nitrogen for 10 min. Both the reaction flask and the addition funnel were maintained under an atmosphere of nitrogen at this stage. The dichloromethane/nitric acid solution was then added dropwise to the porphyrin solution over a period of 2 hours at 0°C with vigorous stirring. During this time the color of the solution changed from deep purple to deep green. On completion of the addition the acid was neutralized by addition of NaHCO_3 (20 g), thus restoring the deep purple color of the neutral porphyrin. The solid was removed by filtration and the

solvent removed *in vacuo* affording 1 g (*ca.* 1.50 mmol) of crude product (yield: > 90 %). The ^1H NMR showed only one porphyrin product, with an estimated > 90 % purity therefore the crude solid was used for further synthesis without any further purification. ^1H NMR δ_{H} (CDCl_3): 8.91 (d, 2H, pyrrole, $J = 5$ Hz), 8.87 (s, 4H, pyrrole), 8.75 (d, 2H, pyrrole, $J = 5$ Hz), 8.64 (d, 2H, $J = 8$ Hz), 8.42 (d, 2H, $J = 8$ Hz), 8.22 (m, 6H), 7.77 (m, 9H), -2.75 (s, 2H) ppm.

H_2 -5-(4-aminophenyl)-10,15,20-triphenylporphyrin. Reduction of H_2 -5-(4-nitrophenyl)-10,15,20-triphenylporphyrin was carried out according to a procedure reported by Barragán et. al.⁷ To concentrated sulphuric acid (30 ml) was added crude H_2 -5-(4-nitrophenyl)-10,15,20-triphenylporphyrin (1 g > 90 % purity, *ca.* 1.50 mmol). This solution was purged with nitrogen before addition of 1.02 g (4.50 mmol) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. The reaction was heated to 70 °C and stirred for 2 hours. After cooling, the reaction mixture was poured onto 100 g of ice. The reaction vessel was placed in an ice bath and the reaction mixture stirred. The reaction mixture was neutralized by dropwise addition of concentrated NH_4OH solution at 0 °C followed by the slow addition of 10 % aqueous NH_4OH to pH 8. The aqueous phase was extracted with 3 x 50 ml portions of dichloromethane. Standard workup and removal of solvent under *in vacuo* resulted in a purple solid. The crude product was purified by silica gel chromatography (CH_2Cl_2) to afford the aminophenyl derivative as a purple solid (800 mg, 1.27 mmol, yield: 85 %). ^1H NMR δ_{H} (CDCl_3): 8.96 (d, 2H, pyrrole, $J = 5$ Hz), 8.86 (s, 6H, pyrrole), 8.25 (m, 6H), 8.01 (d, 2H, $J = 8$ Hz), 7.79 (m, 9H), 7.07 (d, 2H, $J = 8$ Hz), 4.00 (s, 2H, $-\text{NH}_2$), -2.71 (s, 2H) ppm.

H_2 -5-(4-iodophenyl)-10,15,20-triphenylporphyrin. This synthesis was done by adapting a procedure that involves a Sandmeyer reaction on H_2 -5-(4-aminophenyl)-10,15,20-triphenylporphyrin.⁸ Sodium nitrite (60 mg, 0.85 mmol) in water (25 ml) was added dropwise to a solution of H_2 -5-(4-aminophenyl)-10,15,20-triphenylporphyrin (500 mg, 0.85 mmol) in 20 % hydrochloric acid (15 ml) at -5 °C. The solution was stirred at low temperature for 30 minutes before the dropwise addition of an aqueous KI solution (286 mg, 1.7 mmol, in 25 ml of water). The reaction was allowed to reach room temperature and stirred for one further hour before the slow addition of 10 % NH_4OH aq. at 0 °C to increase the pH to 8. The aqueous phase was extracted with dichloromethane (3 x 50 ml). Standard workup and removal of solvent under *in vacuo* resulted in a purple

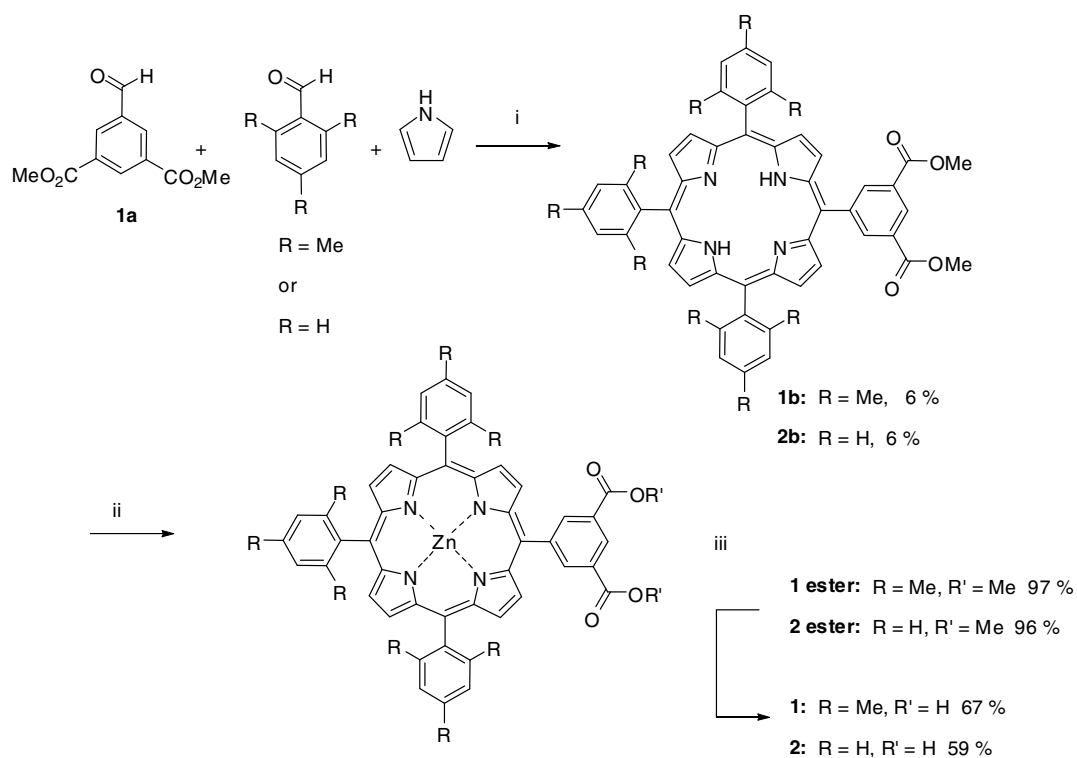
solid. The crude product was purified by silica gel chromatography using CH₂Cl₂:hexane (6:4) to afford the iododerivative as a purple solid (220 mg, 0.30 mmol, yield: 35 %). ¹H NMR δ_H (CDCl₃): 8.87 (m, 8H, pyrrole), 8.24 (m, 6H), 8.10 (d, 2H, *J* = 8 Hz), 7.98 (d, 2H, *J* = 8 Hz), 7.79 (m, 9H), -2.79 (s, 2H) ppm.

Zn(II)-5-(4-iodophenyl)-10,15,20-triphenylporphyrin (*p*-iodo-ZnTPP). H₂-5-(4-iodophenyl)-10,15,20-triphenylporphyrin (0.27 mmol/200 mg) was dissolved in CH₂Cl₂ (60 ml) and the solution was purged with nitrogen for 10 minutes. Zn(OAc)₂ (96 mg, 0.81 mmol, 1.5 equivalents) was first dissolved in MeOH (15 ml) and then added to the porphyrin solution. The reaction mixture was stirred overnight. All solvents were removed *in vacuo* leaving a purple solid. The crude product was dissolved in CH₂Cl₂ and washed repeatedly with 5 % aqueous NaHCO₃, followed by water. The organic layer was dried over MgSO₄ and the solvent removed under *in vacuo*. *p*-iodo-ZnTPP was obtained in quantitative yield following column chromatography silica gel with CH₂Cl₂. ¹H NMR δ_H (CDCl₃): 9.00 (m, 6H, pyrrole), 8.97 (d, 2H, pyrrole *J* = 5.0 Hz), 8.25 (m, 6H), 8.09 (d, 2H, *J* = 8 Hz), 7.99 (d, 2H, *J* = 8 Hz), 7.79 (m, 9H) ppm.

