Supplementary Material

A Supramolecular Photosynthetic Triad of Slipped Cofacial Porphyrin Dimer, Ferrocene, and Fullerene

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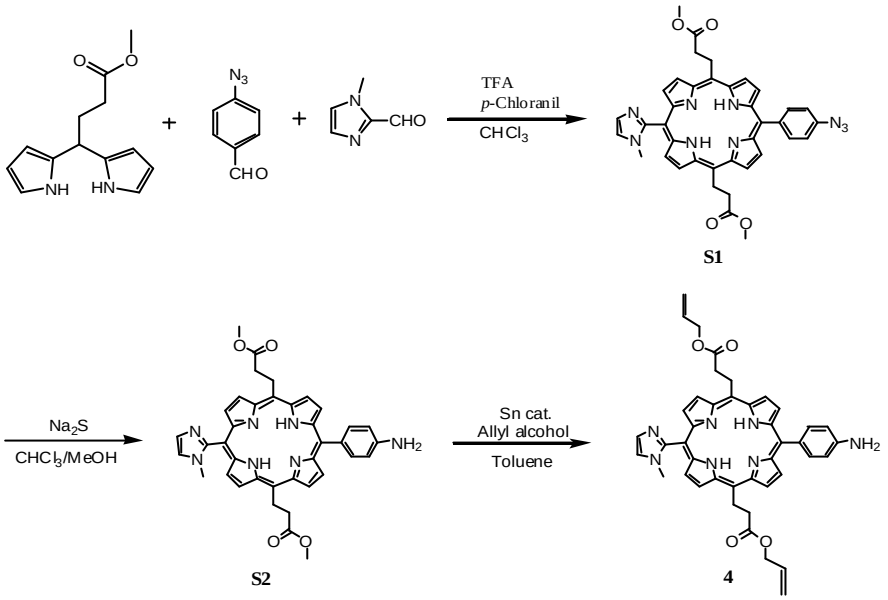
General procedure. General. ^{1}H NMR spectra were measured by JEOL JNM EX 270 and JEOL ECP 600. Matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectra were measured by Per Septive Biosystems Voyager DE-STR. Steady-state UV-visible absorption spectra were recorded on a UV-3100PC (Shimadzu). The edge-to-edge distance (*Ree*) was determined from CPK modeling using WinMOPAC (version 3.9). Analytical gel permeation chromatograms were obtained on Shimadzu LC-workstation M10 equipped with SPD-M10 AVP photo diode array detector using TSK GMH_{HR}-M column (TOSHO Co.). Preparative gel permeation chromatograms were obtained on Japan Analytical Industry Co. LC-908.

Materials. All solvents and chemicals were reagent grade, obtained commercially and used without further purification. Thin-layer chromatography (TLC) and flash column chromatography were performed with Silica gel 60 F_{254} (Merck) and Silica Gel 60 N (KANTO CHEMICAL CO., INC.).

Synthesis and Characterrization.



Synthesis of S1

A solution of 1-methylimidazole-2-carboxyaldehyde (1.1 g, 10.0 mmol), 4-azide benzaldehyde (1.4 g, 10.0 mmol), and *meso*-(methoxycarbonylethyl)dipyrromethane (4.6 g, 20.0 mmol) in chloroform (2000 mL) was degassed by bubbling with nitrogen for 15 min, and then trifluoroacetic acid (2.2 mL, 30.0 mmol) was added. After stirring for 4 h at room temperature, *p*-chloranil (7.5 g, 30.0 mmol) was added and the reaction mixture was stirred for overnight. The reaction solution was washed with aqueous sodium bicarbonate, and then organic layer was evaporated. The desired product was purified by silica gel column chromatography (eluent: chloroform/acetone = 10:1) to yield 0.39 g (0.57 mmol, 2.8% yield): ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.39 (s, 3H), 3.41-3.68 (m, 4H), 3.75 (s, 6H), 5.33 (t, J = 8.3 Hz, 4H), 7.41-7.48 (m, 2H), 7.51 (s, 1H), 7.86 (s, 1H), 8.09-8.17 (m, 2H), 8.82 (d, J = 4.9 Hz, 2H), 8.88 (d, J = 4.9 Hz, 2H), 9.46 (d, J = 5.1 Hz, 2H), 9.50 (d, J = 5.1 Hz, 2H); MALDI-TOFMS *m/z* 680.60 ($M+H^+$).

Synthesis of S2

A solution of freebase porphyrin **S1** (103 mg, 0.15 mmol) and sodium sulfide nonahydrate (144 mg, 0.65 mmol) in chloroform/methanol (20 mL/20 mL) was heated at 60 °C for 6 h. The reaction solution was washed with aqueous sodium bicarbonate, and then organic layer was evaporated. The desired product was purified by silica gel column chromatography (eluent: chloroform/acetone = 5:1) to yield 71 mg (0.11 mmol, 72% yield). : ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.40 (t, *J* = 8.1 Hz, 4H), 3.54 (s, 6H), 5.21 (t, *J* = 8.4 Hz, 4H), 6.93 (d, *J* = 8.3 Hz, 4H), 7.37 (s, 1H), 7.60 (s, 1H), 8.09-8.17 (br.m, 2H), 8.70 (d, *J* = 4.9 Hz, 2H), 8.89 (d, *J* = 4.9 Hz, 2H), 9.32 (d, *J* = 5.1 Hz, 2H), 9.39 (d, *J* = 5.1 Hz, 2H); MALDI-TOFMS *m/z* 654.19 ($M+H^+$).

Synthesis of 4

A solution of free base porphyrin **S2** (71 mg, 0.11 mmol) and allyl alcohol (0.15 mL, 2.2 mmol) in toluene (20 mL) were heated at 70 °C in the presence of distannoxane catalyst[1,2] (909 mg, 1.6 mmol). The reaction was monitored by MALDI-TOF mass spectra. The trans-esterification was completed within 12h. The mixture was cooled to room temperature, and water was added. The mixture was then extracted with $CHCl_3$. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The desired product was purified by silica gel column chromatography (eluent: chloroform/acetone = 5:1) to yield 47 mg (0.66 mmol, 60% yield). : ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.32 (s, 3H), 3.48 (t, *J* = 7.8 Hz, 4H), 4.68 (d, *J* = 5.9 Hz, 4H), 5.19-5.35 (m, 8H), 5.84-5.99 (m, 2H), 7.07 (br.s, 2H), 7.49 (s, 1H), 7.74 (s, 1H), 8.09-8.17 (br.s, 2H), 8.68 (d, *J* = 4.9 Hz, 2H), 8.97 (d, *J* = 4.9 Hz, 2H), 9.33-9.38 (m, 4H) ; MALDI-TOFMS *m/z* 706..22 ($M+H^+$)

