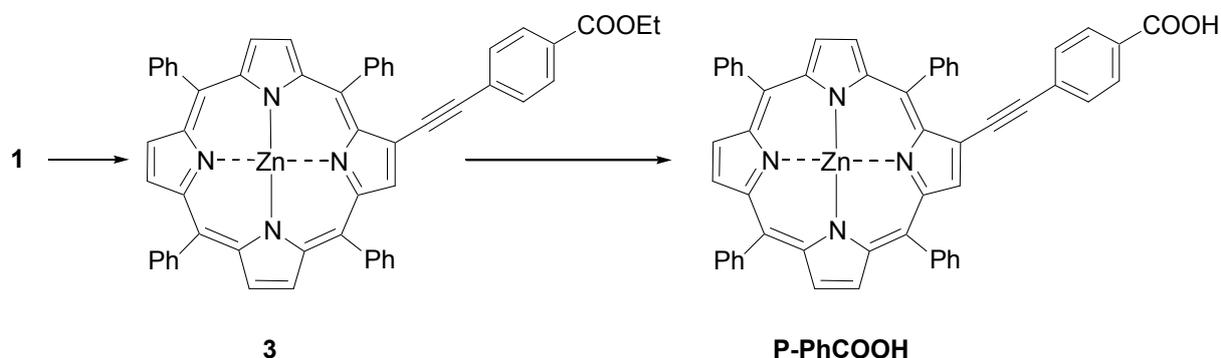




MHz, CDCl<sub>3</sub>):  $\delta$  8.86 (s 2H), 8.80 (d,  $J = 4.6$  Hz, 2H), 8.65 (d,  $J = 4.6$  Hz, 2H), 8.13–8.20 (m, 8H), 7.74–7.96 (m, 12H), 0.21 (s, 18H). ESI-MS:  $m/z$  calcd for C<sub>55</sub>H<sub>36</sub>N<sub>4</sub>O<sub>2</sub>Zn: 868.21 found 869.3 [M+H]<sup>+</sup>.  $\lambda_{\max}/\text{nm}$  (in CH<sub>2</sub>Cl<sub>2</sub>): 437, 563, 604.

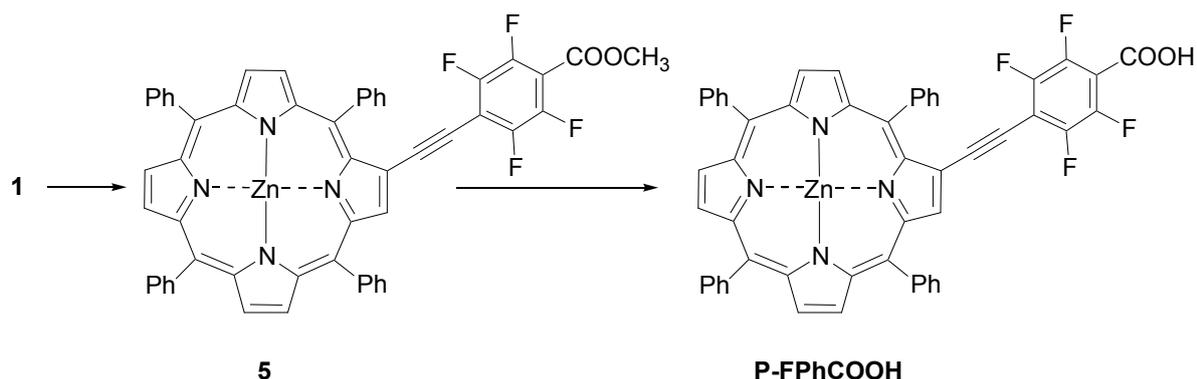


**Zinc 2-(4'-ethoxycarbonyphenylethynyl)-5,10,15,20-tetraphenylporphyrin (3).** To a solution of **1** (50 mg, 0.064 mmol) in THF (10 mL), TBAF (1 mL, 1 M in THF) was added and the solution was stirred at room temperature for 0.5 hour under Ar. After completion of the reaction, the solvent was removed under reduced pressure. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and washed with water twice. The organic solution was washed with brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated. The resulting residue and ethyl 4-iodobenzoate (88 mg, 0.32 mmol) were dissolved in THF (5 mL) and Et<sub>3</sub>N (1 mL) under Ar, and then Pd<sub>2</sub>(dba)<sub>3</sub> (14 mg, 0.016 mmol) and AsPh<sub>3</sub> (48 mg 0.16 mmol) were added to the mixture. The solution was warmed up to 70°C and stirred for 12 h. After completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as eluent. Product (37 mg) was obtained in 68% yield as a purple solid by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH. <sup>1</sup>NMR (600 MHz, THF d<sup>8</sup>):  $\delta$  9.01 (s 1H), 8.80 (s, 2H), 8.79 (s 2H) 8.75 (d,  $J = 4.6$  Hz, 1H), 8.65 (d,  $J = 4.6$  Hz, 1H), 8.32 (d,  $J = 8.3$  Hz, 2H), 8.13–8.20 (m, 8H), 7.74–7.96 (m, 12H), 7.20 (d,  $J = 8.2$  Hz, 2H), 4.23 (m, 2H), 1.32 (t, 3H). ESI-MS:  $m/z$  calcd for C<sub>55</sub>H<sub>36</sub>N<sub>4</sub>O<sub>2</sub>Zn: 848.21, found 849.3 [M+H]<sup>+</sup>.  $\lambda_{\max}/\text{nm}$  (in CH<sub>2</sub>Cl<sub>2</sub>): 431, 557, 594.