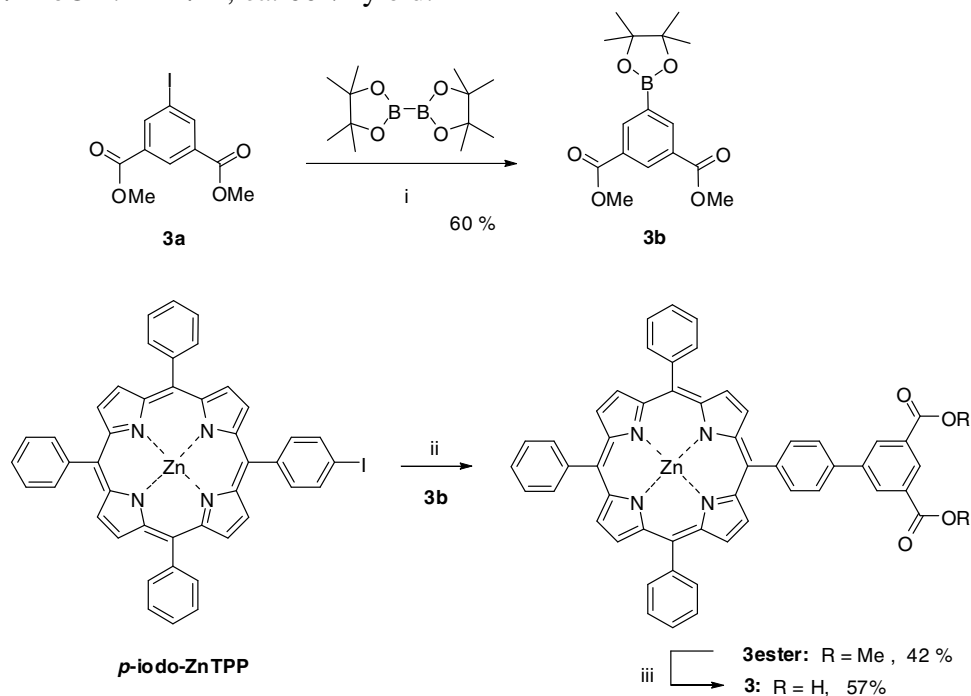
Ib. Synthesis of rigid-rod-Ipa porphyrins

The total yields of porphyrins ZnTMP-Ipe (**1** ester) and ZnTPP-Ipe (**2** ester) were low (6 %) due to the mixed aldehyde porphyrin condensation reaction, which is a statistical step followed by a separation. This route, however, was preferred to a multistep approach.

To prepare the extended rigid-rod-Ipa porphyrin systems we employed the mono-substituted Zn(II)-5-(iodophenyl)-10,15,20-triphenylporphyrin (*p*-iodo-ZnTPP) as the starting material. Although *p*-iodo-ZnTPP was synthesized using known methods,^{7,9} the nitration procedure of H₂-5,10,15,20-tetraphenylporphyrin was optimized using milder nitration conditions, increasing the yield of H₂-5-(4-nitrophenyl)-10,15,20-triphenylporphyrin from 55 to > 90 % yield as described above. This improvement allows the following reduction step to be carried out directly without any prior purification. The biphenyl-based compound, ZnTPP-P-Ipe (ester **3**), was synthesized via a Suzuki coupling reaction of the boronic ester **3b** with *p*-iodo-ZnTPP in 42 % yield, followed by basic hydrolysis to the corresponding acid (Scheme S-4).

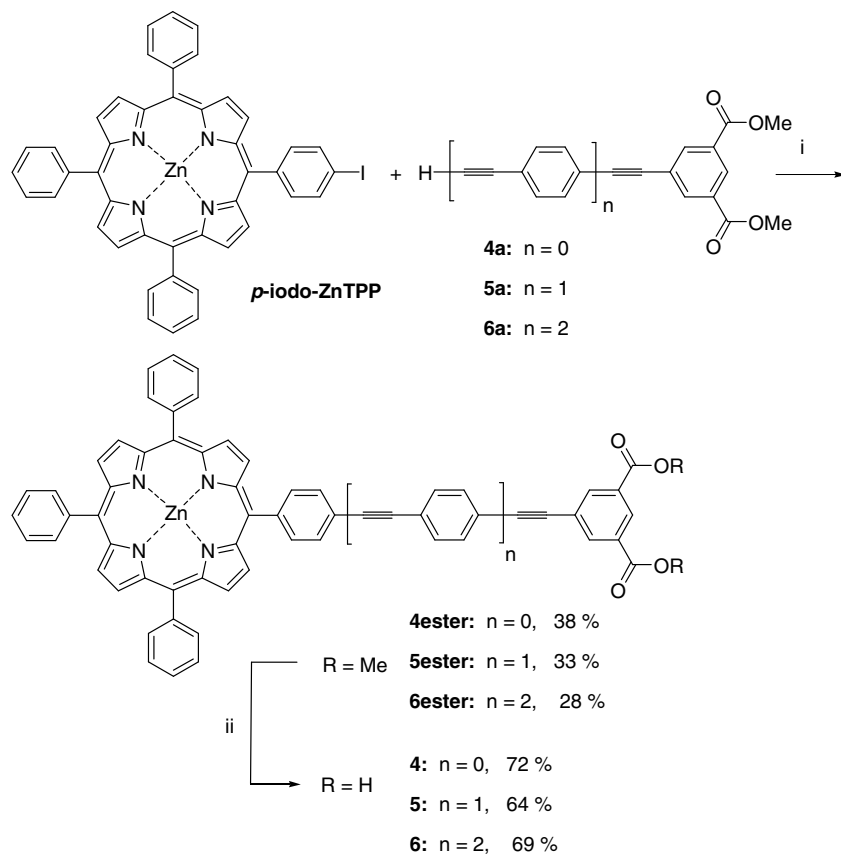


Scheme S-3. Synthetic strategy for the preparation of the porphyrin sensitizers **(1)** ZnTMP-Ipa and **(2)** ZnTPP-Ipa. *Reagents and conditions:* (i) CH_2Cl_2 / TFA / DDQ / r.t. / 12 h; 6 % yield (ii) $\text{Zn}(\text{OAc})_2$ / CH_2Cl_2 / MeOH; r.t. / 12 h; > 95 % yield (iii) 2N aq. NaOH / MeOH:THF / Δ ; ca. 60 % yield.



Scheme S-4. Synthetic strategy followed for the preparation of **(3)** ZnTPP-P-Ipa. *Reagents and conditions:* (i) $\text{Pd}(\text{PPh}_2)\text{Cl}_2$ / KOAc / DMF / 85 °C / 6 h; 60 % yield. (ii) $\text{Pd}(\text{dba})_2$ / K_2CO_3 / THF:H₂O (2:1) / 70 °C / 12 h; 42 % yield. (iii) 2N NaOH / MeOH:THF / 3h; 57 % yield.

Rigid-rod porphyrins ZnTPP-PE-Ipe (**4**), ZnTPP-(PE)₂-Ipe (**5**) and ZnTPP-(PE)₃-Ipe (**6**) were synthesized via Pd-catalyzed coupling of *p*-iodo-ZnTPP with the extended rigid-rod linkers **4a**, **5a** and **6a** respectively using known conditions (Scheme S-5).¹⁰ All porphyrin isophthalate methyl esters (Ipe) were then hydrolyzed under basic conditions to their corresponding isophthalic acid (Ipa) derivatives with yields ranging from 57 – 72 %.