Synthesis of 8

Oxalyl chloride (0.01 mL, 0.1 mmol) was added to a stirred solution of sodium 4-ferrocenylbenzoate (3.3 mg, 10 μmol) in $CHCl_3$ (2 mL) and pyridine (0.01 mL). The resulting solution was stirred for 13h at room temperature, and then refluxed for 5h. Excess oxalyl chloride and solvent were removed under reduced pressure and the residue was redissolved in toluene (5 mL). This solution was added to a stirred solution of **4** (7 mg, 10 μmol) and pyridine (0.01 mL) in toluene (5 mL), and the solution was stirred for 18h. The reaction mixture was evaporated and the desired product was purified by silica gel column chromatography (eluent: chloroform/acetone = 5:1) to yield 6.6 mg (6.3 μmol, 63% yield). : ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.41 (s, 3H), 3.49 (t, *J* = 7.8 Hz, 4H), 3.94 (s, 3H), 4.04 (s, 5H), 4.37 (s, 2H), 4.64 (s, 2H), 4.67 (d, *J* = 5.9 Hz, 4H), 5.18-5.31 (m, 8H), 5.82-5.90 (m, 2H), 7.33 (d, *J* = 1.3 Hz, 1H), 7.49 (s, 1H), 7.53 (d, *J* = 1.9 Hz, 1H), 7.74 (s, 1H), 7.79 (d, *J* = 1.9 Hz, 1H), 7.95 (d, *J* = 1.3 Hz, 1H), 8.09-8.17 (br.s, 2H), 8.68 (d, *J* = 4.9 Hz, 2H), 8.97 (d, *J* = 4.9 Hz, 2H), 9.33-9.38 (m, 4H) ; MALDI-TOFMS *m/z* 994.7 ($M+H^+$)

Synthesis of 2a

To a solution of freebase porphyrin **8** (6.6 mg, 6.3 μmol) in 3 mL of $CHCl_3$ was added 1 mL of saturated solution of zinc acetate dihydrate in methanol. After stirring for 30 min at room temperature, the solution was washed with water, and then organic layer was evaporated to yield 95% of **2a**. : ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.67 (s, 3H), 2.09 (s, 1H), 3.67-3.87 (m, 4H), 4.20 (s, 5H), 4.47 (s, 2H), 4.83-4.90 (m, 6H), 5.32 (d, *J* = 1.2 Hz, 1H), 5.46-5.52 (m, 9H), 6.04-6.10 (m, 2H), 7.73 (d, *J* = 3.9 Hz, 2H), 7.99 (d, *J* = 3.9 Hz, 1H), 8.05 (d, *J* = 3.9 Hz, 2H), 8.16 (d, *J* = 3.9 Hz, 1H), 8.38 (d, *J* = 3.9 Hz, 1H), 8.70 (d, *J* = 3.9 Hz, 1H), 8.95 (d, *J* = 4.9 Hz, 2H), 9.13 (d, *J* = 4.9 Hz, 2H), 9.63 (d, *J* = 4.9 Hz, 2H) ; MALDI-TOFMS *m/z* 1056.7 ($M+H^+$)