**P-PhCOOH.** A mixture of **3** (20 mg) and NaOH (1M, 1mL) in THF (3 mL) and MeOH (1 mL) was refluxed for 2 h. After completion of the reaction, deionized water (100 mL) was added and the mixture was neutralized with HCl (0.1 M, 10 mL). Precipitated product was obtained in 90% yield as a purple solid by filtration after drying in vacuo. <sup>1</sup>NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  9.10 (s 1H), 8.80 (s 2H), 8.77 (s 2H), 8.76 (d,  $J = 4.6$  Hz, 1H), 8.65 (d,  $J = 4.6$  Hz, 1H), 8.40 (d,  $J = 8.3$  Hz, 2H), 8.15–8.24 (m, 8H), 7.68–7.80 (m, 12H), 7.45 (d,  $J = 8.6$  Hz, 2H). HRESI-MS:  $m/z$  calcd for C<sub>53</sub>H<sub>32</sub>N<sub>4</sub>O<sub>2</sub>Zn 819.1744 [M-H]<sup>-</sup>, found 819.1684 [M-H]<sup>-</sup>.



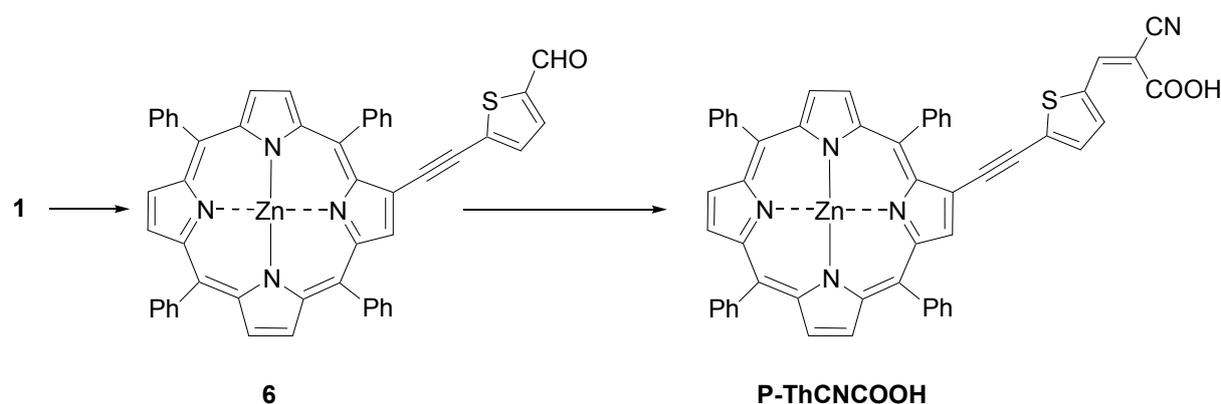
**Methyl 4-bromo-2,3,5,6-tetrafluorobenzoate (4).** To a solution of 4-bromo-2,3,5,6-tetrafluorobenzoate (3 g, 11 mmol) in dry toluene (120 mL),  $\text{SOCl}_2$  (3.2 mL, 44 mmol) was slowly added. The mixture was stirred for 5 h, and then 8 mL of MeOH was added. After 15 min, the solvent was removed under reduced pressure, the residue was dissolved in ethylacetate and washed with  $\text{NaHCO}_3$  aq. The organic solvent was dried with  $\text{Na}_2\text{SO}_4$  and removed by reduced pressure. The residue was purified by silica column chromatography using  $\text{CH}_2\text{Cl}_2$  as eluent. The product (2.6 g) was obtained as white solid in 82% yield.  $^1\text{NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta = 3.98$  (3H, s). ESI-MS:  $m/z$  calcd for  $\text{C}_8\text{H}_3\text{BrF}_4\text{O}_2$  285.93, found 286.9  $[\text{M}+\text{H}]^+$ .



**Zinc 2-(2',3',5',6'-tetrafluoro-4-methoxycarboxyphenylethynyl)-5,10,15,20-tetraphenylporphyrin (5).** To a solution of **1** (50 mg, 0.064 mmol) in THF (10 mL), TBAF (1 mL, 1 M in THF) was added and the solution was stirred at room temperature for 0.5 hour under Ar. After completion of the reaction, the solvent was removed under reduced pressure. The residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and washed with water twice. The organic solution was washed with brine, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated. The resulting residue and **4** (91 mg, 0.32 mmol) were dissolved in THF (5 mL) and  $\text{Et}_3\text{N}$  (1 mL), and degassed by bubbling Ar for 10 min. To the mixture,  $\text{Pd}_2(\text{dba})_3$  (14 mg, 0.016 mmol) and  $\text{AsPh}_3$  (18 mg 0.16 mmol) were added. The solution was warmed up to  $70^\circ\text{C}$  and stirred for 12 h. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by silica column chromatography using  $\text{CH}_2\text{Cl}_2$  as eluent. Product (42 mg) was obtained in 80% yield as a purple solid by recrystallization from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ .  $^1\text{NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$

8.95 (s 1H), 8.80 (s, 2H), 8.74 (d,  $J = 4.7$  Hz, 2H), 8.69 (d,  $J = 4.8$  Hz, 2H) 8.10–8.25 (m, 8H), 7.54–7.76 (m, 12H), 4.32 (s, 3H). ESI-MS:  $m/z$  calcd for  $C_{54}H_{30}F_4N_4O_2Zn$  906.16, found 907.2  $[M+H]^+$ .  $\lambda_{max}/nm$  (in  $CH_2Cl_2$ ): 430, 558, 593.

