Supporting Information for

Self-assembly of aliphatic dipeptides coupled with porphyrin and BODIPY chromophores

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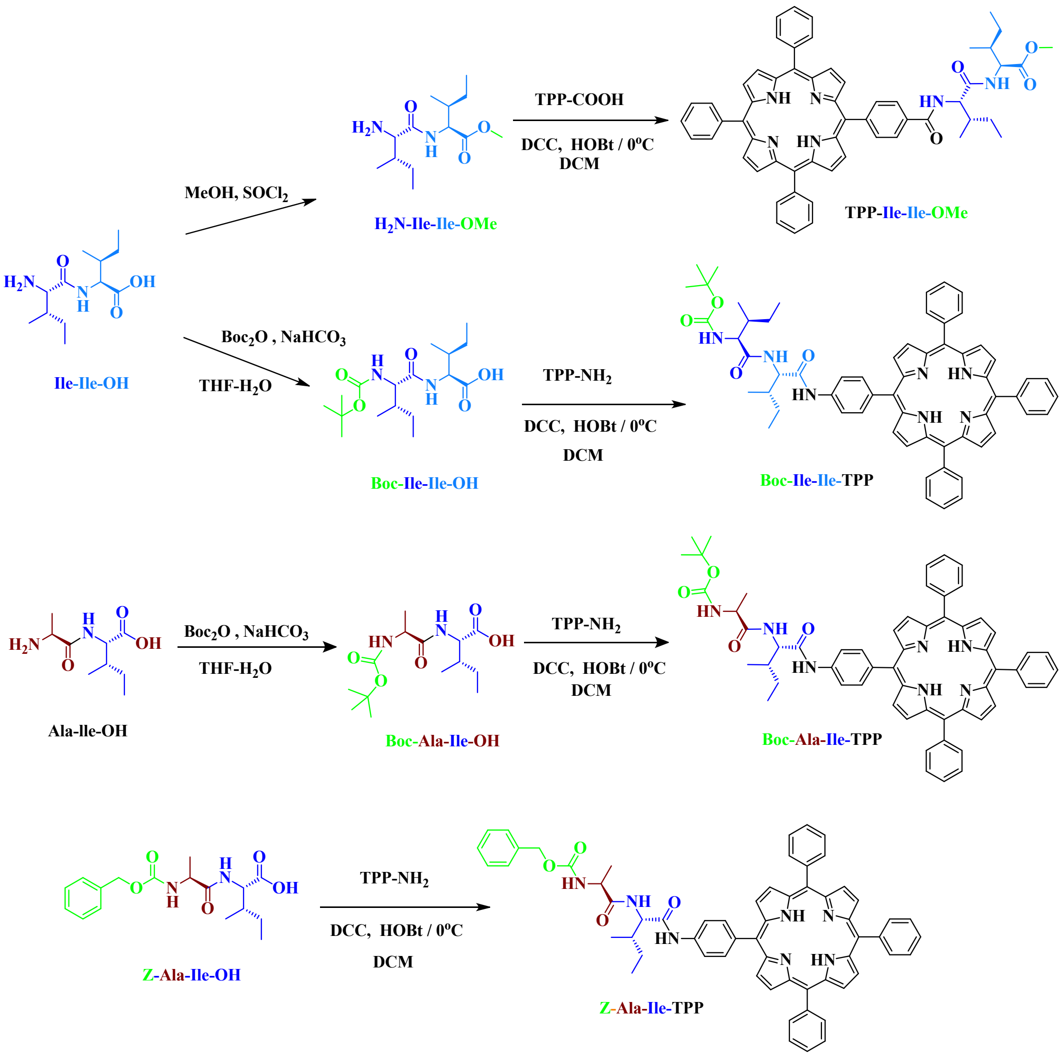
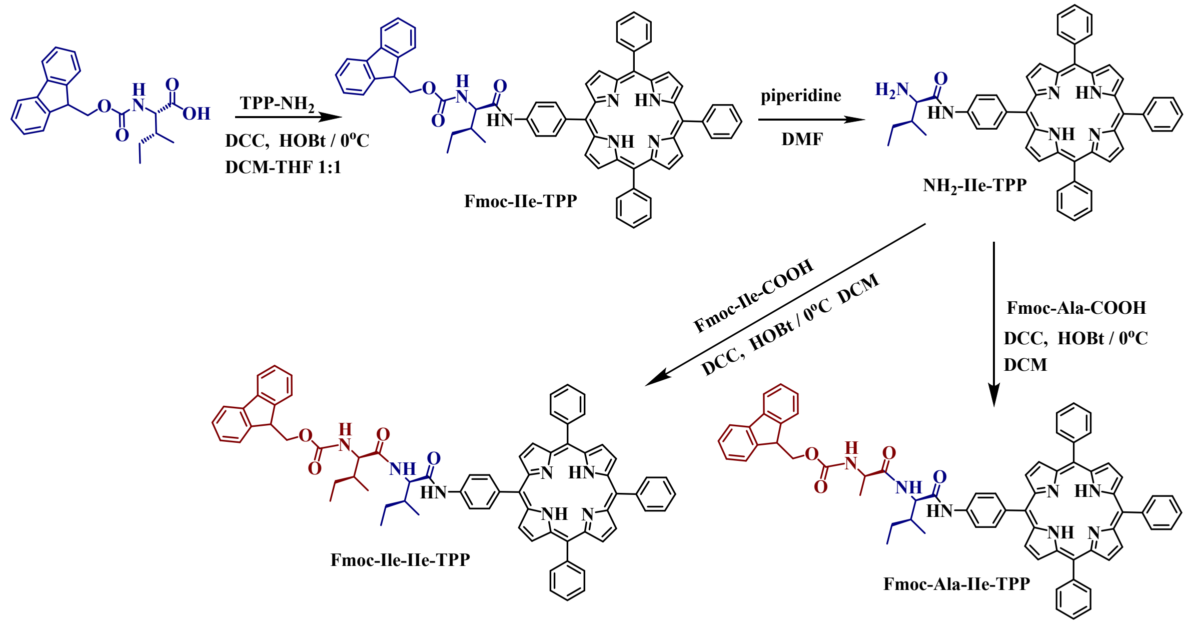
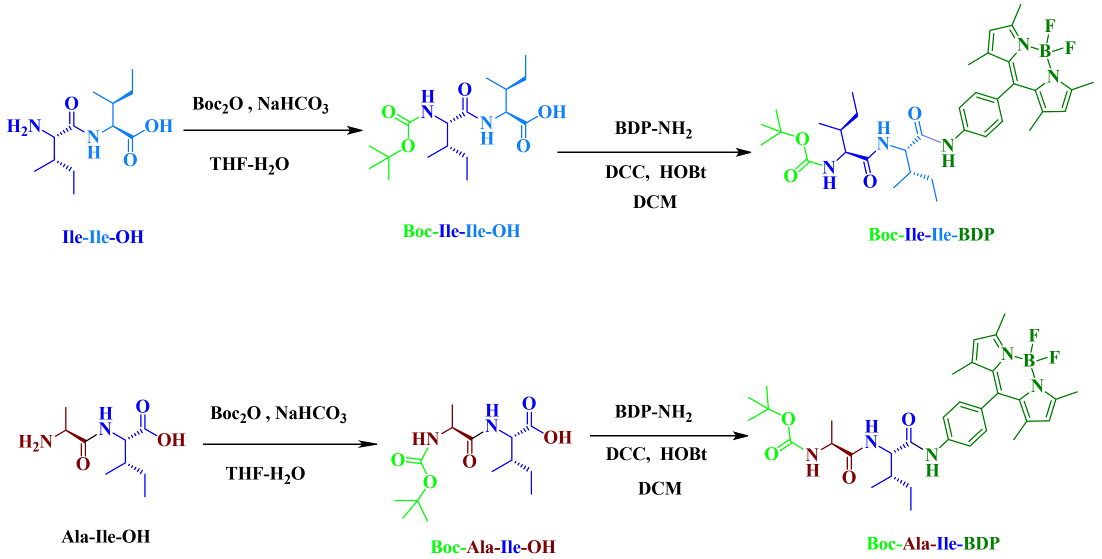


Scheme S1: Synthesis of **Boc-Ala-Ile-TPP**, **Z-Ala-Ile-TPP**, **Boc-Ile-Ile-TPP** and **TPP-Ile-Ile-OMe**.