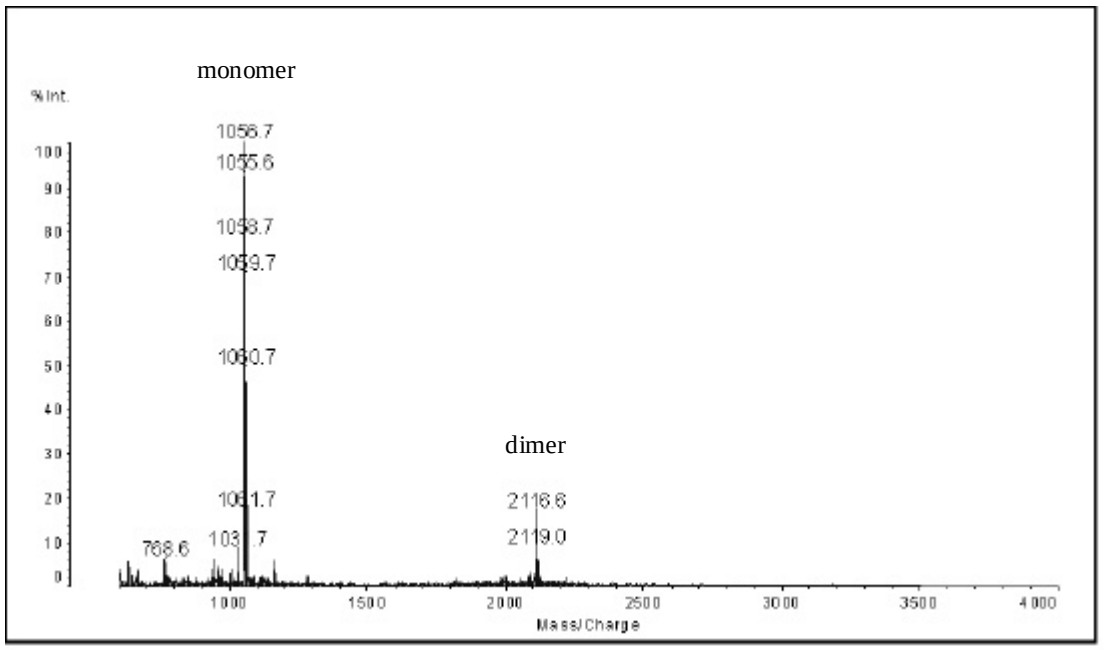


Fig. S1 MALDI-TOF Mass spectrum of **2a**

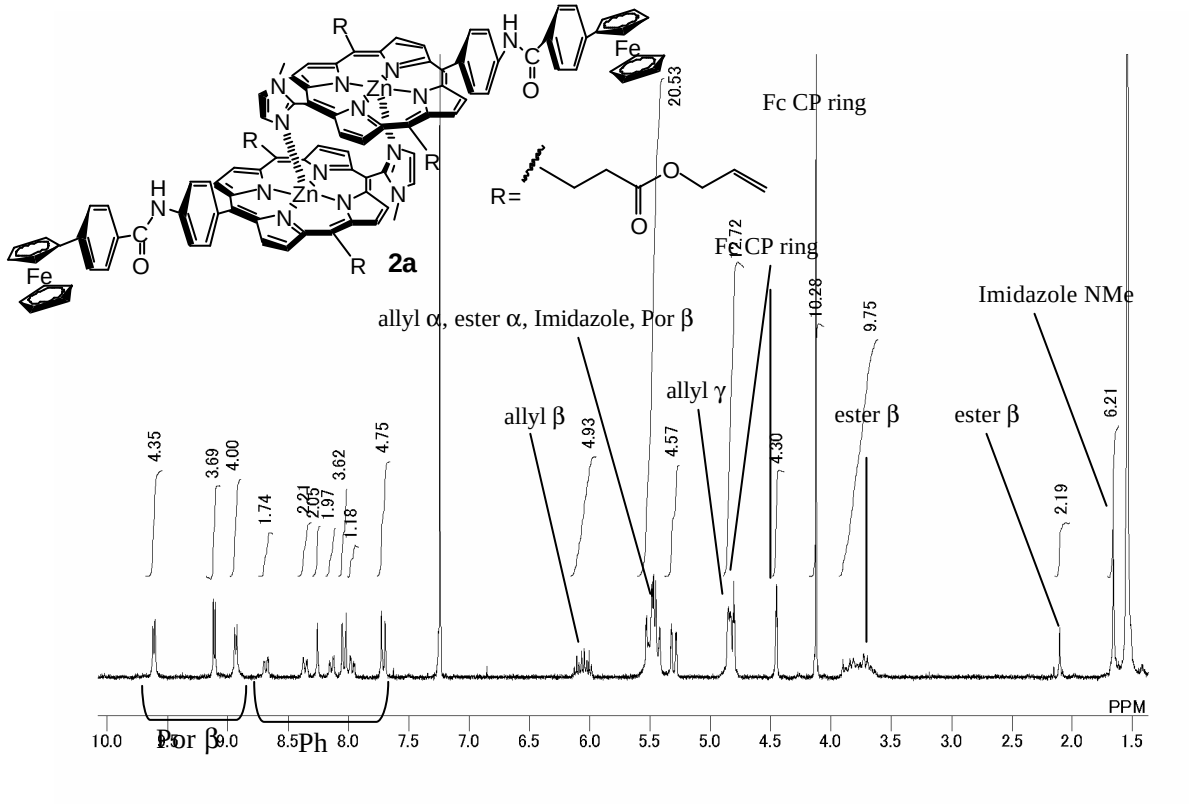


Fig. S2 ^{1}H NMR spectrum of **2a**

Synthesis of 7

A solution of 1-carboxy-1'-(*N*-methyl-2-fulleropyrolidinyl)biphenyl (20 mg, 20.5 μmol), thionyl chloride (15 μL), and pyridine (0.03 mL) in benzene (6 mL) was refluxed for 2h under nitrogen atmosphere. Excess reagents and solvent were removed under reduced pressure, and the residue was redissolved in a mixture of toluene (10 mL) and pyridine (0.01 mL). To the mixture was added a solution of **4** (14.5 mg, 20 μmol) in toluene (10 mL) and pyridine (0.01 mL). The solution was allowed to stir 6h at room temperature under nitrogen atmosphere. The reaction mixture was evaporated and the product was obtained by silica gel column chromatographic separation. (eluent: chloroform/acetone = 20:1) to yield 20.7 mg (68%) : ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.85 (s, 3H), 3.42 (s, 3H), 3.48 (s, 1H), 3.49 (t, *J* = 7.8 Hz, 4H), 3.94 (s, 3H), 4.19-4.37 (s, 2H), 4.64 (s, 2H), 4.67 (d, *J* = 5.9 Hz, 4H), 5.18-5.31 (m, 8H), 5.82-5.90 (m, 2H), 7.33 (d, *J J* = 1.3 Hz, 1H), 7.49 (s, 1H), 7.53 (d, *J* = 1.9 Hz, 1H), 7.74 (s, 1H), 7.79 (d, *J* = 1.9 Hz, 1H), 7.95 (d, *J* = 1.3 Hz, 1H), 8.09-8.17 (br.s, 2H), 8.68 (d, *J* = 4.9 Hz, 2H), 8.97 (d, *J* = 4.9 Hz, 2H), 9.33-9.38 (m, 4H) ; MALDI-TOFMS *m/z* 1661.52 (M^+)

Synthesis of 1a

To a solution of free base porphyrin **7** in 3 mL of $CHCl_3$ was added 1 mL of saturated solution of zinc acetate dihydrate in methanol. After stirring for 30 min at room temperature, the solution was washed with water and then organic layer was evaporated to yield 90% of **1a**. : ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.67 (s, 6H), 2.05 (s, 2H), 2.89 (s, 6H), 3.72-3.85 (m, 8H), 4.22-4.33 (m, 14H), 4.82-4.89 (m, 8H), 5.04 (s, 4H), 5.30 (d, *J* = 10.2 Hz, 4H), 5.45-5.52 (m, 18H), 6.04-6.10 (m, 4H;), 7.49-7.50 (m, 4H), 7.68-7.70 (m, 4H), 7.81 (d, *J* = 5.4 Hz, 2H), 7.89 (d, *J* = 5.4 Hz, 2H), 7.98-7.99 (m, 4H), 8.14-8.18 (m, 5H), 8.26 (s, 1H), 8.35 (d, *J* = 3.9 Hz, 1H), 8.68 (d, *J* =

3.9 Hz, 1H), 8.94 (d, *J* = 4.9 Hz, 4H), 9.10 (d, *J* = 4.9 Hz, 4H), 9.61 (d, *J* = 4.9 Hz, 4H) ; MALDI-TOFMS *m/z* 1727.1 ($M+H^+$)