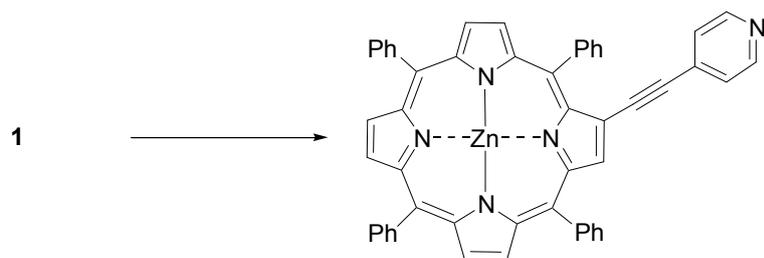
**P-FPhCOOH.** **P-FPhCOOH** was synthesized by hydrolysis of **5** following the same procedure as that of **P-PhCOOH** (88% yield, a purple solid).  $^1NMR$  (600 MHz,  $CDCl_3$ ):  $\delta$  9.01 (s 1H), 8.76 (s, 2H), 8.74 (d,  $J = 4.6$  Hz, 2H), 8.67 (d,  $J = 4.8$  Hz, 2H) 8.10–8.25 (m, 8H), 7.54–7.76 (m, 12H). HRESI-MS:  $m/z$  calcd for  $C_{53}H_{28}F_4N_4O_2Zn$   $[M+H]^+$  893.1513, found 893.1503  $[M+H]^+$ .



**Zinc 2-(5'-formylthienyl-2'-ethynyl)-5,10,15,20-tetraphenylporphyrin (6).** To a solution of **1** (50 mg, 0.064 mmol) in THF (10 mL), TBAF (1 M in THF, 1 mL) was added and the mixture was stirred at room temperature for 0.5 hour under Ar. After completion of the reaction, the solvent was removed under reduced pressure. The residue was dissolved in  $CH_2Cl_2$  and washed with water twice. The organic solution was washed with brine, dried ( $Na_2SO_4$ ), and evaporated. The resulting residue and 2-bromo-5-formylthiophene (54 mg, 0.32 mmol) were dissolved in THF (5 mL) and  $Et_3N$  (1 mL) under Ar, and then  $Pd_2(dba)_3$  (14 mg, 0.016 mmol) and  $AsPh_3$  (48 mg 0.32 mmol) were added to the mixture. The solution was warmed up to  $70^\circ C$  and stirred for 4 h. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by silica column chromatography using  $CH_2Cl_2$  as eluent. Product (35 mg) was obtained in 67% yield as a purple solid by recrystallization from  $CH_2Cl_2/MeOH$ .  $^1NMR$  (600 MHz,  $CDCl_3$ ):  $\delta$  9.20 (s, 1H), 8.90 (s, 2H), 8.87 (d,  $J = 4.4$  Hz, 2H), 8.78 (d,  $J = 4.4$  Hz, 2H), 8.67 (d,  $J = 5.3$  Hz, 1H), 8.10–19 (m, 8H), 7.70–7.84 (m, 12H), 7.67 (d,  $J = 5.3$  Hz, 1H). ESI-MS:  $m/z$  calcd for  $C_{51}H_{30}N_4OSZn$ : 810.14, found 811.2  $[M+H]^+$ .  $\lambda_{max}/nm$  (in  $CH_2Cl_2$ ): 435, 477(sh), 568, 608.

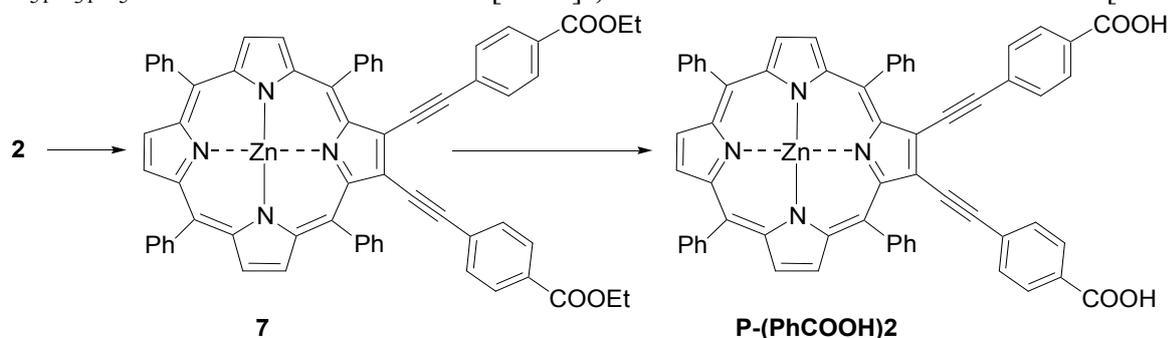
**P-ThCNCOOH.** A solution of **6** (35 mg) and cyanoacetic acid (18 mg, 5 eq) in a mixture of piperidine (0.2 mL) and  $CHCl_3$  (10 mL) was heated under reflux in the atmosphere of Ar for

2 h. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by silica column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/MeOH (9/1) as eluent. Product (11 mg) was obtained in 27% yield as a purple solid. <sup>1</sup>NMR (600 MHz, CDCl<sub>3</sub>): δ 8.88–8.90 (m, 3H), 8.78–8.86 (m, 4H), 8.77 (s, 1H), 8.18–8.22 (m, 8H), 7.92 (s, 1H), 7.70–7.81 (m, 12H), 7.67 (s, 1H). HRESI-MS: *m/z* calcd for C<sub>54</sub>H<sub>31</sub>N<sub>5</sub>O<sub>2</sub>SZn [M+H]<sup>+</sup> 876.0694, found 876.0688 [M+H]<sup>+</sup>.