Scheme S-5. Synthetic strategy followed for the synthesis of (**4**) ZnTPP-PE-Ipa, (**5**) ZnTPP-(PE)₂-Ipa and (**6**) ZnTPP-(PE)₃-Ipa. Reagents and conditions: (i) Pd₂(dba)₃ / AsPh₃ / NEt₃ / THF/ 60 °C / 12 h; 28 – 40 %. (ii) 2N NaOH / MeOH:THF / 3h; 64 - 72 % yield.

General procedure for the synthesis of free base porphyrins 1b and 2b. Pyrrole (0.35 ml, 5 mmol), **1a** (281 mg, 1.25 mmol) and benzaldehyde (0.38 ml, 3.75 mmol) or mesitylaldehyde (0.56 ml, 3.75 mmol), for the synthesis of **1b** or **2b**, respectively, were added to 200 ml CH₂Cl₂ and the solution was purged with nitrogen for 10 minutes. The reaction mixture was then treated with trifluoroacetic acid (0.37 ml, 5 mmol) and stirred overnight (10 - 12 hours) at room temperature, during which time a deep red solution formed. DDQ (852 mg, 3.75 mmol) was then added to the solution and stirring was continued for a further 6 hours. NaHCO₃ (ca. 12 g) was then added, and the reaction mixture was stirred until the acid was neutralized. The reaction mixture was then passed

through a silica gel plug, which was washed with CH₂Cl₂. Most of the solvent was then evaporated and the crude mixture was purified by gravity chromatography over silica gel using CH₂Cl₂ as the eluent. Removal of the solvent *in vacuo* yielded the pure porphyrin as a purple solid.

H₂-5-(dimethyl-3,5-dicarboxyphenyl)-10,15,20-trimesitylporphyrin (1b, H₂TMP-Ipe): (250 mg, 0.30 mmol, yield 6 %) R_f = 0.66 (neat CH₂Cl₂). ¹H NMR δ_H (CDCl₃): 9.29 (s, 1H), 9.20 (s, 2H), 8.87 (d, 2H, pyrrole, *J* = 5.0 Hz), 8.81 (m, 6H, pyrrole), 7.42 (s, 6H), 4.15 (s, 6H), 2.74 (s, 9H), 2.01 (m, 18H), -2.39 (s, 2H) ppm. ¹³C NMR δ_C (CDCl₃): 166.50, 143.14, 139.39, 138.23, 138.16, 138.02, 137.80, 137.78, 130.53, 130.13, 129.24, 127.80, 118.36, 118.35, 116.18, 52.62, 21.81, 21.72, 21.47 ppm. FT-IR-ATR: ν(C=O) 1732 cm⁻¹; ν(C-O) 1240 cm⁻¹. MS (FAB): *m/z* 857.3 [MH⁺]. Calcd. for C₅₇H₅₃N₄O₄: 857.4.

H₂-5-(dimethyl-3,5-dicarboxyphenyl)-10,15,20-triphenylporphyrin (2b, H₂TPP-Ipe): (2.20 mg, 0.30 mmol, yield 6 %) R_f = 0.52 (neat CH₂Cl₂). ¹H NMR δ_H (CDCl₃): 9.17 (s, 1H), 9.10 (s, 2H), 8.89 (m, 6H, pyrrole), 8.74 (d, 2H, pyrrole, *J* = 5.0 Hz), 8.24 (m, 6H), 7.79 (m, 9H), 4.04 (s, 6H), -2.73 (s, 2H) ppm. ¹³C NMR δ_C (CDCl₃): 166.45, 143.13, 142.05, 141.91, 138.51, 134.56, 131.37, 130.15, 129.35, 127.81, 126.72, 120.74, 120.51, 117.09, 52.58 ppm. FT-IR-ATR: ν(C=O) 1732 cm⁻¹; ν(C-O) 1246 cm⁻¹. MS (FAB): *m/z* 731.2 [M⁺]. Calcd. for C₄₈H₃₄N₄O₄: 731.2.

General procedure for metallation of porphyrins. The free base porphyrin (0.30 mmol) was dissolved in 50 ml CH₂Cl₂ and the solution was purged with nitrogen for 10 min. Zn(OAc)₂ (96 mg, 0.45 mmol, 1.5 equiv.) was first dissolved in 10 ml MeOH and then added to the porphyrin solution. The reaction mixture was stirred overnight, and the solvents were removed under *in vacuo* leaving a purple solid. The solid crude product was dissolved in CH₂Cl₂ and washed successively with 5 % aqueous NaHCO₃ and water. The organic layer was dried over MgSO₄ and the solvent removed *in vacuo*. The Zn(II) porphyrins were isolated in quantitative yields following column chromatography on silica gel (CH₂Cl₂).

Zn(II)-5-(dimethyl-3,5-dicarboxyphenyl)-10,15,20-trimesitylporphyrin (1 ester, ZnTMP-Ipe): (267 mg, 0.029 mmol, 97 %) R_f = 0.68 (CH₂Cl₂). ¹H NMR δ_H (CDCl₃): 9.12 (s, 1H), 9.06 (s, 2H), 8.78 (d, 2H, *J* = 4.5 Hz), 8.74 (m, 6H), 7.29 (s, 6H), 4.03 (s, 6H), 2.64 (s, 9H), 1.85 (m, 18H) ppm. ¹³C NMR δ_C (CDCl₃): 166.64, 150.13, 150.04,

149.84, 149.40, 143.91, 139.28, 138.88, 138.17, 137.50, 131.51, 131.38, 131.29, 131.08, 129.89, 129.00, 127.68, 119.20, 52.61, 29.73, 21.84, 21.72, 21.50. ppm. FT-IR-ATR: $\nu(\text{C}=\text{O})$ 1743 cm^{-1} ; $\nu(\text{C}-\text{O})$ 1240 cm^{-1} . MS (FAB): m/z 919.3 $[\text{MH}^+]$. Calcd. for $\text{C}_{57}\text{H}_{50}\text{N}_4\text{O}_4\text{Zn}$: 919.3.

Zn(II)-5-(dimethyl-3,5-dicarboxyphenyl)-10,15,20-triphenylporphyrin (2 ester, ZnTPP-Ipe): (228 mg, 0.29 mmol, 96 %) $R_f = 0.63$ (CH_2Cl_2). ^1H NMR δ_{H} (CDCl_3): 8.99 (m, 6H), 8.81 (d, 2H, $J = 4.5$ Hz), 8.25 (m, 6H), 7.75 (m, 9H), 3.89 (s, 6H) ppm. ^{13}C NMR δ_{C} (CDCl_3): 166.36, 150.44, 150.34, 150.27, 149.65, 143.70, 142.67, 142.62, 138.29, 134.40, 132.49, 132.23, 132.15, 131.31, 129.78, 128.90, 127.51, 126.52, 121.65, 121.41, 118.03, 52.41 ppm. FT-IR-ATR: $\nu(\text{C}=\text{O})$ 1736 cm^{-1} ; $\nu(\text{C}-\text{O})$ 1258 cm^{-1} . MS (FAB): m/z 792.2 $[\text{M}^+]$. Calcd. for $\text{C}_{48}\text{H}_{32}\text{N}_4\text{O}_4\text{Zn}$: 792.2.