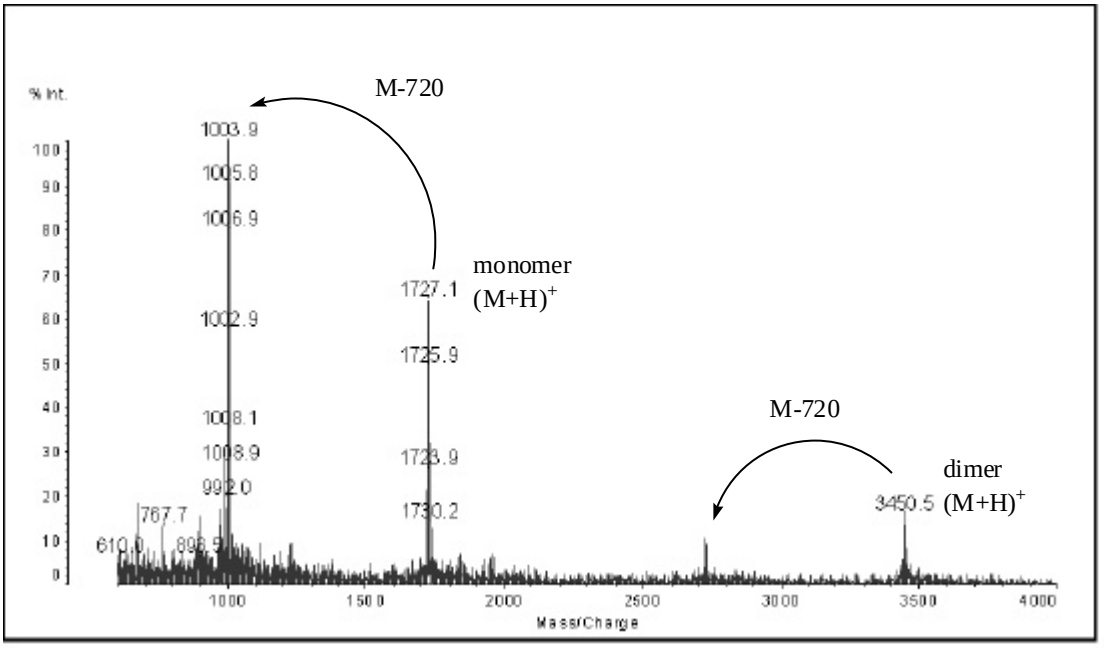


Fig. S3 MALDI-TOF Mass spectrum of **1a**

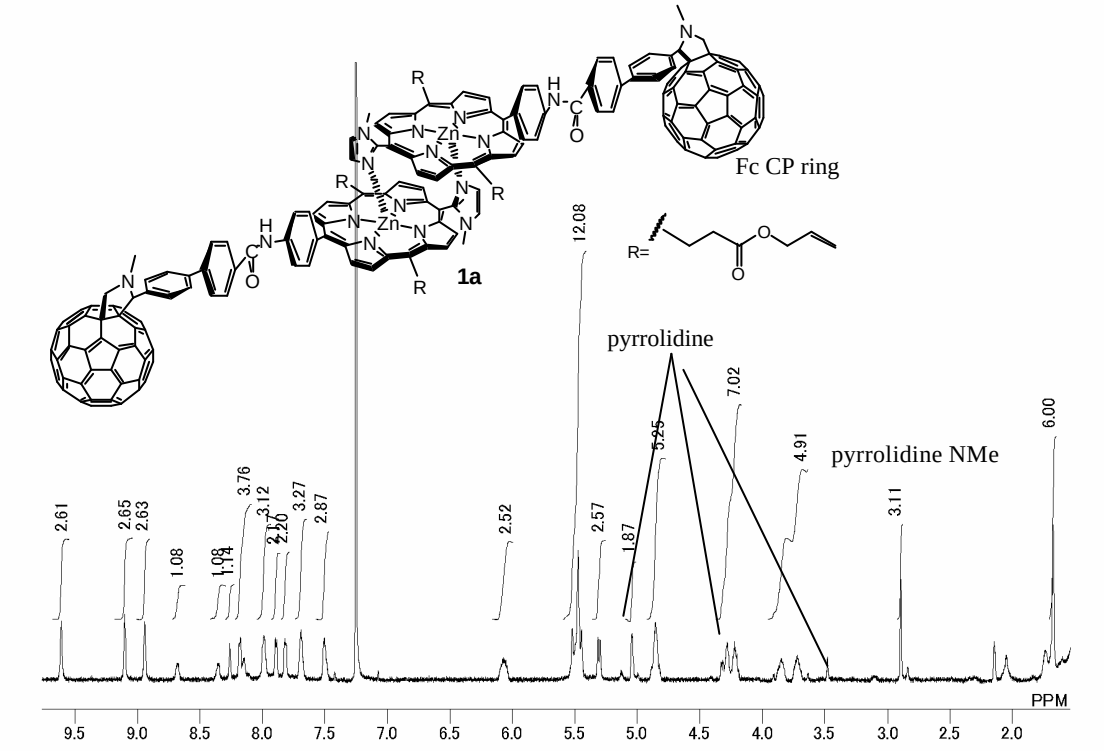


Fig. S4 1H NMR spectrum of **2b**

Synthesis of 3

A solution of **1a** (9 mg, 5.2 μmol) and **2a** (5 mg, 5.2 μmol) in pyridine (50 mL) was stirred for 30 min. The solvent was removed under reduced pressure, and the residue was redissolved in $CHCl_3$ (5 mL). Grubbs catalyst (4 mg, 0.5 eq) was added to the solution, and then the mixture was stirred for 2h at room temperature under nitrogen atmosphere.[2] The reaction mixture was evaporated and the product was purified twice by recycling preparative HPLC (TSK-GEL $G2500H_{HR}$, eluent: chloroform/methanol = 10:1) as shown in Figs. **S5** and **S6** to yield 5.7 mg (42%). Homodimers **1b** (3.5 mg, 20%) and **2b** (2.1 mg, 22%) were also obtained. : ^{1}H NMR (600 MHz, $CDCl_3$) of **3** δ 1.69 (s, 6H; NCH_3 (imidazole)), 2.09 (s, 2H; CH (imidazole ring)), 2.90 (s, 3H; NCH_3 (pyrrolidine)), 3.67-3.87 (m, 4H; ester β), 4.14 (s, 5H; CH (Fc pentacyclodiene ring)), 4.30-4.33 (m, 1H; CH_2 (pyrrolidine)), 4.47 (d, *J* = 1.8 Hz, 2H; CH (Fc pentacyclodiene ring)), 4.82 (d, *J* = 1.8 Hz, 2H; CH (Fc pentacyclodiene ring)), 4.99-5.09 (m, 10H; (2H; pyrrolidine) (8H; allyl α)), 5.39-5.56 (m, 14H(8H; ester α)(2H; imidazole ring)(4H; por β, cis & trans)), 6.40-6.67 (m, 4H; allyl β, cis & trans), 7.73 (d, *J* = 8.4 Hz, 2H; Ph), 7.83 (d, *J* = 7.2 Hz, 2H; Ph), 7.98-7.99 (m, 3H; Ph), 8.05 (d, *J* = 8.4 Hz, 2H; Ph), 8.12-8.14 (m, 2H; Ph), 8.20 (d, *J* = 7.8 Hz, 2H; Ph), 8.28 (s, 1H; NH (amido)), 8.33 (s, 1H; NH (amido)), 8.39-8.41 (m, 2H; Ph), 8.71-8.72 (m, 2H; Ph), 8.97-9.00 (m, 4H; por β, cis & trans), 9.12-9.14 (m, 4H; por β, cis & trans), 9.60-9.63 (m, 4H; por β, cis & trans) ; MALDI-TOFMS *m/z* 2726.3 : ^{1}H NMR of **1b** (600 MHz, $CDCl_3$) δ 1.7 (s, 6H; NCH_3 (imidazole)), 2.10 (s, 2H; CH (imidazole ring)), 2.88 (s, 3H; NCH_3 (pyrrolidine)), 3.67-3.87 (m, 4H; ester β), 4.30-4.33 (m, 2H; CH_2 (pyrrolidine)), 4.99-5.09 (m, 10H; (2H; pyrrolidine) (8H; allyl α)), 5.39-5.56 (m, 14H(8H; ester α)(2H; imidazole ring)(4H; por β, cis & trans)), 6.40-6.67 (m, 4H; allyl β, cis & trans), 7.75 (m, 4H; Ph), 7.83-7.84 (m, 3H; Ph), 7.98-7.99 (m, 3H; Ph), 8.06-8.08 (m, 4H; Ph), 8.24-8.25 (m, 6H;

Ph), 8.28 (s, 2H; NH (amido)), 8.39-8.41 (m, 2H; Ph), 8.71-8.72 (m, 2H; Ph), 8.97-9.00 (m, 4H; por β, cis & trans), 9.12-9.14 (m, 4H; por β, cis & trans), 9.60-9.63 (m, 4H; por β, cis & trans) ; MALDI-TOFMS *m/z* 3392.2 $(M-H)^+$: ^1H NMR (600 MHz, $CDCl_3$) of **2b** δ 1.69 (s, 6H; NCH_3 (imidazole)), 2.09 (s, 2H; CH (imidazole ring)), 3.67-3.87 (m, 4H; ester β), 4.14 (s, 10H; CH (Fc pentacyclodiene ring)), 4.50 (d, *J* = 1.8 Hz, 4H; CH (Fc pentacyclodiene ring)), 4.82 (d, *J* = 1.8 Hz, 4H; CH (Fc pentacyclodiene ring)), 4.99-5.09 (m, 6H; allyl α), 5.39-5.56 (m, 14H(8H; ester α)(2H; imidazole ring)(4H; por β, cis & trans)), 6.40-6.67 (m, 4H; allyl β, cis & trans), 7.73 (d, *J* = 8.4 Hz, 4H; Ph), 7.99 (d, *J* = 7.8 Hz, 2H; Ph), 8.05 (d, *J* = 8.4 Hz, 4H; Ph), 8.20 (d, *J* = 7.8 Hz, 2H; Ph), 8.33 (s, 2H; NH (amido)), 8.40 (d, *J* = 7.8 Hz, 2H; Ph), 8.72 d, *J* = 7.8 Hz, 2H; Ph), 8.97-9.00 (m, 4H; por β, cis & trans), 9.12-9.14 (m, 4H; por β, cis & trans), 9.60-9.63 (m, 4H; por β, cis & trans) ; MALDI-TOFMS *m/z* 2058.6 (M^+)