Scheme S2: Synthesis of **Fmoc-Ala-Ile-TPP** and **Fmoc-Ile-Ile-TPP**.



Scheme S3: Synthesis of **Boc-Ala-Ile-BDP** and **Boc-Ile-Ile-BDP**.

Experimental

UV-Vis absorption and fluorescence spectroscopy

UV-Vis absorption spectra in solution were obtained (in quartz cuvettes of 1 cm path-length) using a Shimadzu UV-1700 spectrophotometer while the spectra in solid state were obtained (onto quartz slides 2x2 cm^2) using a UV/Vis/NIR Lambda 19, Perkin-Elmer spectrophotometer. The emission spectra were measured on a JASCO FP-6500 fluorescence spectrophotometer equipped with a red-sensitive WRE-343 photomultiplier tube (wavelength range: 200–850 nm).

Preparation of self-assembled microstructures

For the preparation of the samples, the corresponding compounds were dissolved in a chaotropic “good” solvent and subsequently a “bad” solvent was introduced. After 24 hours of incubation, 10 μL of each sample were placed on a 12 mm cover glass and left to dry overnight.

Scanning electron microscopy

For SEM and FESEM observations the samples were covered with 10 nm Au/Pd sputtering and were observed directly. SEM experiments were performed by using a JEOL JSM-6390LV microscope operating at 15 and 20 kV (for SEM observations) and a JEOL JSM 7000F (FESEM) operating at 15 kV.

NMR Spectra

The identity and purity of the synthesized compounds were proved by ^{1}H- and ^{13}C NMR spectroscopy, measured on Bruker DPX-300 MHz and Bruker AVANCE III-500 MHz spectrometers. The following chemical shifts are given in ppm.

Mass Spectra

Mass spectra were obtained on a Bruker UltrafleXtreme matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) spectrometer using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as matrix.

Boc-Ala-Ile-TPP

Boc-Ala-Ile-OH (31 mg, 0.102 mmol, 1.2 equiv) was dissolved in DCM (4 mL) and the solution was cooled in an ice bath to 0 °C. *N,N'*-dicyclohexylcarbodiimide (DCC, 21 mg, 0.102 mmol, 1.2 equiv) and 1-hydroxybenzotriazole hydrate (HOBt, 14 mg, 0.102 mmol, 1.2 equiv) were added and stirred for extra 30 min at 0 °C. Subsequently **TPP-NH$_2$** (54 mg, 0.085 mmol, 1 equiv) was added and the resulting mixture was stirred at 8 °C for 48 h. After the completion of the reaction the organic layer was washed with H_2O, dried over Na_2SO_4, filtered and the solvent removed to dryness. The title compound was isolated by column chromatography (silica gel, polarity gradually changed from CH_2Cl_2 to CH_2Cl_2/EtOH, 0.1% *v/v*) as a purple solid (58 mg, 75%).

^{1}H NMR

($CDCl_3$, 500 MHz): δ 8.84 (m, 9H), 8.19 (m, 8H), 8.07 (d, J = 8.0 Hz, 2H), 7.75 (m, 9H), 6.90 (d, J = 8.6 Hz, 1H), 5.04 (bs, 1H), 4.62 (bs, 1H), 4.28 (t, J = 6.1 Hz, 1H), 2.38 (bs, 1H), 1.71 (bs, 1H), 1.53 (s, 9H), 1.50 (d, J = 4.1 Hz, 3H), 1.28 (m, 1H), 1.14 (d, J = 6.8, 2H), 1.10 (d, J = 6.9, 1H), 1.05 (t, J = 7.4, 3H), -2.78 (s, 2H) ppm.

^{13}C NMR

($CDCl_3$, 75 MHz): δ 173.1, 169.9, 156.5, 142.3, 138.2, 137.8, 135.2, 134.7, 131.3, 127.8, 126.8, 120.2, 118.7, 118.4, 81.4, 59.0, 51.5, 36.4, 28.5, 24.8, 17.8, 16.3, 11.8 ppm.

HRMS (MALDI-TOF): m/z calculated for $C_{58}H_{56}N_7O_4$ $[M + H]^+$ 914.4316 ; found 914.4370.

UV-Vis (DCM) λ_{max}, nm (ε, $mM^{-1}cm^{-1}$) 418.5 (425.0), 514.5 (11.4), 551.0 (3.3), 592.0 (1.3), 646.0 (1.0).

Boc-Ile-Ile-TPP

Boc-Ile-Ile-OH (55 mg, 0.16 mmol, 1.2 equiv) was dissolved in DCM (4 mL) and the solution was cooled in an ice bath to 0 °C. DCC (33 mg, 0.16 mmol, 1.2 equiv) and HOBt (22 mg, 0.16 mmol, 1.2 equiv) were added and stirred for extra 30 min at 0 °C. Subsequently **TPP-NH$_2$** (84 mg, 0.133 mmol, 1 equiv) was added and the resulting mixture was stirred at 8 °C for 48 h. After the completion of the reaction the organic layer was washed with H_2O, dried over Na_2SO_4, filtered and the solvent removed to dryness. The title compound was isolated by column chromatography (silica gel, polarity gradually changed from CH_2Cl_2 to CH_2Cl_2/EtOH, 0.2 % *v/v*) as a purple solid (85 mg, 74%).

^{1}H NMR

(CDCl$_3$, 500 MHz): δ 8.84 (m, 9H), 8.21 (m, 6H), 8.17 (d, J = 8.5 Hz, 2H), 8.08 (d, J = 7.8 Hz, 2H), 7.76 (m, 9H), 6.70 (d, J = 7.9 Hz, 1H), 5.03 (bs, 1H), 4.64 (bs, 1H), 4.12 (m, 1H), 2.41 (bs, 1H), 2.09 (m, 1H), 1.69 (m, 1H), 1.62 (m, 1H), 1.53 (s, 8H), 1.48 (s, 1H), 1.26 (m, 2H), 1.14 (d, J = 6.8, 3H), 1.08 (m, 6H), 1.00 (t, J = 7.4, 3H) -2.78 (s, 2H) ppm.

^{13}C NMR

(CDCl$_3$, 75 MHz): δ 171.9, 169.8, 156.8, 142.3, 138.2, 137.8, 135.2, 134.7, 131.2, 127.8, 126.8, 120.2, 119.9, 118.4, 81.4, 60.8, 59.1, 36.6, 36.1, 28.5, 25.1, 24.8, 16.5, 16.2, 11.8 ppm.

HRMS (MALDI-TOF): m/z calculated for $C_{61}H_{62}N_7O_4$ $[M + H]^+$ 956.4863 ; found 956.4897.

UV-Vis: (DCM) λ_{max}, nm (ε, mM^{-1}cm^{-1}) 418.5 (445.0), 514.5 (14.4), 551.0 (8.0), 593.0 (4.3), 646.0 (3.3).