Dimethyl-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalate (3b). Dimethyl 5-iodobenzene-1,3-dicarboxylate **3a** (768 mg, 2.4 mmol) and bis(pinacolato)diboron (640 mg, 2.5 mmol) were both dissolved in DMF (10 ml) and the solution was purged with nitrogen for 30 min. To the solution was then added KOAc (706 mg, 7.2 mmol) and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (50 mg, 0.072 mmol), and the resulting mixture was heated at 85 °C for 6 h. After cooling to room temperature, 50 ml of water were added and the product was extracted with CH_2Cl_2 (3 x 25 ml), dried over Na_2SO_4 and filtered. The solvent was removed *in vacuo*. The resulting crude solid was purified by silica gel column chromatography using a 1:2 mixture of EtOAc:hexane to yield **3b** as a pale yellow solid (460 mg, 1.44 mmol, yield: 60 %). Analytical data was in agreement with previously reported data.¹¹ $R_f = 0.59$. ^1H NMR δ_{H} (CDCl_3): 8.77 (s, 1H), 8.64 (s, 2H), 3.95 (s, 6H), 1.37 (s, 12H) ppm. ^{13}C NMR δ_{C} (CDCl_3): 166.32, 139.92, 133.32, 130.06, 84.43, 52.32, 24.88 ppm. ^{11}B NMR δ_{B} (CDCl_3): 30.16 ppm. FT-IR-ATR: $\nu(\text{C}=\text{O})$ 1729 cm^{-1} ; $\nu(\text{C}-\text{O})$ 1240 cm^{-1} . MS (FAB): m/z 321.1 $[\text{MH}^+]$. Calcd. for $\text{C}_{16}\text{H}_{22}\text{BO}_6$: 321.1.

Zn(II)-5-[4-(dimethyl-3,5-dicarboxyphenyl)phenyl]-10,15,20-triphenylporphyrin (3 ester, ZnTPP-P-Ipe). A flask was charged with **3b** (45 mg, 0.14 mmol), *p*-iodo-ZnTPP (100 mg, 0.125 mmol), $\text{Pd}(\text{dba})_2$ (7.5 mg, 0.013 mmol), K_2CO_3 (55 mg, 0.40 mmol), THF (20 ml) and water (10 ml). The solution was stirred vigorously and purged with nitrogen for 30 min, and then heated at 70 °C for 12 h. After cooling water was added (10 ml) and the product was extracted with CH_2Cl_2 (3 x 25 ml). The organic phase was dried with Na_2SO_4 , filtered and the solvent then removed *in vacuo*. The crude solid

was passed through a silica gel column using neat CH₂Cl₂ affording a purple powder following removal of the solvent (48 mg, 0.055 mmol, 42 %) R_f = 0.42 (CH₂Cl₂). ¹H NMR δ_H (CDCl₃): 9.02 (d, 2H, *J* = 4.8 Hz), 8.97 (m, 6H), 8.54 (s, 1H), 8.50 (s, 2H), 8.35 (d, 2H, *J* = 7.8 Hz), 8.23 (m, 6H), 7.98 (d, 2H, *J* = 7.8 Hz), 7.76 (m, 9H), 3.85 (s, 6H) ppm. ¹³C NMR δ_C (CDCl₃): 166.05, 150.19, 149.97, 143.03, 142.87, 141.61, 137.97, 135.09, 134.42, 132.30, 132.07, 131.96, 131.72, 131.01, 129.23, 127.43, 126.48, 125.28, 121.10, 120.08, 52.30 ppm. FT-IR-ATR: ν(C=O) 1727 cm⁻¹; ν(C-O) 1237 cm⁻¹. MS (FAB): *m/z* 868.1 [M⁺]. Calcd. for C₅₄H₃₆N₄O₄Zn: 868.2.

Zn(II)-5-[4-(dimethyl-3,5-dicarboxyphenyl)ethynyl]phenyl]-10,15,20-triphenylporphyrin (4 ester, ZnTPP-PE-Ipe). A 25 ml round bottom flask containing a magnetic stirrer was placed under vacuum and flame dried. After cooling the flask was filled with nitrogen gas using a double manifold. While maintaining an inert nitrogen atmosphere, the flask was charged with *p*-iodo-ZnTPP (80 mg, 0.10 mmol), **4a** (26 mg, 0.12 mmol), Pd₂(dba)₃ (14 mg, 0.015 mmol), AsPh₃ (37 mg, 0.12 mmol), THF (10 ml) and NEt₃ (2 ml). The reaction mixture was stirred for 6 hours at 60 °C. After cooling, water was added (10 ml) and the product was extracted with CH₂Cl₂ (3 x 25 ml). The organic phase was dried with Na₂SO₄, filtered and the solvent removed under *in vacuo*. The crude solid was passed through a silica gel column using CH₂Cl₂ as the eluent. Removal of the solvent *in vacuo* afforded **4 ester** as a purple powder (34 mg, 0.038 mmol, 38 %) R_f = 0.46 (CH₂Cl₂). ¹H NMR δ_H (CDCl₃): 9.02 (m, 8H), 8.33 (d, 2H, *J* = 8.0 Hz), 8.28 (m, 7H), 8.00 (s, 2H), 7.97 (d, 2H, *J* = 8.0 Hz), 7.80 (m, 9H), 3.71 (m, 6H) ppm. ¹³C NMR δ_C (CDCl₃): 165.14, 150.25, 150.20, 150.17, 149.78, 143.68, 142.81, 142.79, 136.16, 134.68, 134.46, 132.22, 132.03, 131.68, 130.28, 129.99, 129.51, 127.46, 126.52, 124.08, 121.63, 121.26, 119.95, 91.40, 88.23, 52.26 ppm. FT-IR-ATR: (C≡C) 2216 cm⁻¹; ν(C=O) 1727 cm⁻¹; ν(C-O) 1243 cm⁻¹. MS (FAB): *m/z* 892.0 [M⁺]. Calcd. for C₅₆H₃₆N₄O₄Zn: 892.2.

Zn(II)-5-[4-(4-(dimethyl-3,5-dicarboxyphenyl)ethynyl)phenyl]ethynyl]phenyl]-10,15,20-triphenylporphyrin (5 ester, ZnTPP-(PE)₂-Ipe). A 25 ml round bottom flask containing a magnetic stirrer was placed under vacuum and flame dried. After cooling the flask was filled with nitrogen using a double manifold. While maintaining an inert nitrogen atmosphere, the flask was charged with *p*-iodo-ZnTPP (80 mg, 0.10 mmol), **5a** (38 mg, 0.12 mmol), Pd₂(dba)₃ (14 mg, 0.015 mmol), AsPh₃ (37 mg, 0.12 mmol), THF

(10 ml) and NEt₃ (2 ml). The reaction mixture was stirred for 6 hours at 60 °C, and cooled. Water was added (10 ml) and the product was extracted with CH₂Cl₂ (3 x 25 ml). The organic phase was dried with Na₂SO₄, filtered and the solvent removed *in vacuo*. The crude solid was passed through a silica gel column using CH₂Cl₂:EtOAc (98:2) to afford **5 ester** as a purple powder (33 mg, 0.033 mmol, 33 %) following removal of the solvent *in vacuo*. R_f = 0.53. ¹H NMR δ_H (CDCl₃): 8.98 (m, 8H), 8.67 (s, 1H), 8.41 (s, 2H), 8.24 (m, 8H), 7.96 (d, 2H, *J* = 8.0 Hz), 7.78 (m, 9H), 7.69 (d, 2H, *J* = 8.0 Hz), 7.64 (d, 2H, *J* = 8.0 Hz), 4.00 (s, 6H) ppm. ¹³C NMR δ_C (CDCl₃): 165.43, 150.31, 150.28, 150.22, 149.84, 143.30, 142.74, 136.38, 136.16, 134.54, 134.42, 132.23, 132.06, 131.77, 131.74, 131.68, 130.82, 130.03, 129.90, 127.54, 126.56, 124.09, 123.83, 122.38, 122.18, 121.36, 121.28, 120.09, 91.72, 90.96, 90.01, 89.17, 52.46 ppm. FT-IR-ATR: (C≡C) 2209 cm⁻¹; ν(C=O) 1732 cm⁻¹; ν(C-O) 1246 cm⁻¹. MS (FAB): *m/z* 992.2 [M⁺]. Calcd. for C₆₄H₄₀N₄O₄Zn: 992.2.