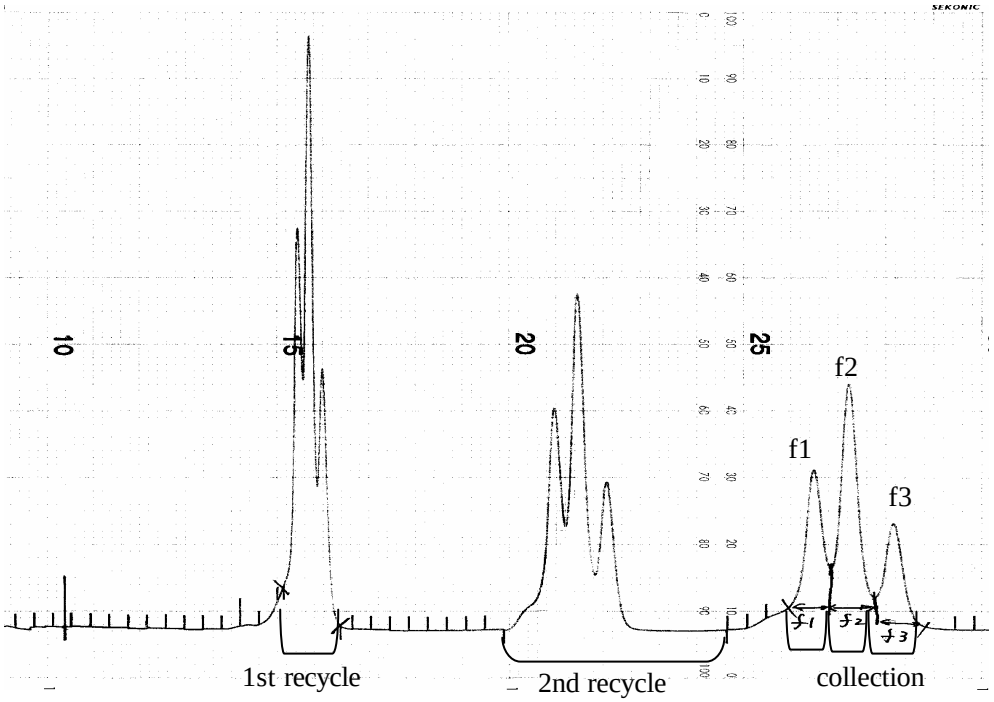


Fig. S5 Chromatograms of covalently linked macrorings using recycling preparative HPLC systems. After two recycling processes, fractions 1-3 were collected.

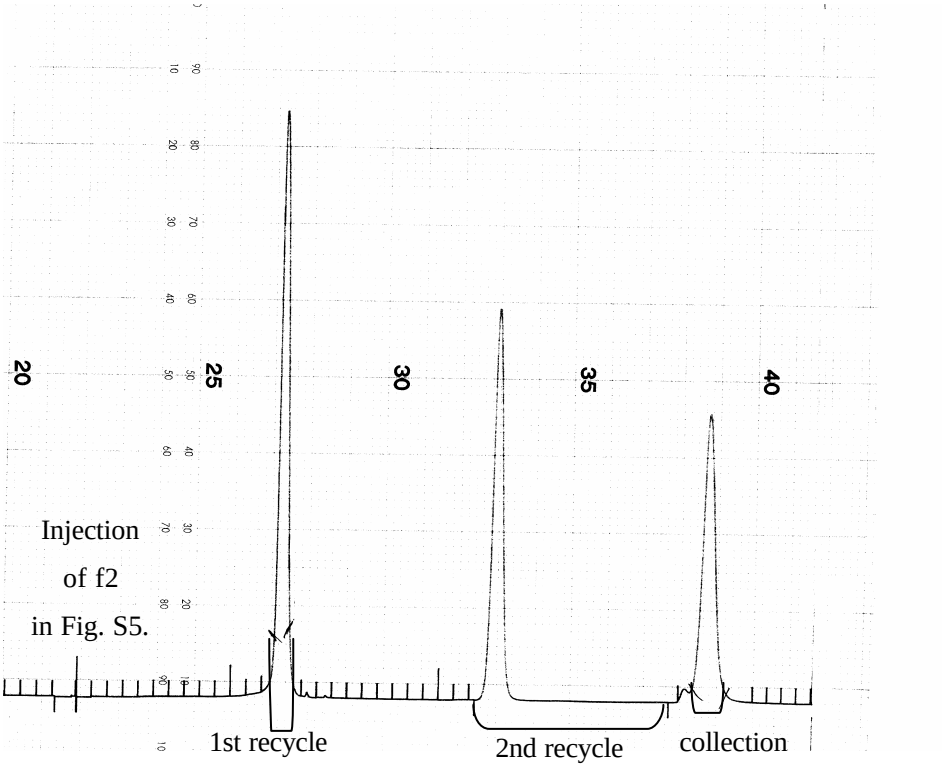


Fig. S6 Recycling GPC chart of **3** (f2)