**P-Py**

**P-Py.** To a solution of **1** (50 mg, 0.064 mmol) in THF (10 mL), TBAF (1 M in THF, 1 mL) was added and the mixture was stirred at room temperature for 0.5 hour under Ar. After completion of the reaction, the solvent was removed under reduced pressure. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and washed with water twice. The organic solution was washed with brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated. The resulting residue and 4-iodopyridine (66 mg, 0.32 mmol) were dissolved in THF (5 mL) and Et<sub>3</sub>N (1 mL) under Ar, and then Pd<sub>2</sub>(dba)<sub>3</sub> (14 mg, 0.016 mmol) and AsPh<sub>3</sub> (48 mg 0.16 mmol) were added to the mixture. The solution was warmed up to 70°C and stirred for 12 h. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by silica column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as eluent. Product (40 mg) was obtained as a purple solid in 79 % yield by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH. <sup>1</sup>NMR (600 MHz, CDCl<sub>3</sub>): δ 8.97 (s, 1H), 8.81 (s, 2H), 8.79 (d, *J* = 4.6 Hz, 2H), 8.65 (d, *J* = 4.6 Hz, 2H), 8.31 (d, *J* = 5.1 Hz, 2H), 8.16–8.22 (m, 8H), 7.76–7.88 (m, 12H), 7.17 (d, *J* = 5.5 Hz, 2H). HRESI-MS: *m/z* calcd for C<sub>51</sub>H<sub>31</sub>N<sub>5</sub>Zn 778.1944 [M+H]<sup>+</sup>, 778.1933 found [M+H]<sup>+</sup>.



**7**

**P-(PhCOOH)<sub>2</sub>**

**Zinc 2,3-bis(4'-ethoxycarbonyphenylethynyl)-5,10,15,20-tetraphenylporphyrin (7).** To a solution of **2** (50 mg, 0.057 mmol) in THF (10 mL), TBAF (1 mL, 1 M in THF) was added

and the solution was stirred at room temperature for 0.5 hour under Ar. After completion of the reaction, the solvent was removed under reduced pressure. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and washed with water twice. The organic solution was washed with brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated. The resulting residue and ethyl 4-iodobenzoate (58 mg, 0.28 mmol) were dissolved in THF (5 mL) and Et<sub>3</sub>N (1 mL) under Ar, and then Pd<sub>2</sub>(dba)<sub>3</sub> (10 mg, 0.011 mmol) and AsPh<sub>3</sub> (34 mg 0.11 mmol) were added to the mixture. The solution was warmed up to 70°C and stirred for 12 h. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by silica column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as eluent. Product (37 mg) was obtained in 72% yield as green solid by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH. <sup>1</sup>NMR (600 MHz, CDCl<sub>3</sub>): δ 8.86 (s, 2H), 8.84 (d, *J* = 4.7 Hz, 2H), 8.80 (d, *J* = 4.6 Hz, 2H), 8.15 (d, *J* = 7.2 Hz, 4H), 8.13 (d, *J* = 7.2 Hz, 4H), 7.73–7.79 (m, 8H), 7.52–7.61 (m, 12H), 4.23 (m, 4H), 1.32 (t, 6H). ESI-MS: *m/z* calcd for C<sub>66</sub>H<sub>44</sub>N<sub>4</sub>O<sub>4</sub>Zn: 1020.27, found 1021.3 [M+H]<sup>+</sup>. λ<sub>max</sub>/nm (in CH<sub>2</sub>Cl<sub>2</sub>): 447, 566, 609.

**P-(PhCOOH)2.** A mixture of **7** (20 mg) and NaOH (1M, 1 mL) in THF (3 mL) and MeOH (1 mL) was refluxed for 2 h. After completion of the reaction, deionized water (100 mL) was added and the mixture was neutralized with HCl (0.1 M, 10 mL). Precipitated product (16 mg) was obtained as a green solid in 85% yield after filtration and drying in vacuo. <sup>1</sup>NMR (600 MHz, THF d<sup>8</sup>): δ 8.90 (s, 2H), 8.80 (d, *J* = 4.7 Hz, 2H), 8.74 (d, *J* = 4.6 Hz, 2H), 8.10 (d, *J* = 7.2 Hz, 4H), 8.08 (d, *J* = 7.2 Hz, 4H), 7.70–7.75 (m, 8H), 7.51–7.58 (m, 12H). HRESI-MS: *m/z* calcd for C<sub>62</sub>H<sub>36</sub>N<sub>4</sub>O<sub>4</sub>Zn 963.1955 [M-H]<sup>-</sup>, found 963.1932 [M-H]<sup>-</sup>.

### Spectroscopic Measurements

UV-vis absorption measurements were performed using a V-570 UV-vis spectrophotometer (Jasco). Steady-state fluorescence spectra were recorded using 1 cm path length quartz cell on a RF-503A spectrophotometer (Shimadzu).

### Electrochemical Measurements.

Electrochemical measurements were performed by the differential pulse voltammetry (DPV) method on a BAS100 electrochemical analyzer. Voltammograms were recorded under argon flow using 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte. Two compartment cells connected by a salt bridge was employed, where a porphyrin in dehydrated THF, a platinum disk (BAS) working electrode and a Pt wire counter electrode were put in the one cell, and a saturated calomel (SCE) reference electrode was put in the other cell. Ferrocene/ferrocenium (0.56 V vs SCE)<sup>S2</sup> was used as the external potentiometric standard.