Zn(II)-5-[4-(4-(4-(dimethyl-3,5-dicarboxyphenyl)ethynyl)phenyl)ethynyl]phenyl-10,15,20-triphenylporphyrin (6 ester, ZnTPP-(PE)₃-Ipe). A 25 ml round bottom flask containing a magnetic stirrer was placed under vacuum and flame dried. After cooling the flask was filled with nitrogen gas using a double manifold. While maintaining an inert nitrogen atmosphere, the round bottomed flask was charged with *p*-iodo-ZnTPP (50 mg, 0.063 mmol), **6a** (32 mg, 0.076 mmol), Pd₂(dba)₃ (8 mg, 0.009 mmol), AsPh₃ (23 mg, 0.08 mmol), THF (10 ml) and NEt₃ (2 ml). The reaction mixture was stirred for 6 hours at 60 °C, and then cooled. Water was added (10 ml) and the product was extracted with CH₂Cl₂ (3 x 25 ml). The organic phase was dried with Na₂SO₄, filtered and the solvent removed *in vacuo*. The crude solid was passed through a silica gel column using CH₂Cl₂:EtOAc (98:2) affording **6 ester** as a purple powder (19 mg, 0.018 mmol, 28 %) following removal of the solvent. R_f = 0.51. ¹H NMR δ_H (CDCl₃): 8.86 (m, 8H), 8.62 (s, 1H), 8.36 (s, 2H), 8.19 (m, 8H), 7.90 (d, 2H, *J* = 7.5 Hz), 7.72 (m, 9H), 7.60 (d, 2H, *J* = 7.5 Hz), 7.58 (d, 2H, *J* = 7.5 Hz), 7.54 (s, 4H), 3.96 (s, 6H) ppm. ¹³C NMR δ_C (CDCl₃): 165.77, 151.26, 151.18, 150.81, 145.27, 144.66, 136.98, 135.73, 135.52, 135.01, 133.55, 132.83, 132.72, 132.64, 132.54, 132.44, 132.09, 130.81, 130.64, 129.75, 128.30, 127.35, 125.17, 124.88, 124.77, 124.08, 123.71, 123.19, 121.93, 121.81, 120.57, , 92.66, 92.18,

91.72, 90.74, 90.14, 52.84 ppm. FT-IR-ATR: (C≡C) 2208 cm⁻¹; ν(C=O) 1728 cm⁻¹; ν(C-O) 1249 cm⁻¹. MS (FAB): *m/z* 1092.2 [M⁺]. Calcd. for C₇₂H₄₄N₄O₄Zn: 1092.3.

General procedure for hydrolysis of the porphyrins esters to acids: The porphyrin ester was dissolved in 4 ml of a 1:1 MeOH:THF mixture and 2 N aq. NaOH (5 ml) was then added in one portion. The solution was refluxed for 3 hours.¹² After cooling, the organic phase was solvent was removed under *in vacuo* and any unreacted ester was extracted with chloroform. The acid was precipitated by the slow addition of 2 N aq. HCl to the aqueous phase. The precipitate was filtered and thoroughly washed with water and diethyl ether.

Zn(II)-5-(3,5-dicarboxyphenyl)-10,15,20-trimesitylporphyrin (1, ZnTMP-Ipa): (26 mg, 0.030 mmol, 60 %) ¹H NMR δ_H (CD₃OD): 9.08 (s, 1H), 8.98 (s, 2H), 8.66 (s, 4H), 8.62 (s, 4H), 7.28 (s, 6H), 2.60 (s, 9H), 1.85 (s, 18H) ppm. HRMS (FAB): *m/z* 890.2817 [MH⁺]. Calcd. for C₅₅H₄₆N₄O₄Zn: 890.2811.

Zn(II)-5-(3,5-dicarboxyphenyl)phenyl-10,15,20-triphenylporphyrin (2, ZnTPP-Ipa): (25 mg, 0.034 mmol, 67 %) ¹H NMR δ_H (CD₃OD): 9.13 (s, 1H), 9.05 (s, 2H), 8.93 (2H, d, *J* = 4.5 Hz), 8.87 (s, 4H), 8.79 (d, 2H, *J* = 4.5 Hz), 8.25 (m, 6H), 7.81 (m, 9H) ppm. FT-IR-ATR: ν(C=O) 1687 cm⁻¹; ν(C-O) 1270 cm⁻¹. HRMS (FAB): *m/z* 764.1399 [M⁺]. Calcd. for C₄₆H₂₈N₄O₄Zn: 764.1402.

Zn(II)-5-[4-(3,5-dicarboxyphenyl)phenyl]-10,15,20-triphenylporphyrin (3, ZnTPP-P-Ipa): (19 mg, 0.023 mmol, 57 %) ¹H NMR δ_H (CD₃OD): 8.94 (s, 2H), 8.77 – 8.87 (m, 9H), 8.34 (d, 2H, *J* = 7.5 Hz), 8.20 (m, 6H), 8.16 (d, 2H, *J* = 7.5 Hz), 7.74 (m, 9H) ppm. FT-IR-ATR: ν(C=O) 1696 cm⁻¹; ν(C-O) 1262 cm⁻¹. HRMS (FAB): *m/z* 840.1722 [M⁺]. Calcd. for C₅₂H₃₂N₄O₄Zn: 840.1715.

Zn(II)-5-[4-(dimethyl-3,5-dicarboxyphenyl)ethynyl]phenyl]-10,15,20-triphenylporphyrin (4, ZnTPP-PE-Ipa): (28 mg, 0.032 mmol, 72 %) ¹H NMR δ_H (CD₃OD): 8.86 – 8.88 (dd, 4H *J* = 7.5 Hz), 8.84 (s, 4H), 8.69 (s, 1H), 8.49 (s, 2H), 8.25 (d, 2H, *J* = 7.5 Hz), 8.19 (m, 6H), 8.00 (d, 2H, *J* = 7.5 Hz), 7.75 (m, 9H) ppm. FT-IR-ATR: (C≡C) 2213 cm⁻¹; ν(C=O) 1700 cm⁻¹; ν(C-O) 1269 cm⁻¹. HRMS (FAB): *m/z* 864.1720 [M⁺]. Calcd. for C₅₄H₃₂N₄O₄Zn: 864.1715.

Zn(II)-5-[4-(4-(dimethyl-3,5-dicarboxyphenyl)ethynyl)phenyl]ethynyl]phenyl-10,15,20-triphenylporphyrin (5, ZnTPP-(PE)₂-Ipa): (22 mg, 0.022 mmol, 64 %) ¹H NMR δ_H (CD₃OD): 8.86 – 8.88 (dd, 4H *J* = 7.0 Hz), 8.84 (s, 4H), 8.65 (s, 1H), 8.38 (s,

2H), 8.24 (d, 2H, $J = 7.5$ Hz), 8.19 (m, 6H), 7.95 (d, 2H, $J = 7.5$ Hz), 7.75 (m, 9H), 7.71 (d, 2H, $J = 8.0$ Hz), 7.67 (d, 2H, $J = 8.0$ Hz) ppm. FT-IR-ATR: (C≡C) 2210 cm^{-1} ; $\nu(\text{C=O})$ 1698 cm^{-1} ; $\nu(\text{C-O})$ 1265 cm^{-1} . HRMS (FAB): m/z 964.2022 [M^+]. Calcd. for $\text{C}_{62}\text{H}_{36}\text{N}_4\text{O}_4\text{Zn}$: 964.2028.