^{1}H NMR and MALDI TOF Mass of **3, 1b, 2b**

Fc-$(ZnP)_2$-C_{60} **3**

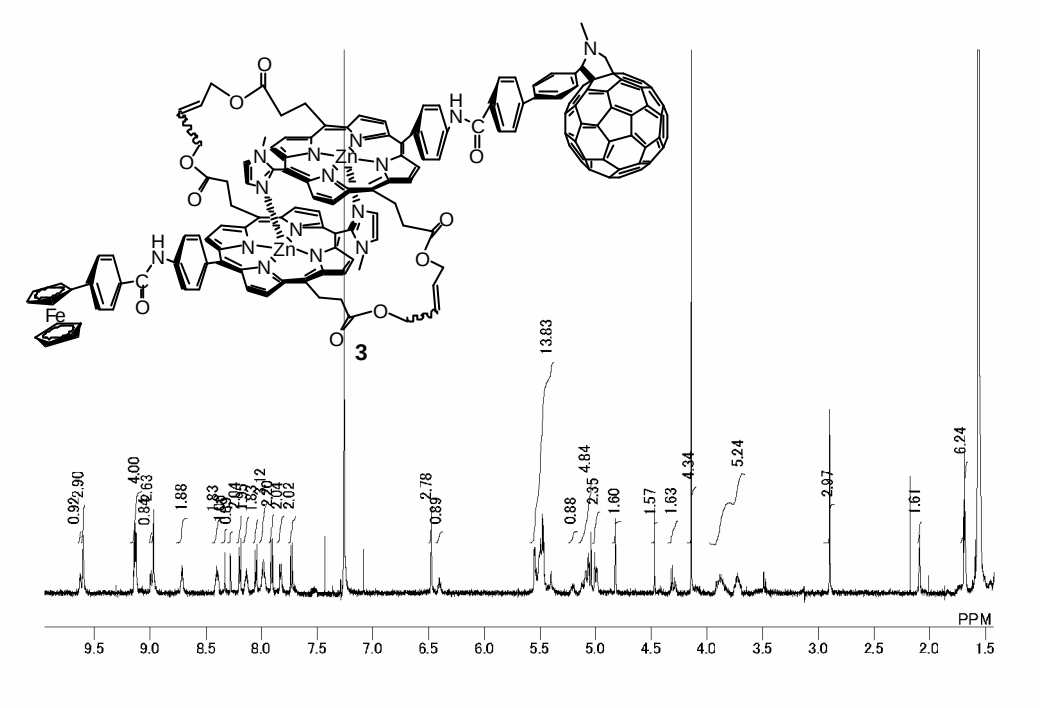


Fig. S7 ^{1}H NMR of **3**

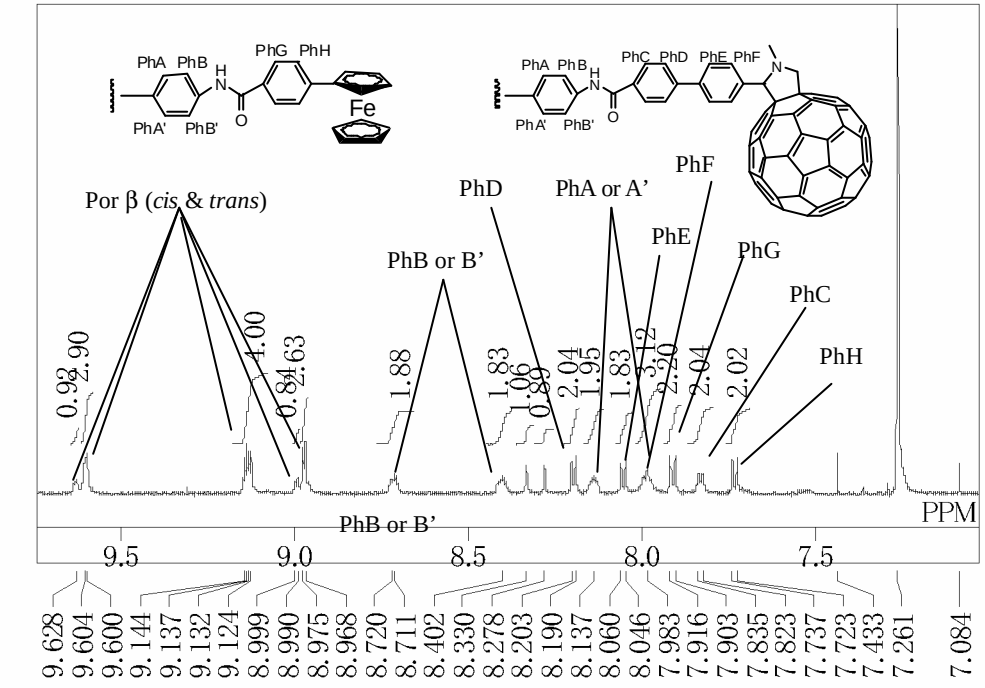


Fig. S8 ^{1}H NMR of **3** (7.0 ppm-9.7 ppm)

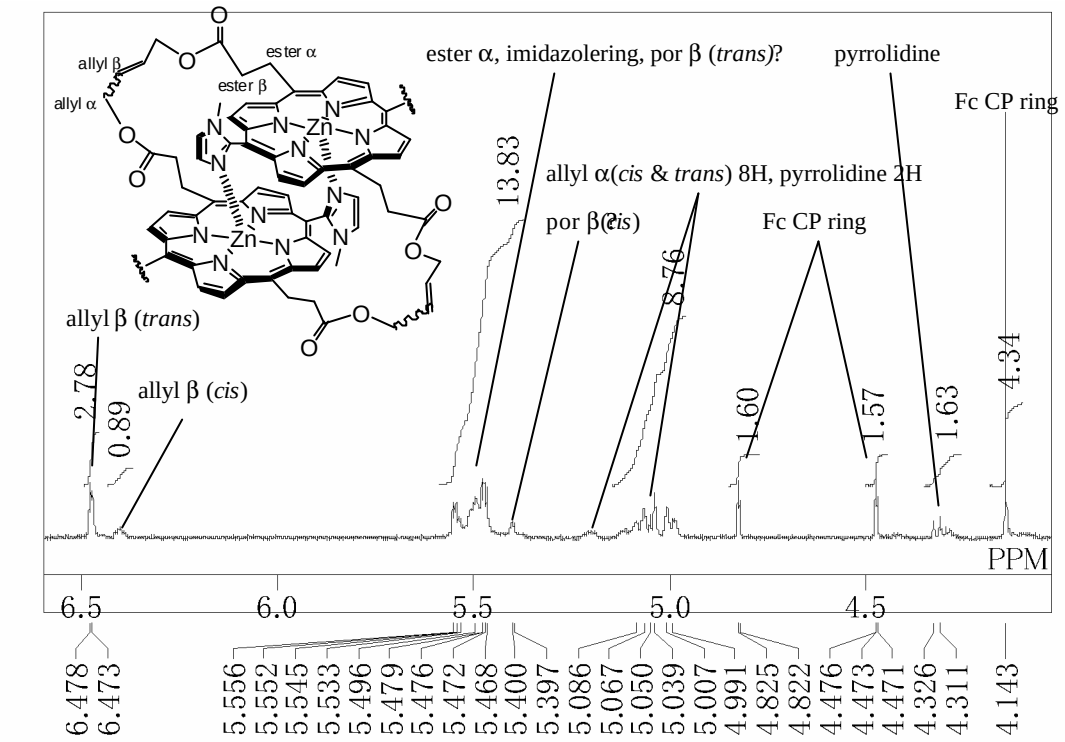


Fig. S9 ^{1}H NMR of **3** (4.0 ppm-6.5 ppm)

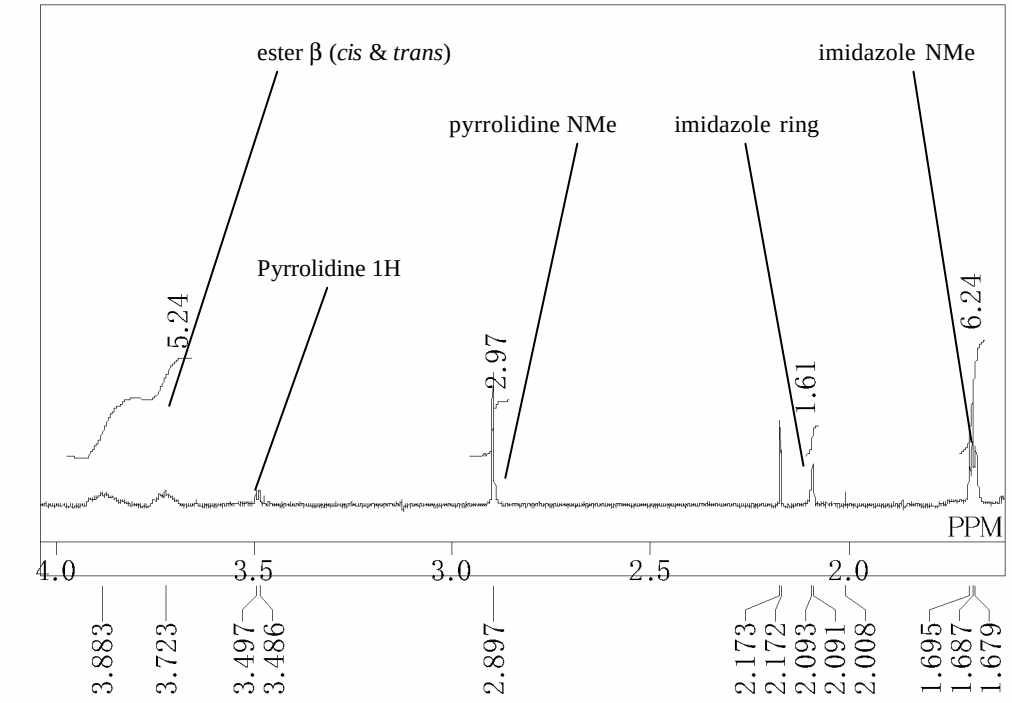


Fig. S10 ^{1}H NMR of **3** (1.5 ppm-4.0 ppm)