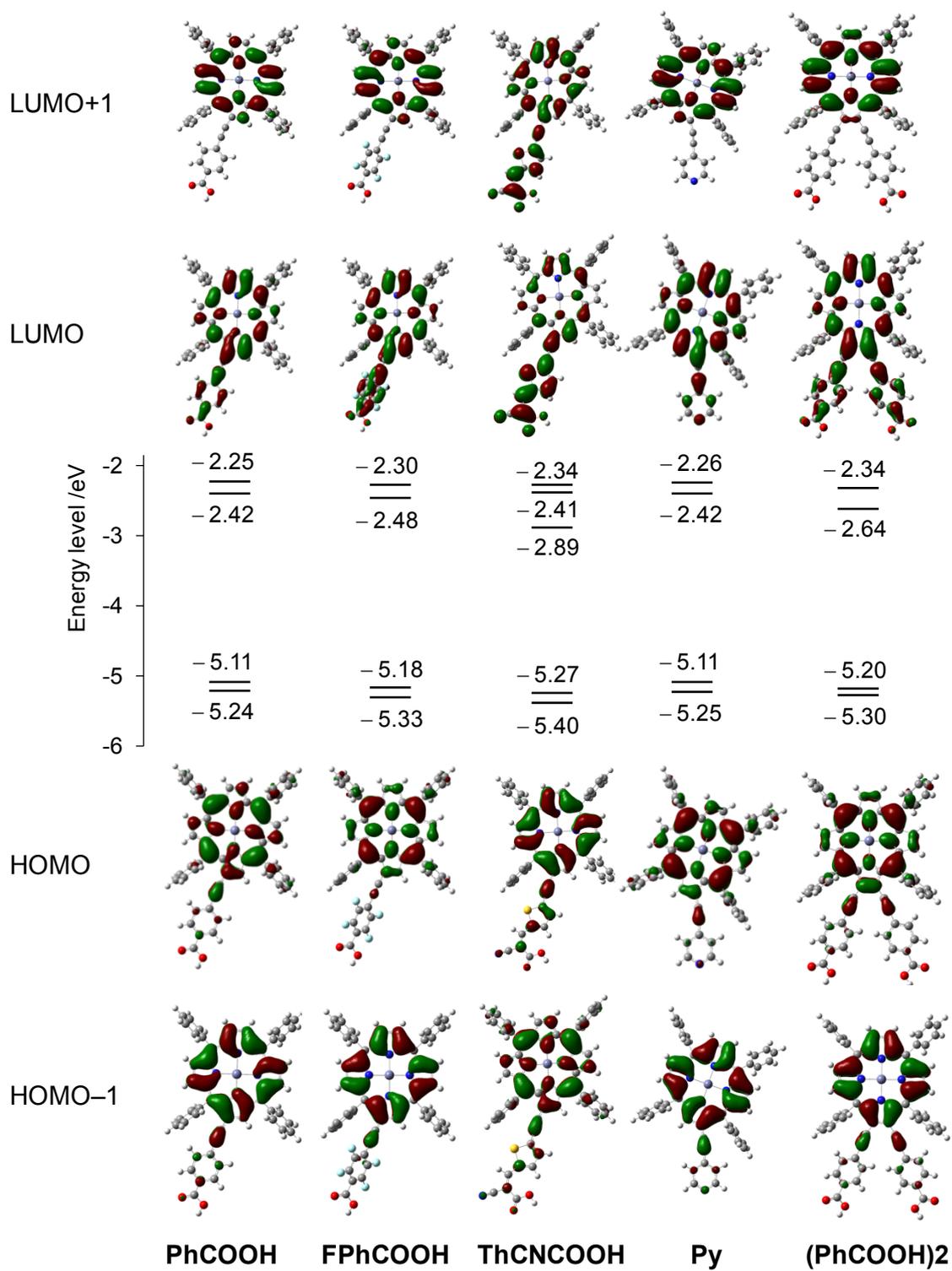
### **Density functional theory (DFT) calculations**

Geometry optimization and electronic structure calculations of the porphyrins were performed at the B3LYP/6-31G(d)\* level of theory using the Gaussian 09 program package.<sup>S3</sup>

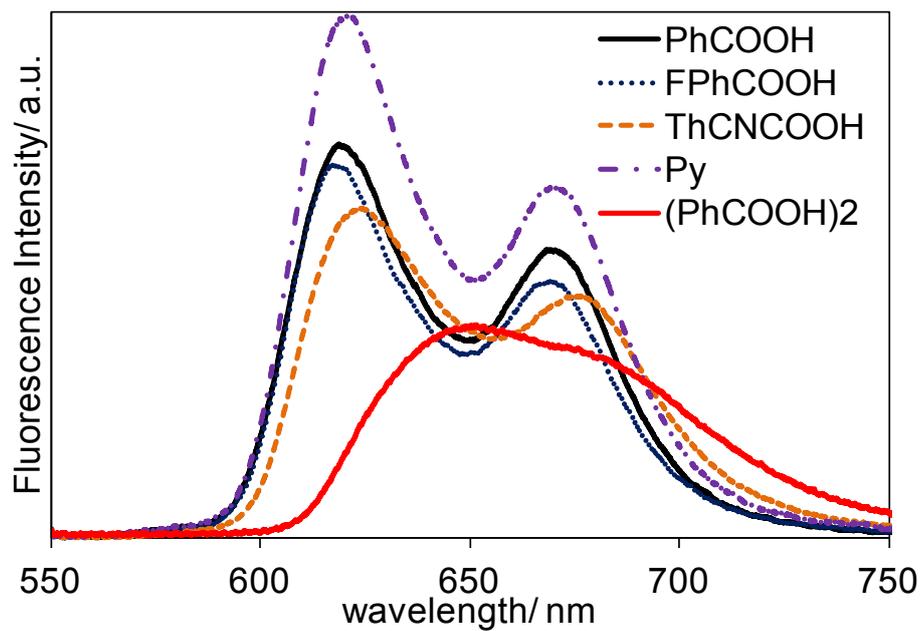
### **Device Fabrication and Photovoltaic Measurements**