Zn(II)-5-[4-(4-(4-(3,5-dicarboxyphenyl)ethynyl)phenyl)ethynyl)phenyl)ethynyl]phenyl-10,15,20-triphenylporphyrin (6, ZnTPP-(PE)₃-Ipa): (18 mg, 0.017 mmol, 69 %) ^1H NMR δ_{H} (CD_3OD): 8.87 (s, 4H), 8.84 (s, 4H), 8.63 (s, 1H), 8.21 – 8.24 (m, 10H), 7.93 (d, 2H, $J = 8.0$ Hz), 7.78 (m, 9H), 7.67 (d, 2H, $J = 8.0$ Hz), 7.62 (d, 2H, $J = 8.0$ Hz), 7.59 (dd, 4H) ppm. FT-IR-ATR: (C≡C) 2209 cm^{-1} ; $\nu(\text{C=O})$ 1698 cm^{-1} ; $\nu(\text{C-O})$ 1265 cm^{-1} . HRMS (FAB): m/z 1064.2349 [M^+]. Calcd. for $\text{C}_{70}\text{H}_{40}\text{N}_4\text{O}_4\text{Zn}$: 1064.2341.

II. FT-IR-ATR Spectra

The broad bands observed at ~ 3000 cm^{-1} in the spectra of the compounds bound to TiO_2 and ZnO films are assigned to adsorbed moisture on the films.

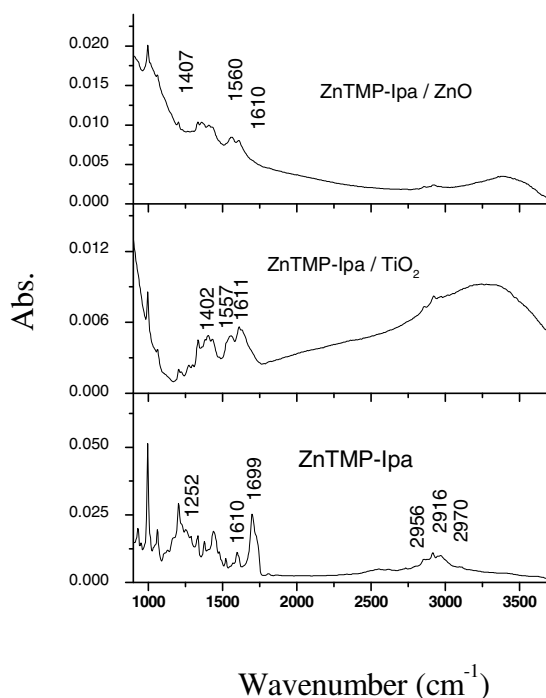


Figure S-1. FT-IR-ATR spectra of ZnTMP-Ipa (**1**) as a solid (bottom) and bound to TiO_2 and ZnO (middle and top, respectively).

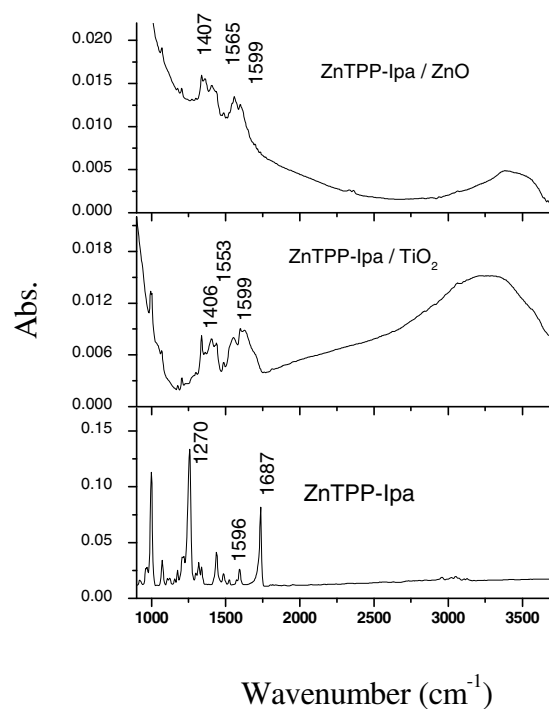


Figure S-2. FT-IR-ATR spectra of ZnTPP-Ipa (**2**) as a solid (bottom) and bound to TiO_2 and ZnO (middle and top, respectively).

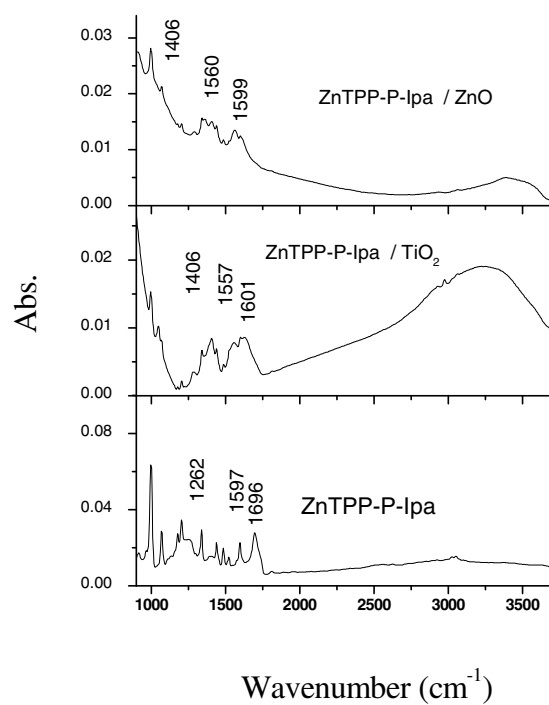


Figure S-3. FT-IR-ATR spectra of ZnTPP-P-Ipa (**3**) as a solid (bottom) and bound to TiO_2 and ZnO (middle and top, respectively).

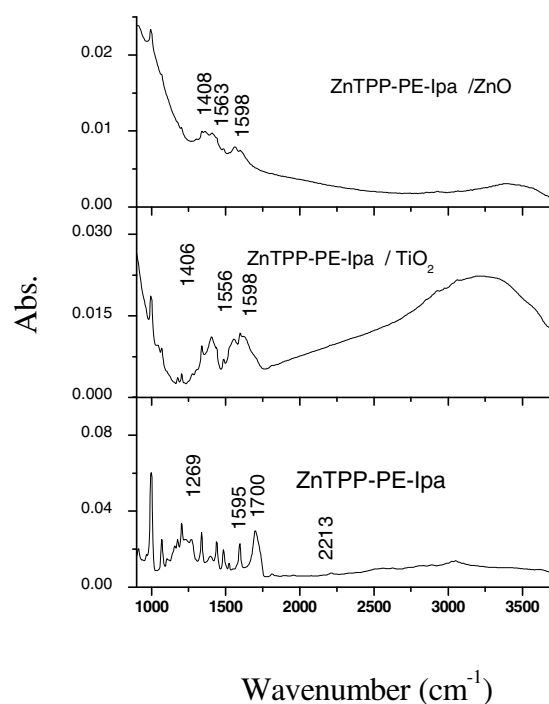


Figure S-4. FT-IR-ATR spectra of ZnTPP-PE-Ipa (**4**) as the neat solid (bottom) and adsorbed on TiO_2 and ZnO (middle and top, respectively). The broad bands observed at $\sim 3000 \text{ cm}^{-1}$ for the TiO_2 and ZnO samples are assigned to adsorbed moisture on the films.