Fmoc-Ile-Ile-TPP

Fmoc-Ile-OH (74 mg, 0.21 mmol, 1.2 equiv) was dissolved in CH_2Cl_2 (4 mL) and the solution was cooled in an ice bath to 0 °C. DCC (44 mg, 0.21 mmol, 1.2 equiv) and HOBt (28 mg, 0.21 mmol, 1.2 equiv) were added and stirred for extra 30 min at 0 °C. Subsequently **TPP-NH$_2$** (110 mg, 0.175 mmol, 1 equiv) was added and the resulting mixture was stirred at 8 °C for 48 h. After the completion of the reaction the organic layer was washed with H_2O, dried over Na_2SO_4, filtered and the solvent removed to dryness. **Fmoc-Ile-TPP** was isolated by column chromatography (silica gel, CH_2Cl_2/EtOH, 0,5% *v/v*) as a purple solid (150 mg, 89%). Deprotection of the Fmoc group with 3 mL piperidine in 10 mL DMF was conducted at room temperature for 2h. DMF was evaporated under vacuum and two extractions with DCM/H_2O followed. **NH$_2$-Ile-TPP** was isolated by column chromatography (silica gel, CH_2Cl_2/EtOH, 1 % *v/v*). For the final amide coupling Fmoc-Ile-OH (23 mg, 0.065 mmol, 1.2 equiv) was dissolved in DCM (4 mL) and the solution was cooled in an ice bath to 0 °C. DCC (14 mg, 0.065 mmol, 1.2 equiv) and HOBt (9 mg, 0.065 mmol, 1.2 equiv) were added and stirred for extra 30 min at 0 °C. Subsequently **NH$_2$-Ile-TPP** (40 mg, 0.054 mmol, 1 equiv) was added and the resulting mixture was stirred at 8 °C for 48 h. The title compound was isolated by column chromatography (silica gel, CH_2Cl_2/EtOH, 0.2 % *v/v*) as a purple solid (45 mg, 77%).

^{1}H NMR

($CDCl_3$, 500 MHz): *δ* 8.81 (m, 8H), 8.65 (s, 1H), 8.18 (m, 8H), 8.01 (d, *J* = 7.4 Hz, 2H), 7.74 (m, 11H), 7.60 (m, 2H), 7.36 (m, 2H), 7.30 (bs, 2H) 6.79 (d, *J* = 7.0 Hz, 1H), 5.46 (bs, 1H), 4.62 (m, 1H), 4.54 (d, J = 6.7 Hz, 2H), 4.25 (m, 2H), 2.28 (m, 1H), 2.04 (m, 1H), 1.69 (m, 2H), 1.26 (m, 2H), 1.12 (d, *J* = 6.7, 3H), 1.00 (m, 9H), -2.80 (s, 2H) ppm.

^{13}C NMR

($CDCl_3$, 75 MHz): *δ* 172.0, 169.8, 157.2, 143.9, 142.4, 141.6, 138.5, 137.6, 135.3, 134.8, 131.6, 128.7, 128.1, 127.9, 127.4, 126.9, 125.1, 120.3, 119.7, 118.5, 67.5, 60.7, 59.2, 47.4, 37.4, 36.6, 25.2, 25.1, 16.2, 16.0, 11.7 ppm.

HRMS (MALDI-TOF): m/z calculated for $C_{71}H_{64}N_7O_4$ $[M + H]^+$ 1078.5020 ; found 1078.5062.

UV-Vis: (DCM) λ_{max}, nm (ε, $mM^{-1}cm^{-1}$) 418.5 (430.0), 514.5 (12.1), 551.0 (6.8), 591.0 (3.8), 646.0 (2.5).

Fmoc-Ala-Ile-TPP

Fmoc-Ala-OH (23 mg, 0.07 mmol, 1.2 equiv) was dissolved in DCM (4 mL) and the solution was cooled in an ice bath to 0 °C. DCC (14.5 mg, 0.07 mmol, 1.2 equiv) and HOBt (9.5 mg, 0.07 mmol, 1.2 equiv) were added and stirred for extra 30 min at 0 °C. Subsequently **NH_2-Ile-TPP** (43 mg, 0.058 mmol, 1 equiv) was added and the resulting mixture was stirred at 8 °C for 48 h. After the completion of the reaction the organic layer was washed with H_2O, dried over Na_2SO_4, filtered and the solvent removed to dryness. The title compound was isolated by column chromatography (silica gel, CH_2Cl_2/EtOH, 0.3 % *v/v*) as a purple solid (50 mg, 83%).

^{1}H NMR

($CDCl_3$, 500 MHz): *δ* 8.81 (m, 8H), 8.69 (s, 1H), 8.18 (m, 8H), 8.03 (d, *J* = 7.0 Hz, 2H), 7.74 (m, 11H), 7.60 (t, *J* = 7.1 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.28 (bs, 2H) 6.93 (d, *J* = 7.3 Hz, 1H), 5.50 (bs, 1H), 4.63 (m, 1H), 4.54 (m, 2H), 4.41 (m, 1H), 4.26 (t, *J* = 6.7 Hz, 1H), 2.28 (bs, 1H), 1.68 (m, 1H), 1.53 (d, *J* = 6.4 Hz, 3H), 1.26 (m, 1H), 1.13 (d, *J* = 6.7, 3H), 1.00 (t, *J* = 7.3, 3H), -2.79 (s, 2H) ppm.

^{13}C NMR

($CDCl_3$, 75 MHz): *δ* 172.9, 169.8, 156.8, 144.0, 143.7, 142.3, 141.5, 138.4, 137.6, 135.2, 134.7, 131.2, 128.0, 127.8, 127.3, 126.8, 125.0, 120.2, 119.6, 118.4, 67.5, 59.1, 51.6, 47.2, 36.7, 25.0, 18.4, 16.0, 11.6 ppm.

HRMS (MALDI-TOF): m/z calculated for $C_{68}H_{58}N_7O_4$ $[M + H]^+$ 1036.4550; found 1036.4565.

UV-Vis: (DCM) λ_{max}, nm (ε, $mM^{-1}cm^{-1}$) 418.5 (433.0), 514.5 (13.4), 551.0 (7.2), 591.0 (4.0), 647.0 (2.9).

Z-Ala-Ile-TPP

Z-Ala-Ile-OH (20 mg, 0.057 mmol, 1.2 equiv) was dissolved in DCM (2.5 mL) and the solution was cooled in an ice bath to 0 °C. *N,N'*-dicyclohexylcarbodiimide (DCC, 12 mg, 0.057 mmol, 1.2 equiv) and 1-hydroxybenzotriazole hydrate (HOBt, 8 mg, 0.057 mmol, 1.2 equiv) were added and stirred for extra 30 min at 0 °C. Subsequently **TPP-NH$_2$** (30 mg, 0.051 mmol, 1 equiv) was added and the resulting mixture was stirred at r.t for 24 h. After the completion of the reaction the organic layer was washed with H_2O, dried over Na_2SO_4, filtered and the solvent removed to dryness. The title compound was isolated by column chromatography (silica gel, polarity gradually changed from CH_2Cl_2 to CH_2Cl_2/EtOH, 2% *v/v*) as a purple solid (38 mg, 79%).

^{1}H NMR

($CDCl_3$, 500 MHz): δ 8.84 (m, 8H), 8.61 (bs, 1H), 8.19 (m, 8H), 8.03 (d, J = 7.9 Hz, 2H), 7.75 (m, 9H), 7.35 (m, 5H), 6.76 (d, J = 8.6 Hz, 1H), 5.30 (m, 2H), 5.16 (d, J = 12.1 Hz, 2H), 4.59 (t, J = 6.7 Hz, 1H), 4.35 (t, J = 6.4 Hz, 1H), 2.30 (m, 1H), 1.65 (m, 1H), 1.52 (d, J = 7.2 Hz, 3H), 1.25 (bs, 1H), 1.09 (d, J = 6.8, 3H), 1.00 (t, J = 7.3, 3H), -2.79 (s, 2H) ppm.

^{13}C NMR

($CDCl_3$, 75 MHz): δ 172.7, 169.7, 156.8, 142.3, 138.4, 137.6, 135.9, 135.2, 134.7, 131.3, 128.8, 128.7, 128.4, 127.8, 127.3, 126.8, 120.2, 118.4, 67.8, 59.0, 51.8, 36.5, 24.8, 18.2, 16.1, 11.7 ppm.

HRMS (MALDI-TOF): m/z calculated for $C_{61}H_{54}N_7O_4$ $[M + H]^+$ 948.4237; found 948.4260.