DSSCs were constructed by assembling a porphyrin-adsorbed TiO<sub>2</sub> film and a Pt counter electrode with a spacer, where an electrolyte was injected into the gap of the electrodes. For the counter electrode, commercially available Pt coated FTO plate (Geomatec Co., Ltd) was used and two holes were drilled for electrolyte injection. For the spacer, a 30 μm plastic film (Himilan, DuPont) was used. TiO<sub>2</sub> films were prepared by repeatedly screen printing TiO<sub>2</sub> pastes (Solaronix) with mean particle sizes of 13 nm or 400 nm onto F-doped SnO<sub>2</sub> (FTO, Nippon Sheet Glass) substrates. After the printing, the films were calcined at 500 °C for 30 min, followed by immersion in TiCl<sub>4</sub> solution at 70 °C for 30 min and re-calcination. All TiO<sub>2</sub> films composed of a ~6 μm transparent layer (13 nm) and a ~4 μm scattering layer (400 nm). Dye immersion of the TiO<sub>2</sub> films was conducted in ~0.2 mM porphyrins (with deoxycholic acid) in THF at 30°C for 0.5 h. The films were rinsed with the immersing solvent before use. For the electrolyte, 0.1 M LiI, 0.6 M 1,2-dimethyl-3-propylimidazolium iodide and 0.025 M I<sub>2</sub> and 0.5 M 4-*tert*-butyl pyridine in acetonitrile were used. The active area of the cells was 0.16 cm<sup>2</sup>.

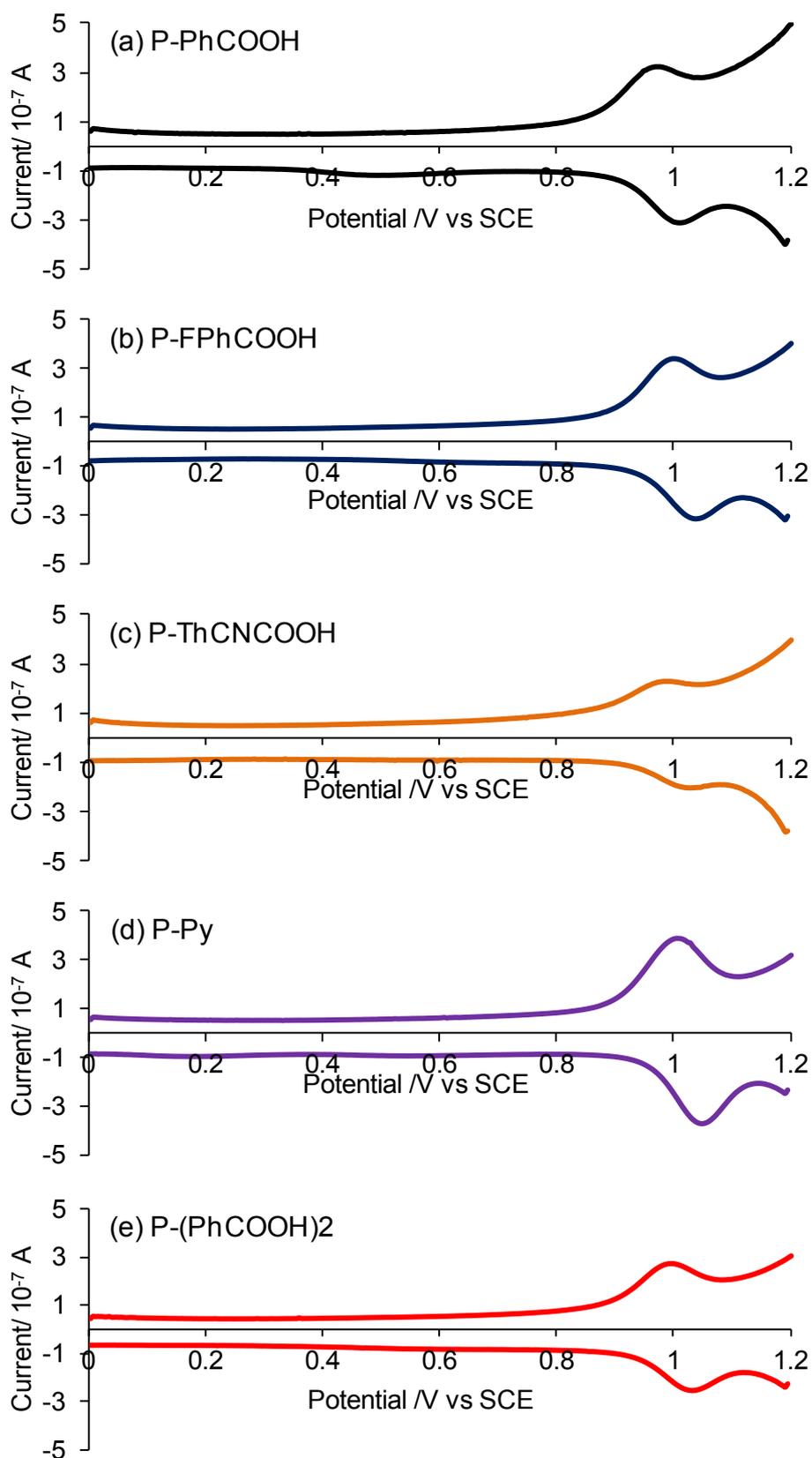
The current–voltage characteristics of sample cells were measured under AM 1.5 G illumination with a solar simulator (CEP-25TF, Bunkoukeiki Co., Ltd). The light intensity was calibrated by a standard silicon cell (BS-520 S/N 235, Bunkoukeiki Co., Ltd). Data were collected by a source meter (Keithley 2400). The power conversion efficiency ( $\eta$ ) was obtained according to the equation  $\eta = J_{sc} \times V_{oc} \times FF/P_{in}$ , where  $J_{sc}$  is the short-circuit photocurrent density,  $V_{oc}$  is the open-circuit voltage,  $ff$  is the fill factor and  $P_{in}$  is the incident radiation power. The incident photon-to-current conversion efficiency (IPCE) spectra were measured by an IPCE measurement system (SM-250E, Bunkoukeiki Co., Ltd). A standard silicon solar cell (SiPD S1337-1010BQ, Bunkoukeiki Co., Ltd) was used as a reference.