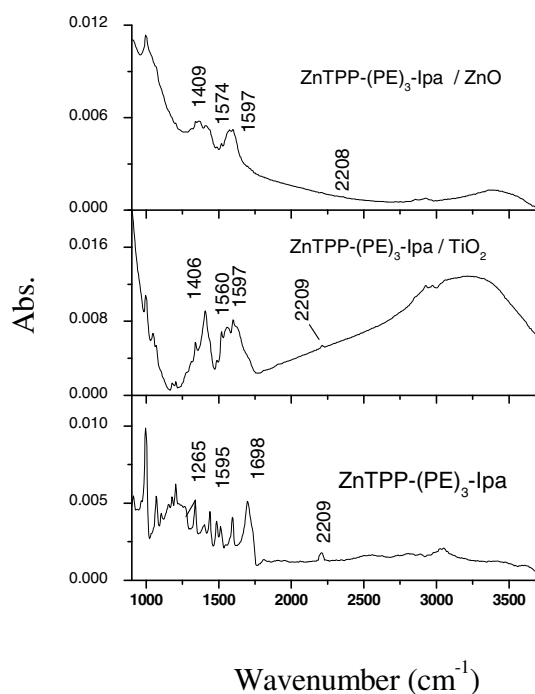


Figure S-5. FT-IR-ATR spectra of ZnTPP-(PE)₃-Ipa (**5**) as the neat solid (bottom) and adsorbed on TiO_2 and ZnO (middle and top, respectively).

III. Fluorescence emission spectra in Solution

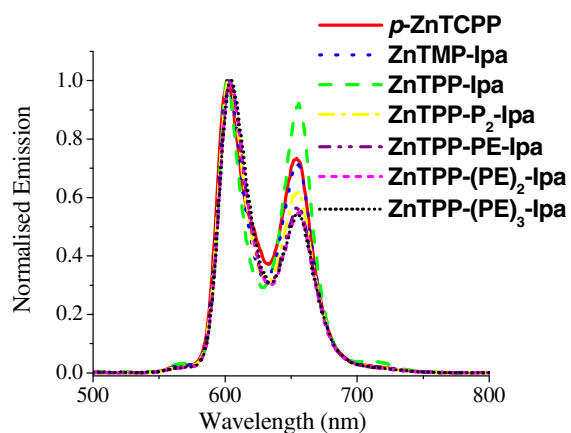


Figure S-6. Fluorescence spectra of *p*-ZnTCPP and the rigid-rod-Ipa porphyrins recorded in MeOH.

IV. UV-Vis Absorption on TiO₂ and ZrO₂

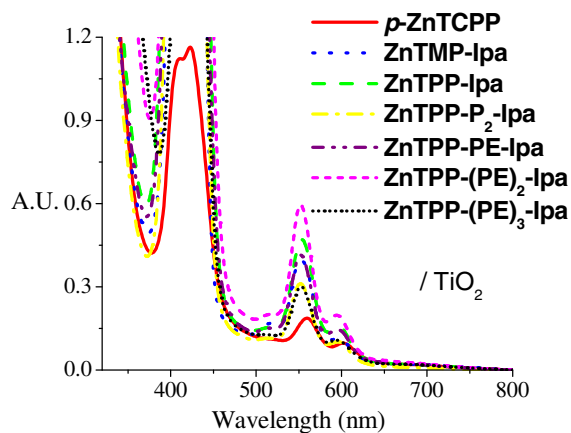


Figure S-7. UV-Vis absorption spectra of reference compound *p*-ZnTCPP (solid red line) and the rigid-rod-Ipa porphyrins bound to TiO₂ films.

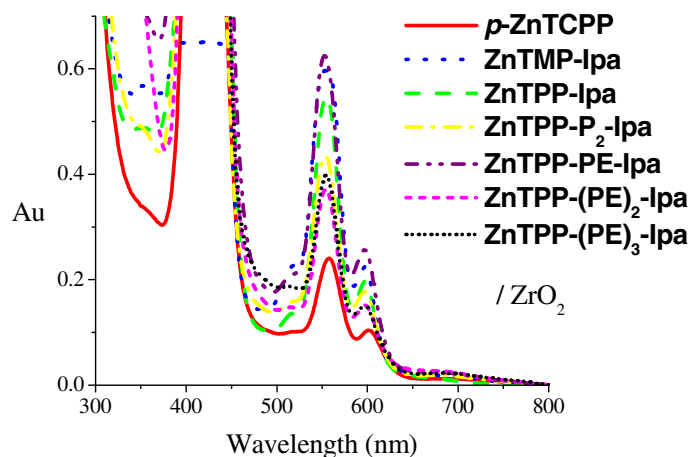


Figure S-8. UV-Vis absorption spectra of reference compound *p*-ZnTCPP (solid red line) and the rigid-rod-Ipa porphyrins bound to ZrO_2 films.

V. Fluorescence emission on TiO_2 and plot of ‘emission quantum efficiency’ vs. porphyrin rods length on TiO_2

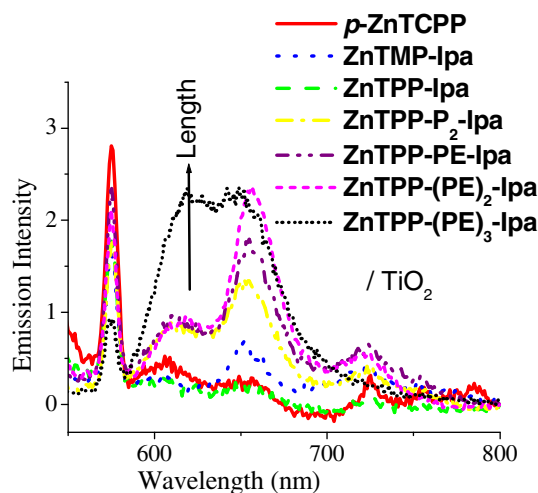


Figure S-9. Residual fluorescence emission observed for porphyrins ZnTPP-P-Ipa, ZnTPP-PE-Ipa, ZnTPP-(PE)₂-Ipa and ZnTPP-(PE)₃-Ipa bound to TiO_2 and reference porphyrins.

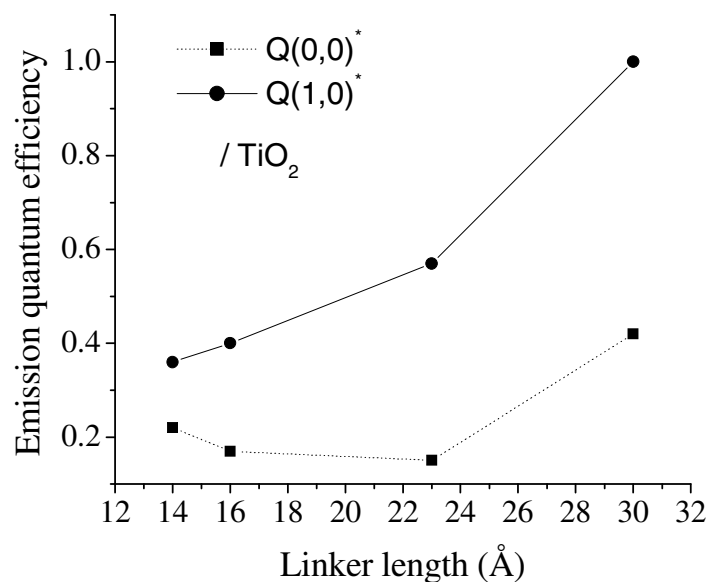


Figure S-10. Plot of ‘emission quantum efficiency’ vs. porphyrin rods length for both the $Q(0,0)^*$ and $Q(1,0)^*$ emission bands of the porphyrins ZnTPP-P-Ipa, ZnTPP-PE-Ipa, ZnTPP-(PE)₂-Ipa and ZnTPP-(PE)₃-Ipa bound to TiO₂.