UV-Vis: (DCM) λ_{max}, nm (ε, $mM^{-1}cm^{-1}$) 418.5 (402.0), 514.5 (11.3), 551.0 (6.5), 591.0 (3.8), 647.0 (2.6).

TPP-Ile-Ile-OMe

TPP-COOH (40 mg, 0.061 mmol, 1 equiv) was dissolved in DCM (4 mL) and the solution was cooled in an ice bath to 0 °C. *N,N'*-dicyclohexylcarbodiimide (DCC, 14 mg, 0.067 mmol, 1.2 equiv) and 1-hydroxybenzotriazole hydrate (HOBt, 9 mg, 0.067 mmol, 1.2 equiv) were added and stirred for extra 60 min at 0 °C. Subsequently $ClNH_3^+$-Ile-Ile-OMe (23 mg, 0.091 mmol, 1.5

equiv) and 20 μL Et_3N were added and the resulting mixture was stirred at r.t for 24 h. After the completion of the reaction the organic layer was washed with H_2O, dried over Na_2SO_4, filtered and the solvent removed to dryness. The title compound was isolated by column chromatography (silica gel, polarity gradually changed from CH_2Cl_2 to CH_2Cl_2/EtOH, 0.8% *v/v*) as an purple solid (41 mg, 75%).

^{1}H NMR

($CDCl_3$, 500 MHz): δ 8.86 (m, 6H), 8.81 (d, J = 4.7 Hz, 2H), 8.32 (d, J = 8.1 Hz, 2H), 8.22 (m, 8H), 7.76 (m, 9H), 7.20 (d, J = 8.6 Hz, 1H), 6.55 (d, J = 8.4 Hz, 1H), 4.78 (dd, J_1 = 8.4 Hz, J_2 = 7.1 Hz, 1H), 4.71 (dd, J_1 = 8.4 Hz, J_2 = 4.8 Hz, 1H), 3.81 (s, 3H), 2.16 (m, 1H), 2.03 (m, 1H), 1.81 (m, 1H), 1.53 (m, 1H), 1.45 (m, 1H), 1.30 (m, 1H), 1.16 (d, J = 6.8 Hz, 3H), 1.08 (t, J = 7.4 Hz, 3H), 1.00 (m, 6H), -2.77 (s, 2H) ppm.

^{13}C NMR

($CDCl_3$, 75 MHz): δ 172.2, 171.3, 167.6, 146.0, 142.2, 134.7, 133.5, 131.4, 127.9, 126.8, 125.6, 120.6, 120.5, 118.6, 58.4, 56.8, 52.4, 38.2, 38.0, 25.5, 25.4, 15.7, 15.6, 11.8, 11.6 ppm.

HRMS (MALDI-TOF): m/z calculated for $C_{61}H_{54}N_7O_4$ $[M + H]^+$ 899.4285; found 899.4257.

UV-Vis: (DCM) λ_{max}, nm (ε, $mM^{-1}cm^{-1}$) 418.5 (408.0), 514.5 (11.6), 551.0 (6.8), 591.0 (3.8), 647.0 (2.7).

Boc-Ala-Ile-BDP

Boc-Ala-Ile-OH (22 mg, 0.073 mmol, 1.2 equiv) was dissolved in DCM (4 mL) and the solution was cooled in an ice bath to 0 °C. *N,N'*-dicyclohexylcarbodiimide (DCC, 15 mg, 0.073 mmol, 1.2 equiv) and 1-hydroxybenzotriazole hydrate (HOBt, 10 mg, 0.073 mmol, 1.2 equiv) were added and stirred for extra 30 min at 0 °C. Subsequently **BDP-NH$_2$** (21 mg, 0.061 mmol, 1 equiv) was added and the resulting mixture was stirred at r.t for 24 h. After the completion of the reaction the organic layer was washed with H_2O, dried over Na_2SO_4, filtered and the solvent removed to dryness. The title compound was isolated by column chromatography (silica gel, CH_2Cl_2/EtOH, 0.8% *v/v*) as an orange solid (30 mg, 79%).

1H NMR

($CDCl_3$, 500 MHz): δ 8.72 (s, 1H), 7.82 (d, J = 7.9 Hz 2H), 7.20 (d, J = 8.0 Hz, 2H), 6.75 (d, J = 8.4 Hz, 1H), 5.97 (s, 2H), 4.98 (bs, 1H), 4.49 (bs, 1H), 4.17 (bs, 1H), 2.54 (s, 6H), 2.30 (bs, 1H), 1.54 (m, 1H), 1.44 (s, 3H), 1.43 (s, 9H), 1.41 (s, 6H), 1.15 (m, 1H), 1.01 (d, J = 6.8 Hz 3H), 0.96 (t, J = 7.3, 3H) ppm.

^{13}C NMR

(CDCl$_3$, 75 MHz): δ 173.0, 169.6, 156.4, 155.5, 143.3, 141.6, 138.9, 131.7, 130.6, 128.6, 121.7, 121.3, 120.5, 81.5, 58.6, 51.7, 36.0, 28.3, 24.5, 17.7, 16.2, 14.8, 14.7, 11.8 ppm.

HRMS (MALDI-TOF): m/z calculated for $C_{33}H_{44}BF_2N_5O_4$ [M]$^+$: 623.3454; found: 623.3462.

UV-Vis (DCM): λ (ε, mM^{-1}cm^{-1}) = 501 (47.2) nm.

Boc-Ile-Ile-BDP

Boc-Ile-Ile-OH (25 mg, 0.072 mmol, 1.2 equiv) was dissolved in DCM (4 mL) and the solution was cooled in an ice bath to 0 °C. DCC (14.8 mg, 0.072 mmol, 1.2 equiv) and HOBt (9.7 mg, 0.072 mmol, 1.2 equiv) were added and stirred for extra 30 min at 0 °C. Subsequently **BDP-NH$_2$** (20 mg, 0.06 mmol, 1 equiv) was added and the resulting mixture was stirred at 8 °C for 48 h. After the completion of the reaction the organic layer was washed with H_2O, dried over Na_2SO_4, filtered and the solvent removed to dryness. The title compound was isolated by column chromatography (silica gel, polarity gradually changed from CH_2Cl_2 to CH_2Cl_2/EtOH, 1 % *v/v*) as a purple solid (30 mg, 75%).

^{1}H NMR

(CDCl$_3$, 500 MHz): δ 8.75 (s, 1H), 7.83 (d, J = 7.4 Hz 2H), 7.20 (d, J = 8.5 Hz, 2H), 6.57 (d, J = 7.4 Hz, 1H), 5.97 (s, 2H), 4.96 (bs, 1H), 4.50 (bs, 1H), 4.03 (bs, 1H), 2.54 (s, 6H), 2.34 (bs, 1H), 2.00 (bs, 1H), 1.53 (m, 2H), 1.42 (m, 15H), 1.17 (m, 2H), 1.01 (t, J = 7.6 Hz, 6H), 0.95 (m, 6H), ppm.

^{13}C NMR

(CDCl$_3$, 75 MHz): δ 171.7, 169.6, 156.8, 155.5, 143.3, 141.6, 138.9, 131.7, 130.5, 128.6, 121.3, 120.5, 81.4, 60.8, 58.8, 36.5, 35.6, 28.3, 25.0, 24.5, 16.5, 16.1, 14.8, 14.7, 11.8 ppm.

HRMS (MALDI-TOF): m/z calculated for $C_{36}H_{50}BF_2N_5O_4$ [M]$^+$: 665.3924; found: 665.3945.

UV-Vis (DCM): λ (ε, mM^{-1}cm^{-1}) = 501 (50.2) nm.