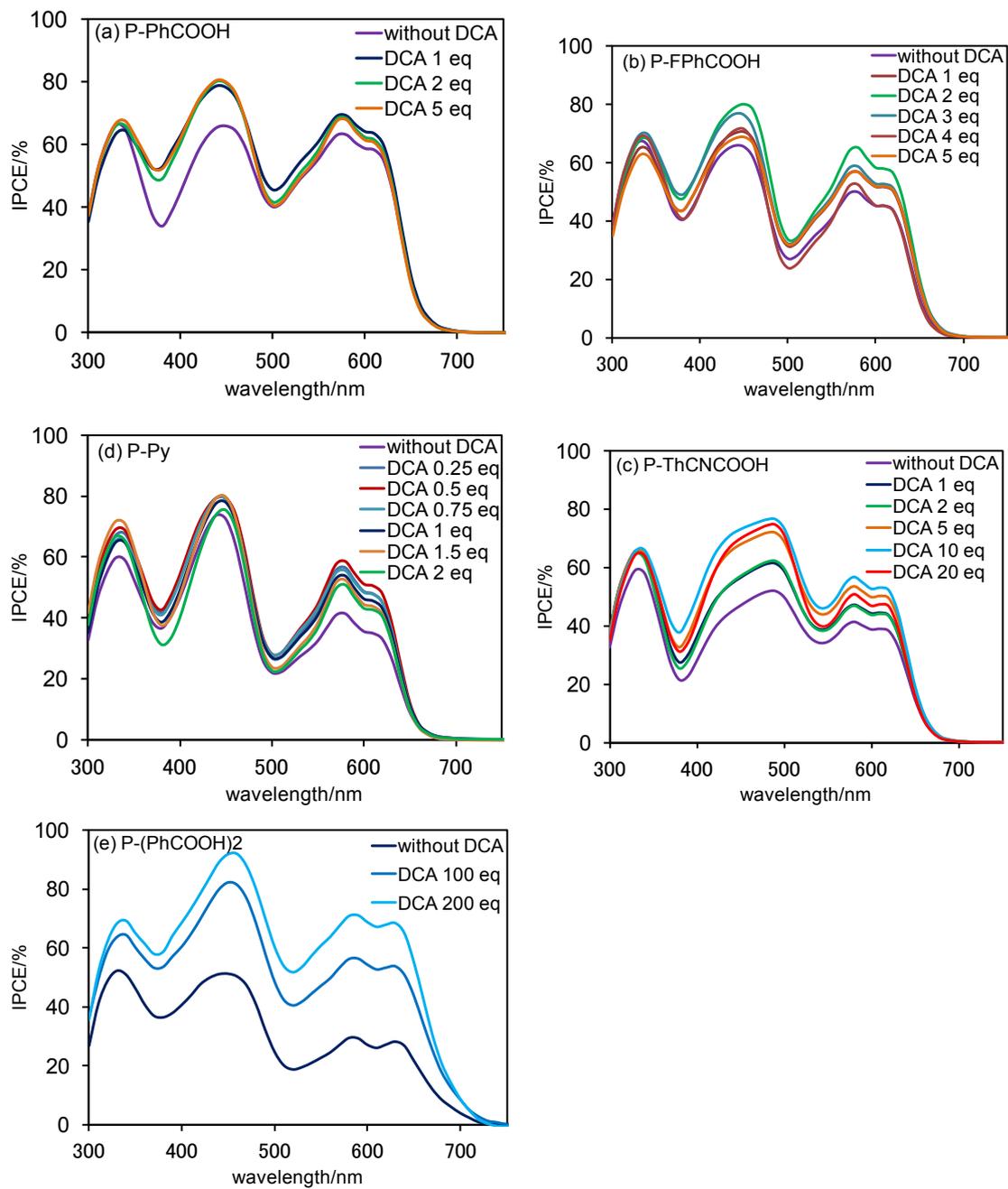
**Figure S1.** Structures and energies of molecular orbitals obtained by DFT calculations with B3LYP/6-31G(d)\*.



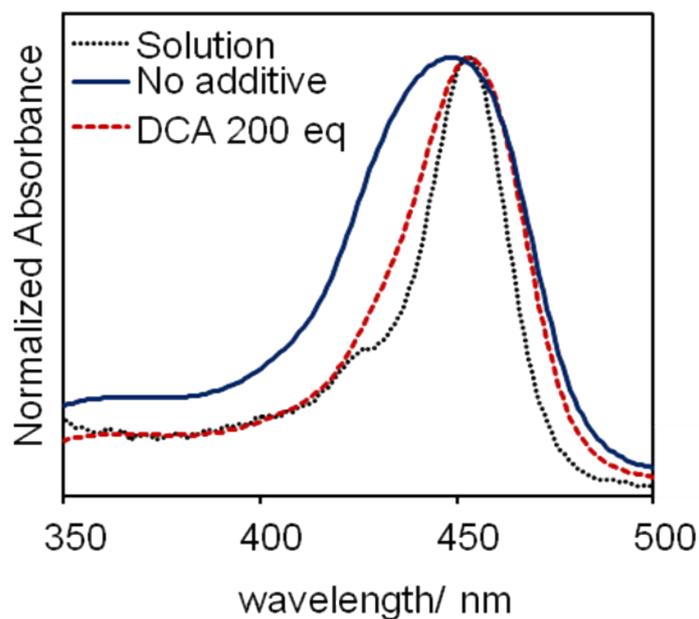
**Figure S2.** Steady-state fluorescence spectra of the porphyrins in THF. The excitations were performed at the Soret bands, where the wavelengths were chosen to irradiate identical absorbance.