VI. Cyclic Voltammograms

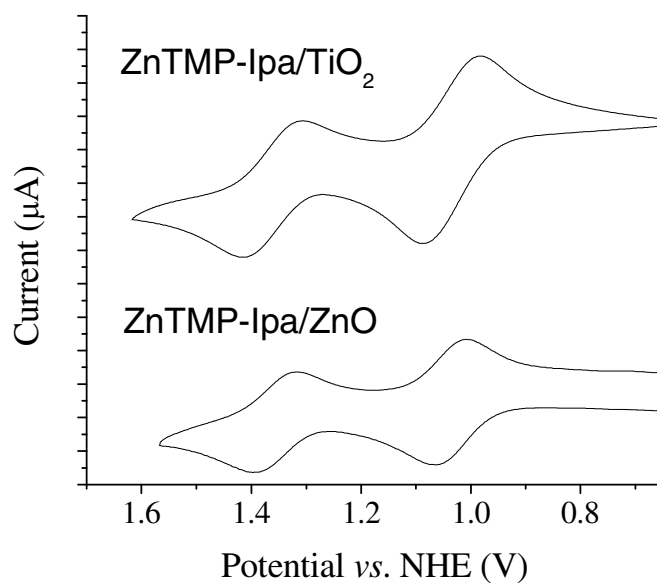


Figure S-11. Cyclic voltammogram scans of ZnTMP-Ipa bound to TiO₂/ITO (*top*) and ZnO/ITO (*bottom*) electrodes (0.1 M Bu₄NClO₄ / CH₂Cl₂ / scan rate: 100 mVs⁻¹).

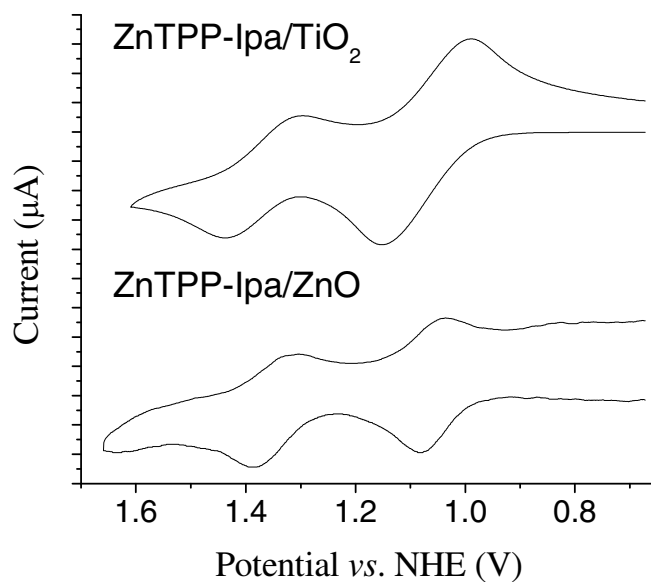


Figure S-12. Cyclic voltammogram scans of ZnTPP-Ipa bound to TiO₂/ITO (*top*) and ZnO/ITO (*bottom*) electrodes (0.1 M Bu₄NClO₄ / CH₂Cl₂ / scan rate: 100 mVs⁻¹).

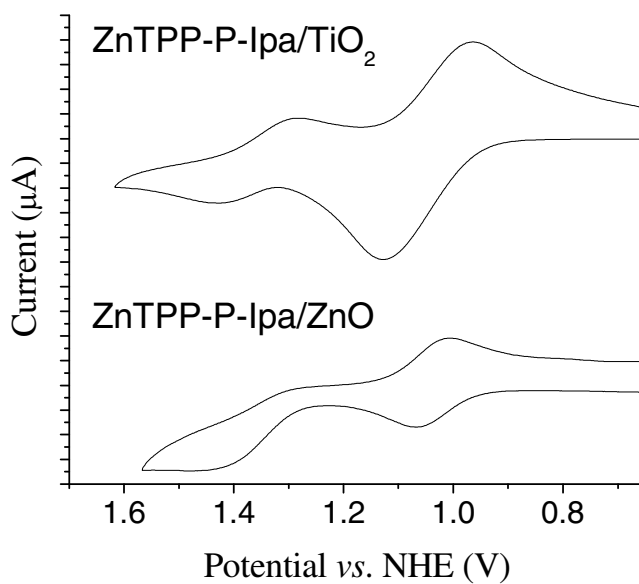


Figure S-13. Cyclic voltammogram scans of ZnTPP-P-Ipa bound to TiO₂/ITO (*top*) and ZnO/ITO (*bottom*) electrodes (0.1 M Bu₄NClO₄ / CH₂Cl₂ / scan rate: 100 mVs⁻¹).

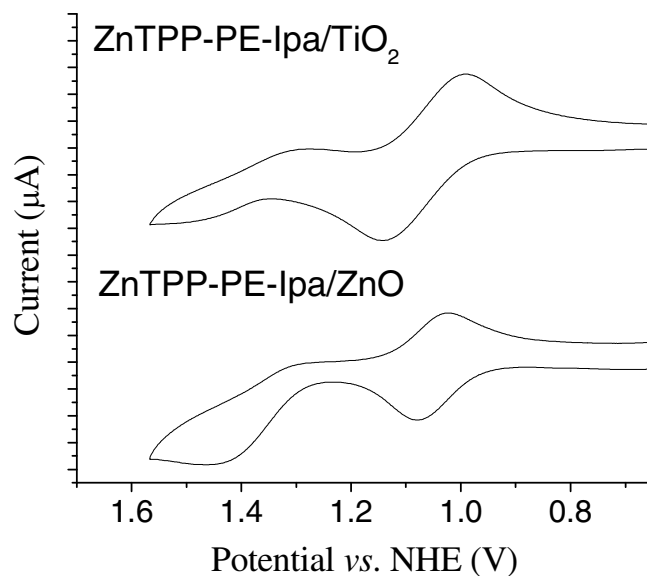


Figure S-14. Cyclic voltammogram scans of ZnTPP-PE-Ipa bound to TiO₂/ITO (*top*) and ZnO/ITO (*bottom*) electrodes (0.1 M Bu₄NClO₄ / CH₂Cl₂ / scan rate: 100 mVs⁻¹).

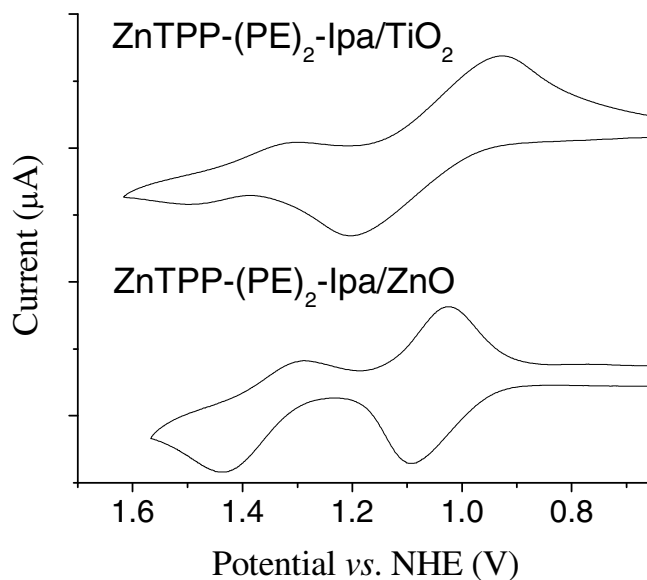


Figure S-15. Cyclic voltammogram scans of ZnTPP-(PE)₂-Ipa bound to TiO₂/ITO (*top*) and ZnO/ITO (*bottom*) electrodes (0.1 M Bu₄NClO₄ / CH₂Cl₂ / scan rate: 100 mVs⁻¹).

VII. Complete Ref. 1b

Adams, D. M.; Brus, L.; Chidsey, C. E. D.; Creager, S.; Creutz, C.; Kagan, C. R.; Kamat, P. V.; Lieberman, M.; Lindsay, S.; Marcus, R. A.; Metzger, R. M.; Michel-Beyerle, M. E.; Miller, J. R.; Newton, M. D.; Rolison, D. R.; Sankey, O.; Schanze, K. S.; Yardley, J.; Zhu, X. *J. Phys. Chem. B.* **2003**, *107*, 6668.

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- 12) The hydrolysis of ZnTMP-Ipe to the corresponding carboxylic acid required a reaction time of 12 h.