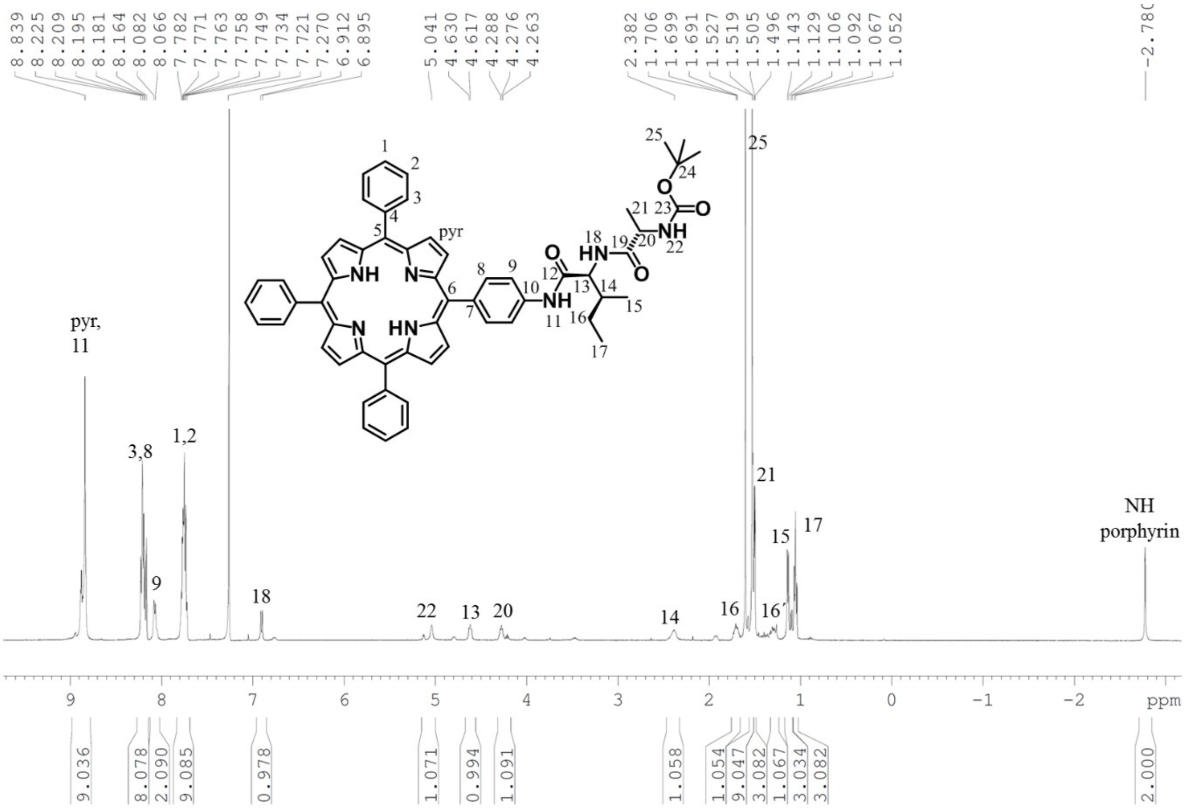


Fig. S1 ^{1}H NMR spectrum of **Boc-Ala-Ile-TPP** (500 MHz, $CDCl_3$).

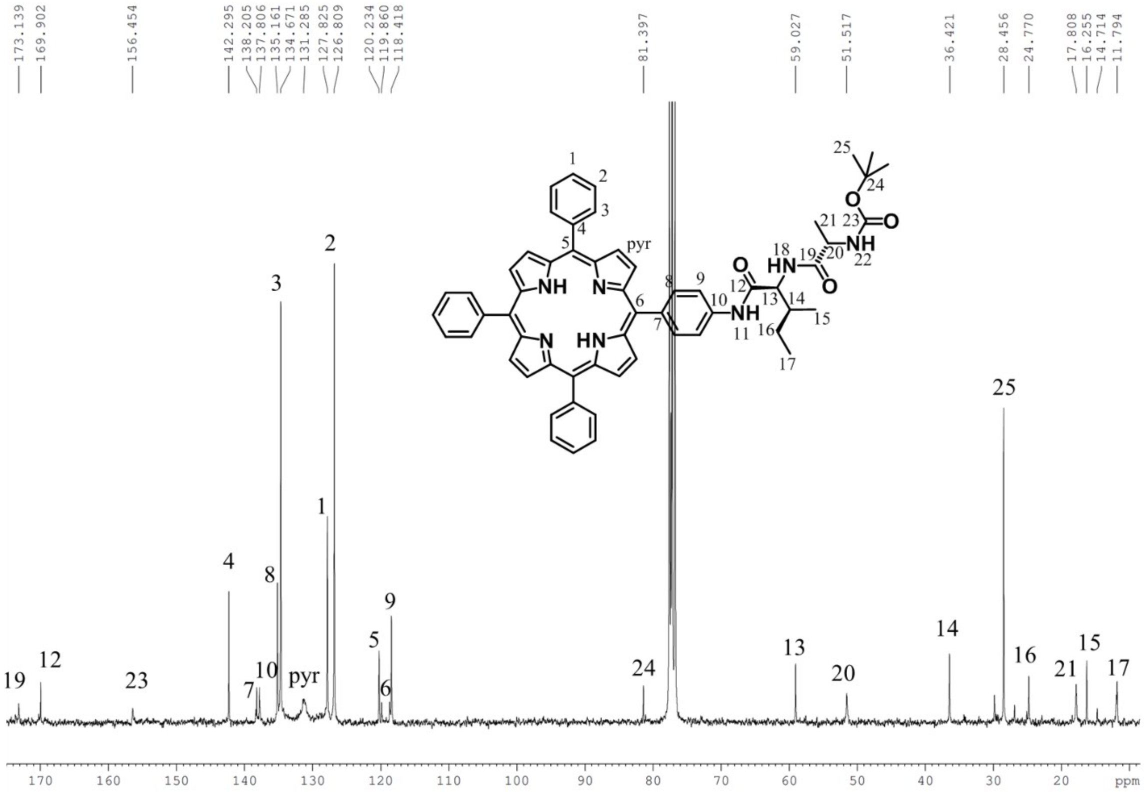


Fig. S2 ^{13}C NMR spectrum of **Boc-Ala-Ile-TPP** (75 MHz, $CDCl_3$).