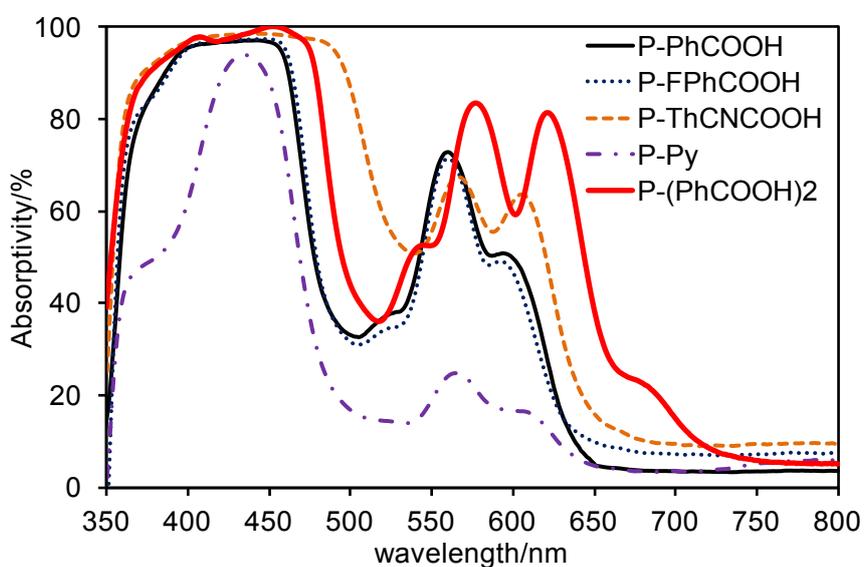
**Figure S3.** Differential pulse voltammograms of the porphyrins in THF with 0.1 M  $n\text{-Bu}_4\text{NPF}_6$  as the supporting electrolyte.



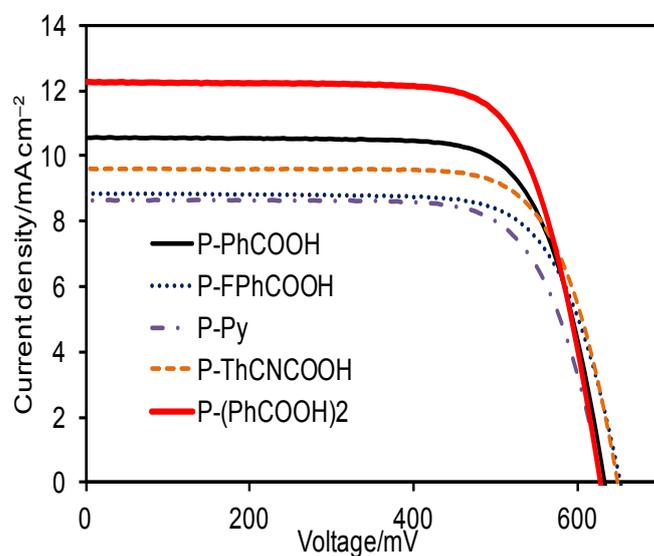
**Figure S4.** IPCE spectra of the porphyrin-sensitized solar cells at various ratios of DCA to porphyrin.



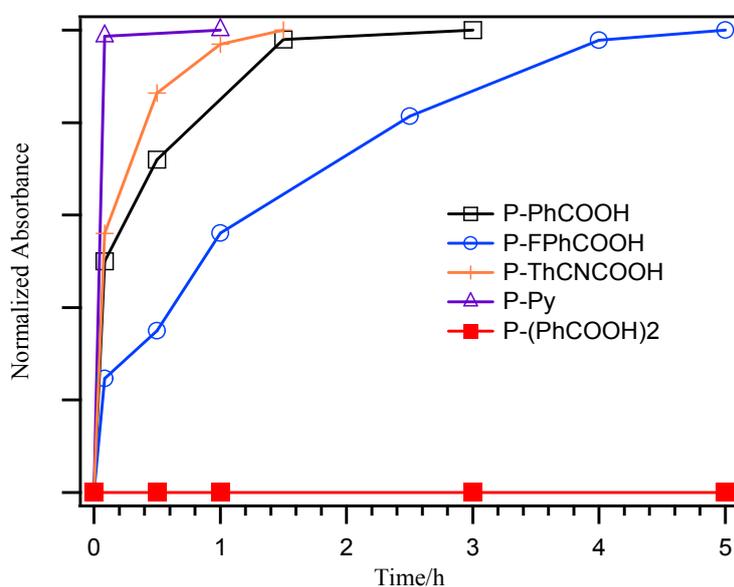
**Figure S5.** UV-vis spectra of **P-(PhCOOH)<sub>2</sub>** in acetonitrile (dotted line) and on TiO<sub>2</sub> with (dashed line) or without (solid line) addition of DCA in acetonitrile.



**Figure S6.** UV-vis absorption spectra of the porphyrins adsorbed on a transparent TiO<sub>2</sub> film with a thickness of  $\sim 4$   $\mu\text{m}$ . The optimized ratios of DCA were used for dye adsorption. In the DSSCs, most photons with energies corresponding to the Soret bands are mostly harvested due to the presence of a scattering layer.



**Figure S7.** Photocurrent-voltage curves of the porphyrin-sensitized solar cells at the optimized DCA conditions under AM 1.5 illumination ( $100 \text{ mW cm}^{-2}$ ).



**Figure S8.** Time courses of absorbance of dissolved porphyrins from porphyrin-adsorbed  $\text{TiO}_2$  films in THF with 0.01 M NaOH. 1 cm path length optical cell was used, where the  $\text{TiO}_2$  films were put off the probe light pathway. The optimized ratios of DCA were used for dye adsorption. Without DCA, a similar tendency was observed.

### **Additional references**

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S2. N. G. Connelly and W. E. Geiger, *Chem. Rev.* 1996, **96**, 877.

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