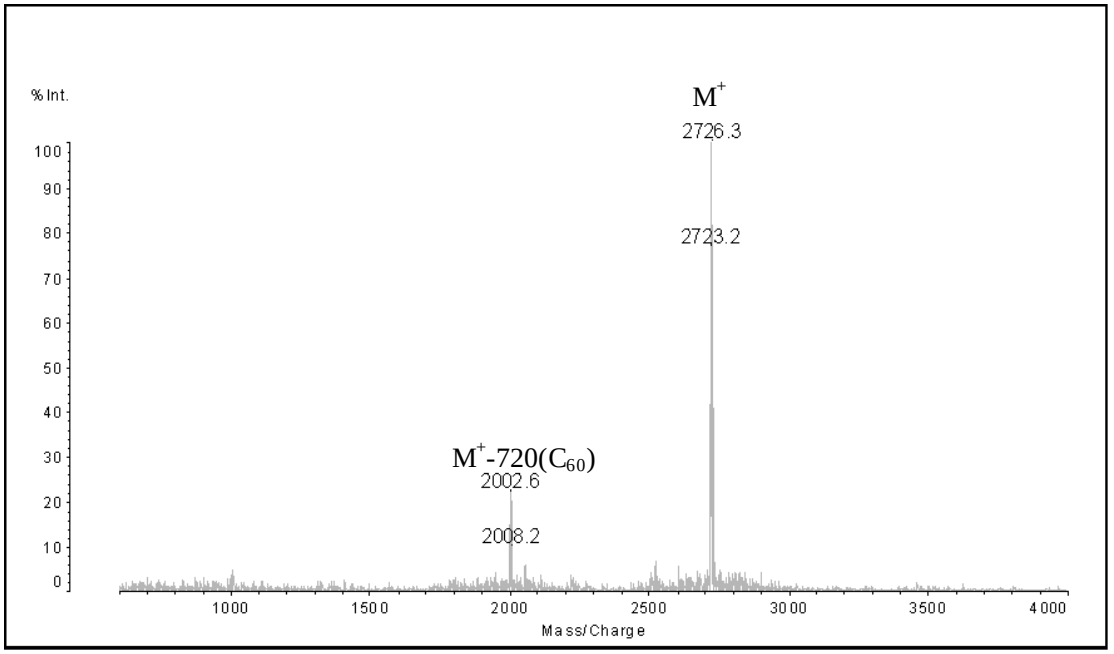


Fig. S11 MALDI-TOF Mass spectrum of **3**

C_{60}-$(ZnP)_2$-C_{60} **1b**

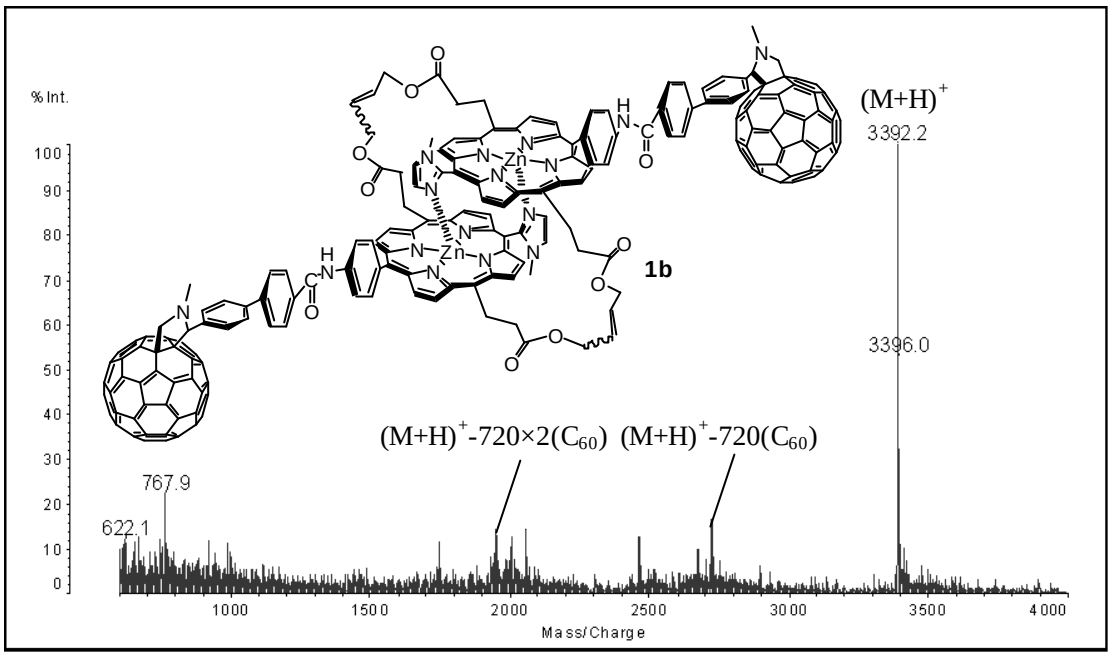


Fig. S12 MALDI-TOF Mass spectrum of **1b**

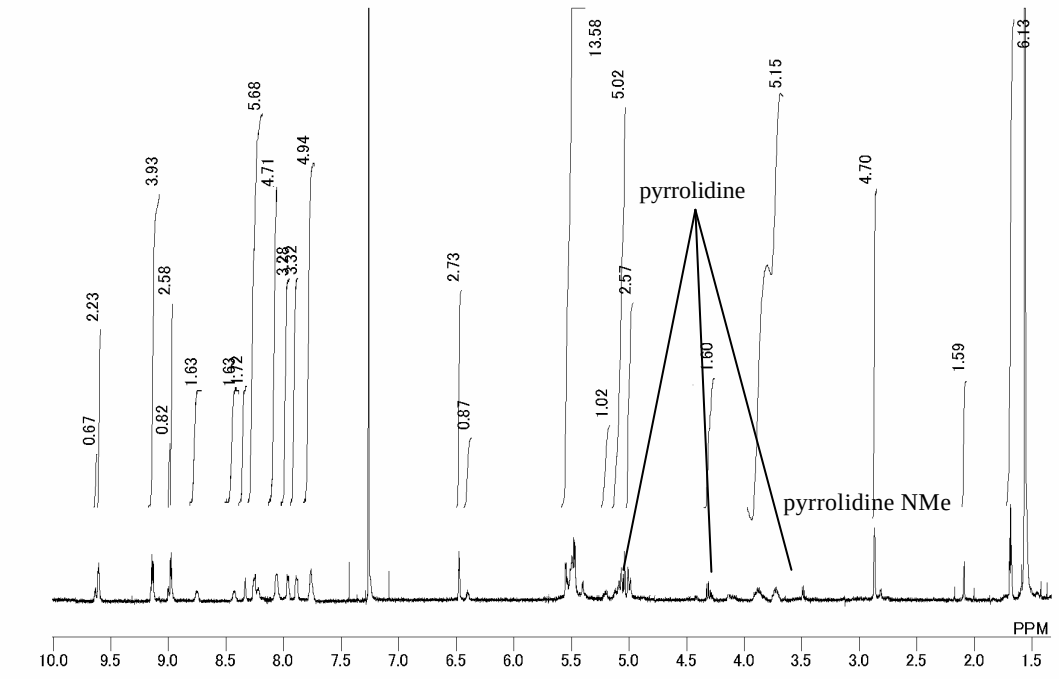


Fig. S13 ^{1}H NMR of **1b**

Fc-$(ZnP)_2$-Fc **2b**

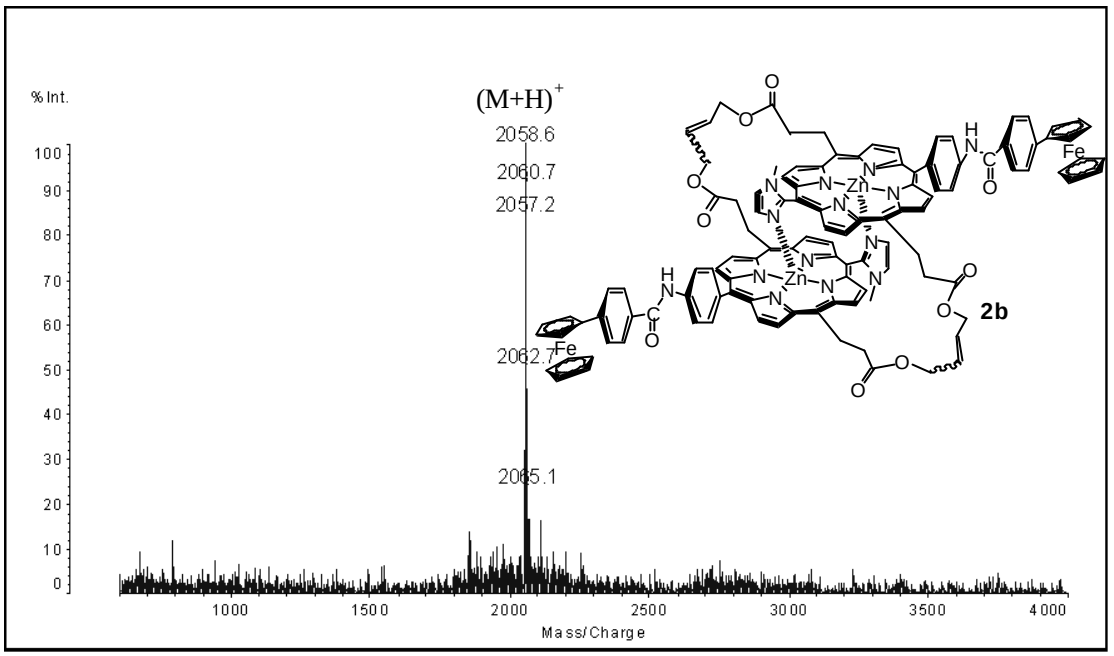


Fig. S14 MALDI-TOF Mass spectrum of **2b**

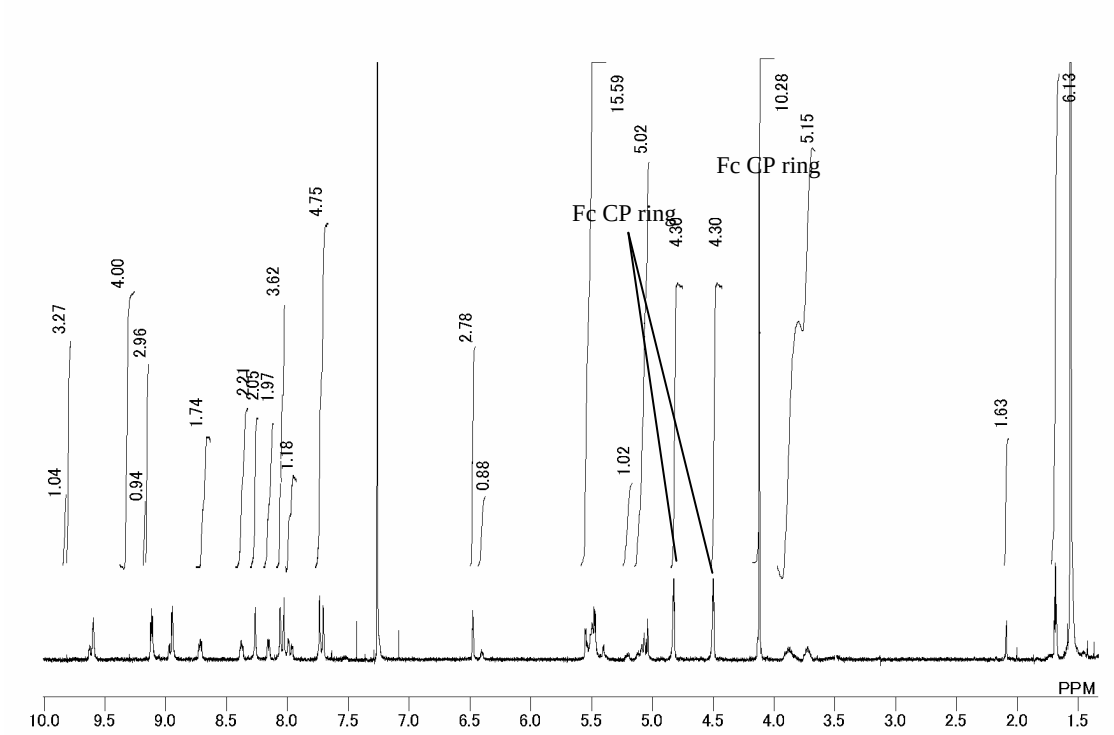


Fig. S15 ^{1}H NMR of **2b**