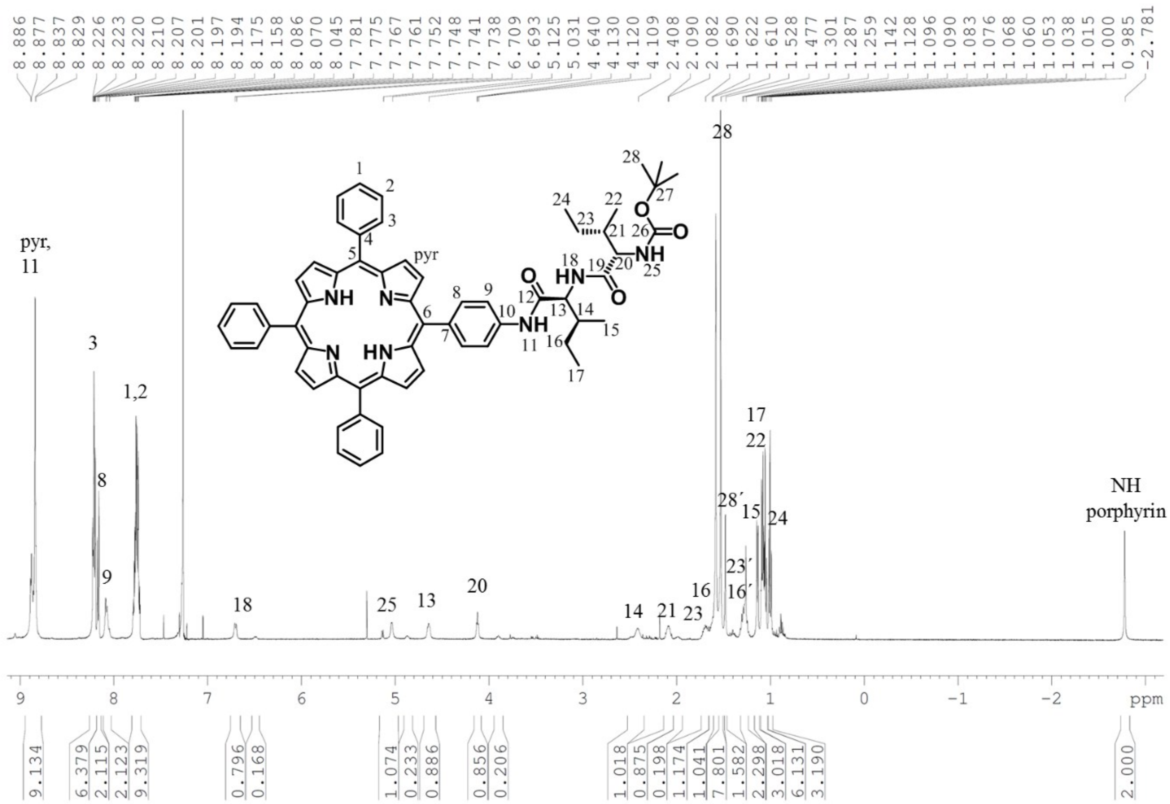


Fig. S3 ^{1}H NMR spectrum of **Boc-Ile-Ile-TPP** (500 MHz, $CDCl_3$).

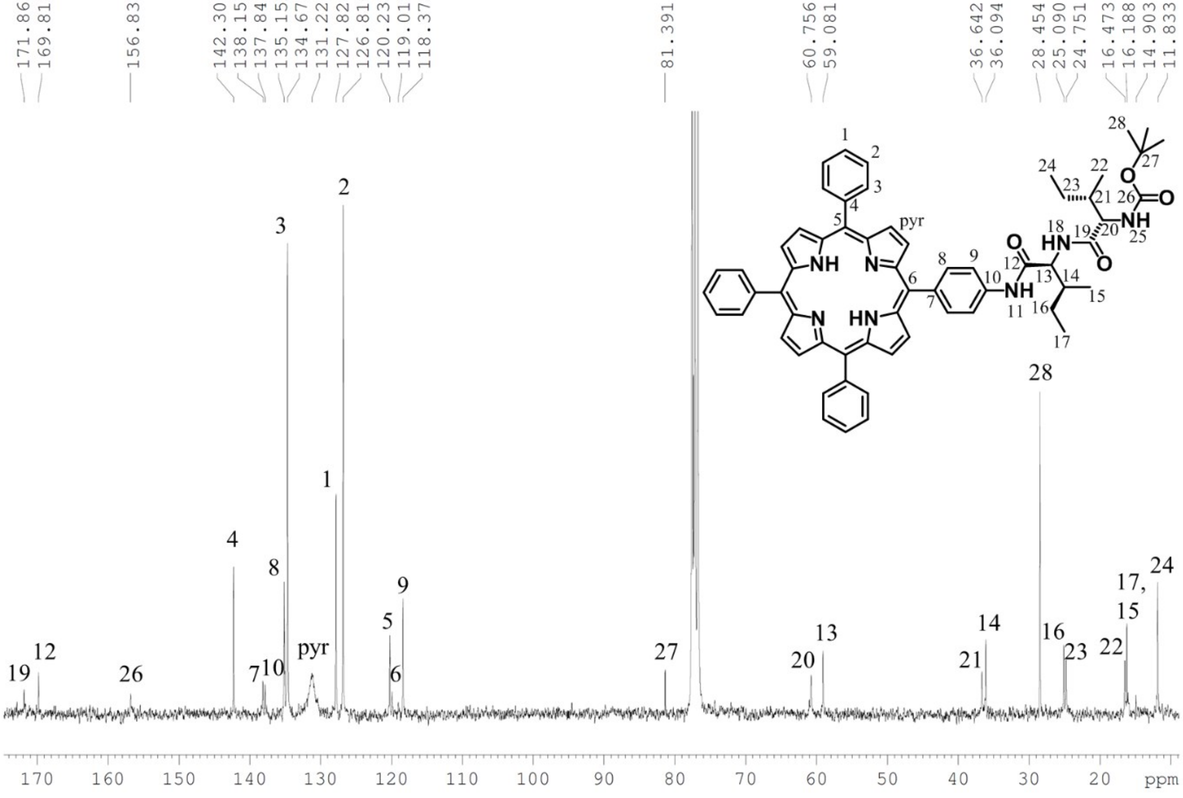


Fig. S4 ^{13}C NMR spectrum of **Boc-Ile-Ile-TPP** (75 MHz, $CDCl_3$).

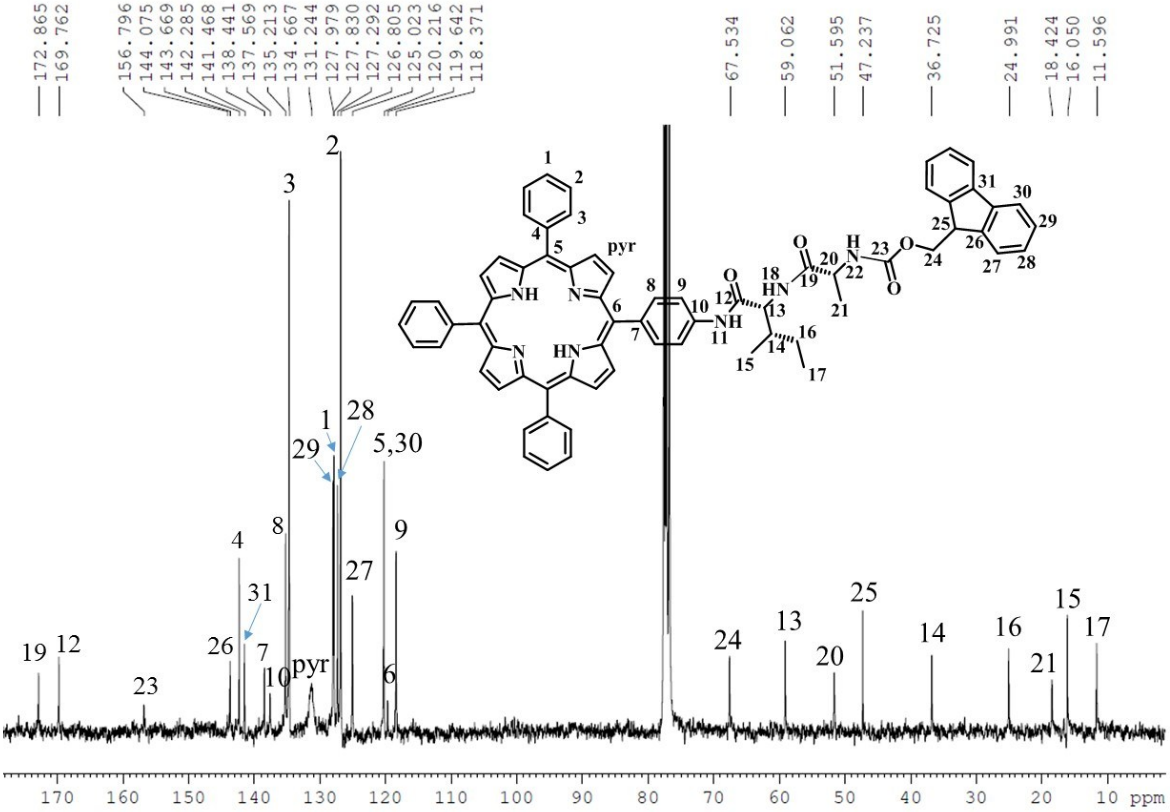


Fig. S5 ^{13}C NMR spectrum of **Fmoc-Ala-Ile-TPP** (75 MHz, $CDCl_3$).