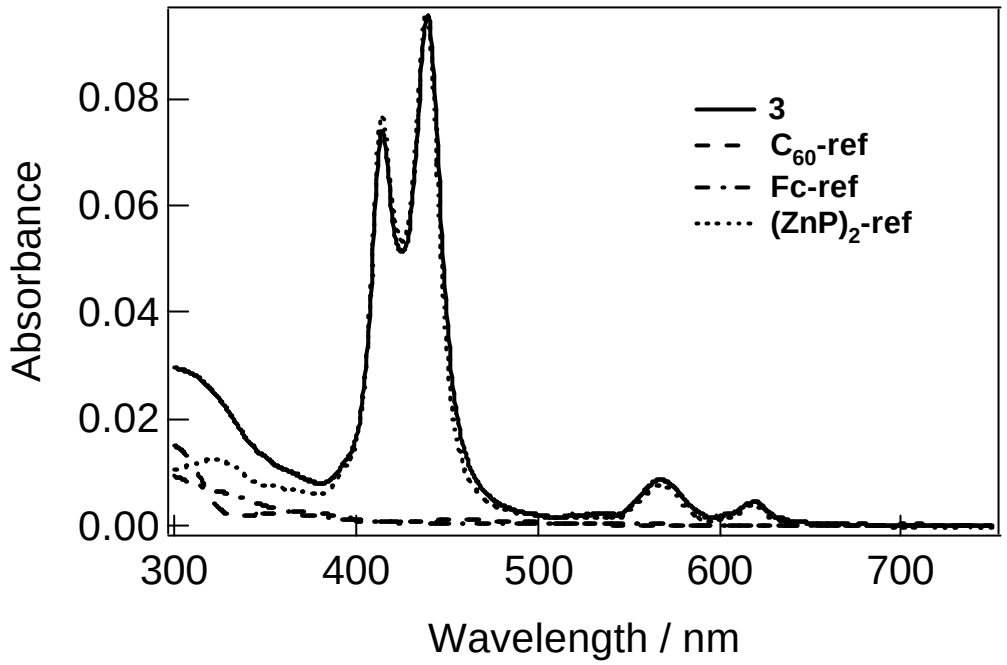


Fig. S16 UV-visible absorption spectra of **3**, **C_{60}-ref**, **Fc-ref**, **and $(ZnP)_2$-ref**. The spectrum of **3** was a superposition of the spectral sum of the components, **C_{60}-ref**, **Fc-ref**, **and $(ZnP)_2$-ref**.

Reference for supporting information

[1] Otera, J.; Danoh, N.; Nozaki, H. *J. Org. Chem.* **1991**, *56*, 5307-5311.

[2] Ohashi, A.; Satake, A.; Kobuke, Y. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 365–374.