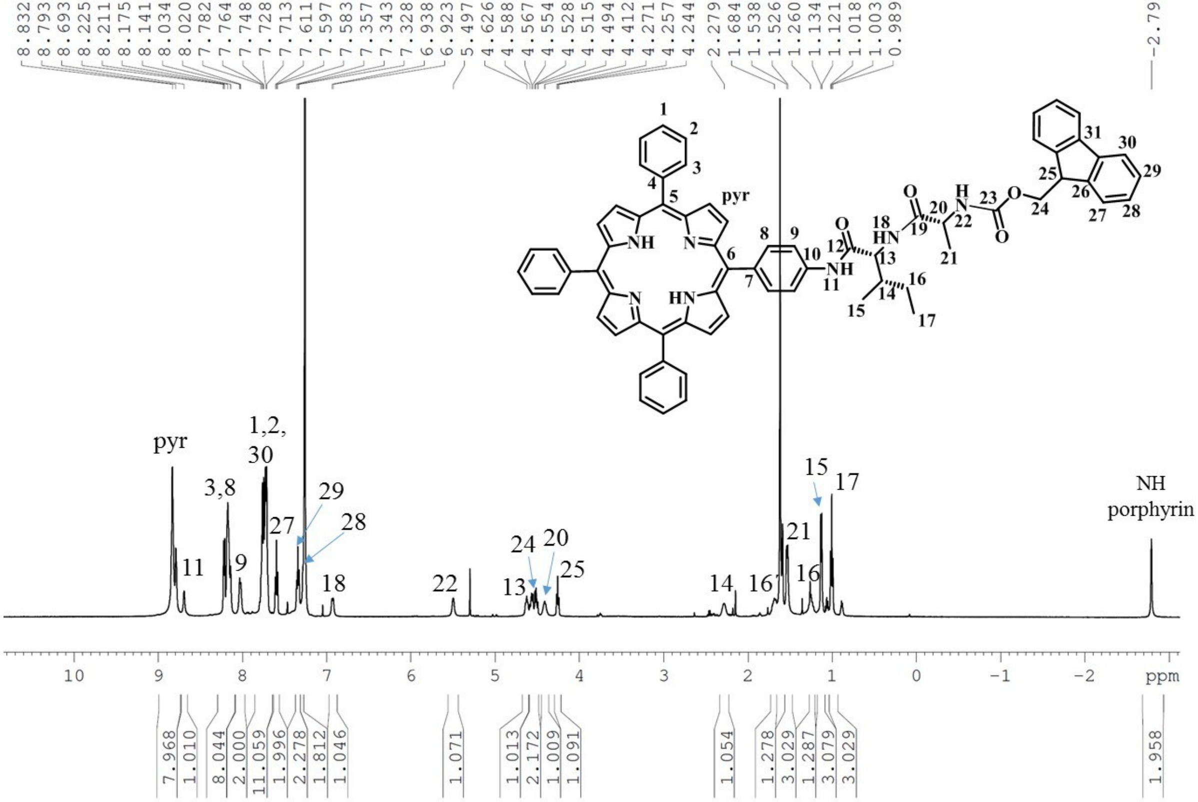


Fig. S6 ^{1}H NMR spectrum of **Fmoc-Ala-Ile-TPP** (500 MHz, $CDCl_3$).

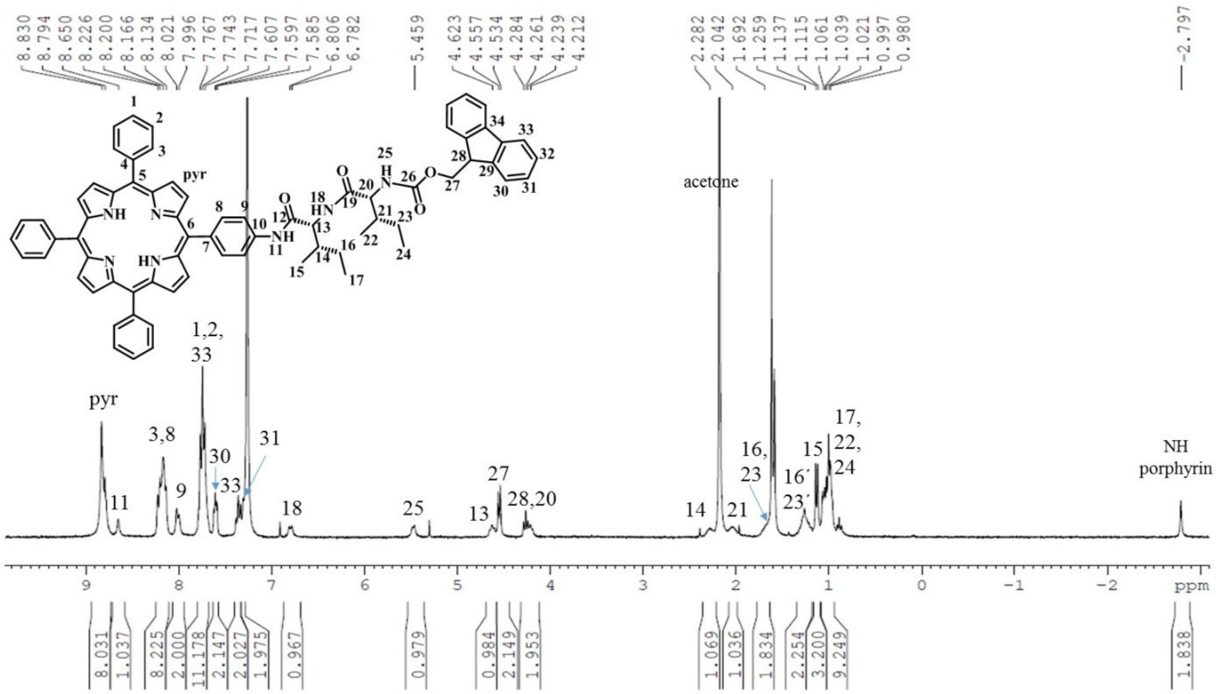


Fig. S7 ^{1}H NMR spectrum of **Fmoc-Ile-Ile-TPP** (500 MHz, $CDCl_3$).

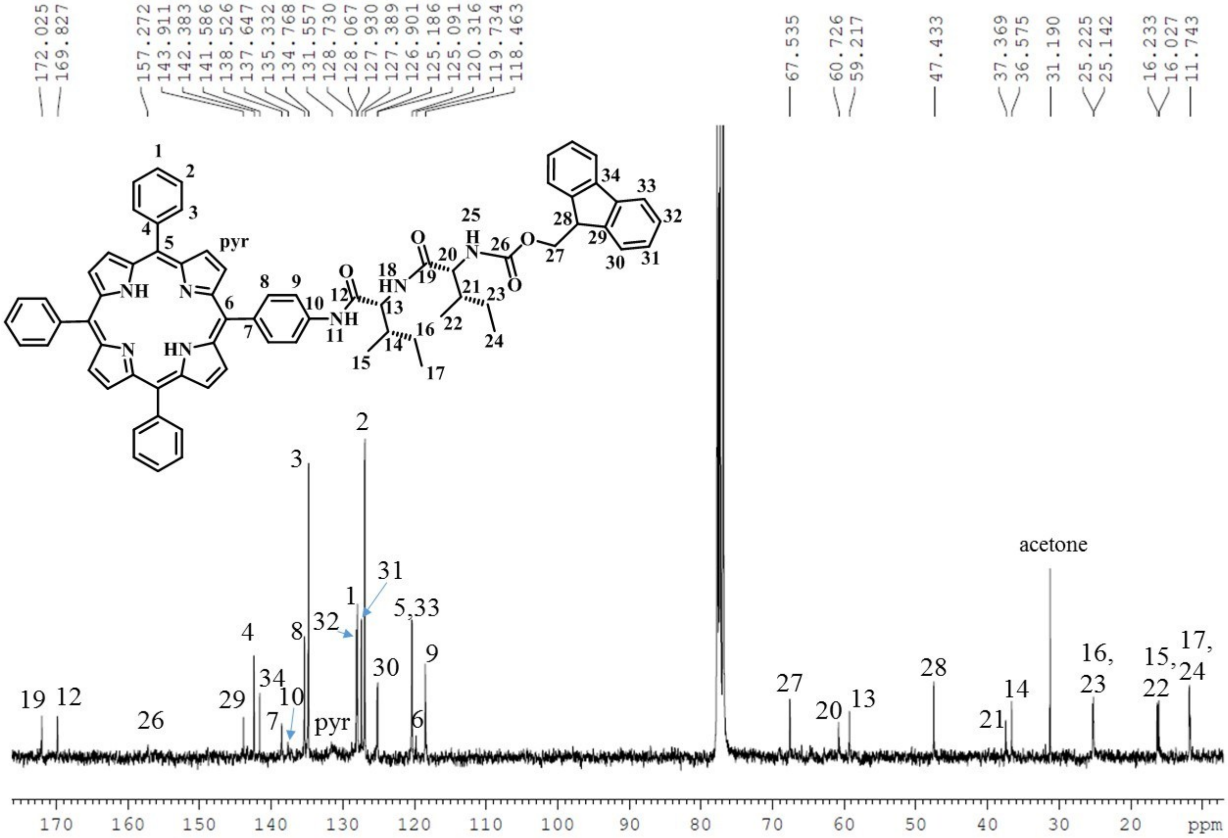


Fig. S8 ^{13}C NMR spectrum of **Fmoc-Ile-Ile-TPP** (75 MHz, $CDCl_3$).

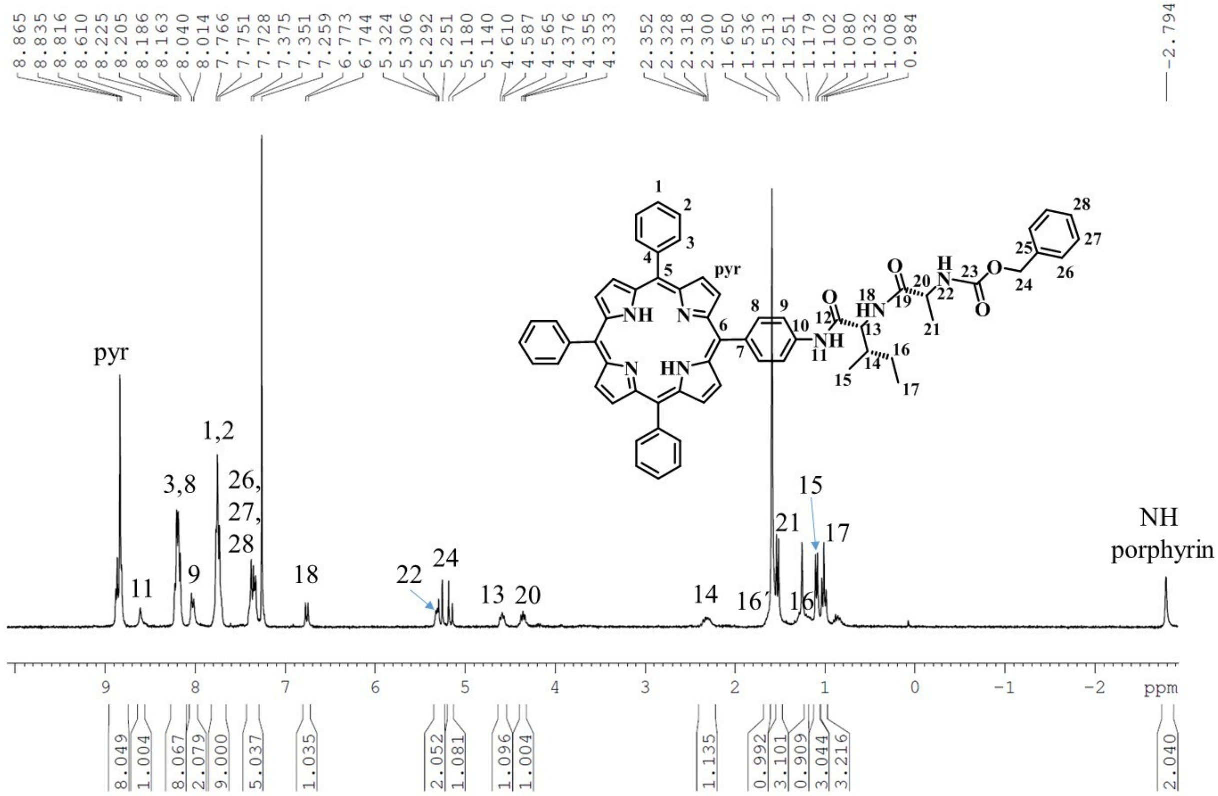


Fig. S9 ^{1}H NMR spectrum of **Z-Ala-Ile-TPP** (500 MHz, CDCl$_3$).

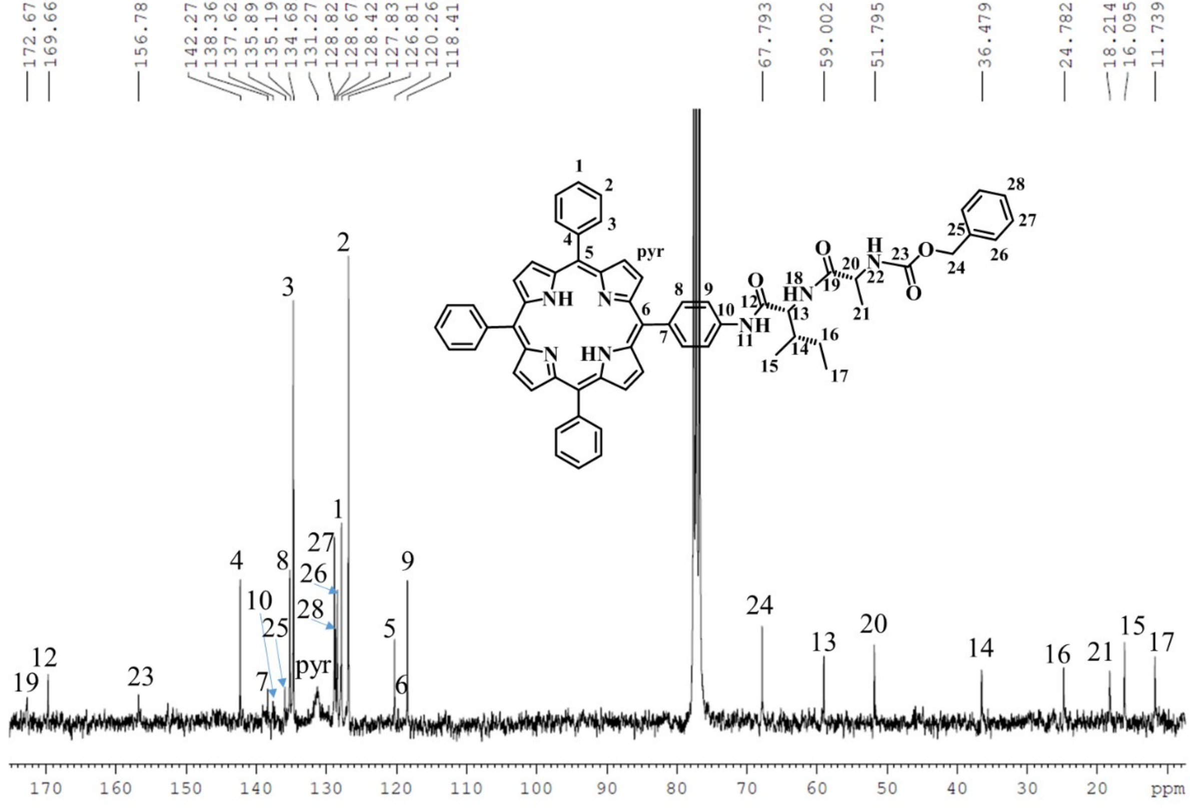


Fig. S10 ^{13}C NMR spectrum of **Z-Ala-Ile-TPP** (75 MHz, CDCl$_3$).

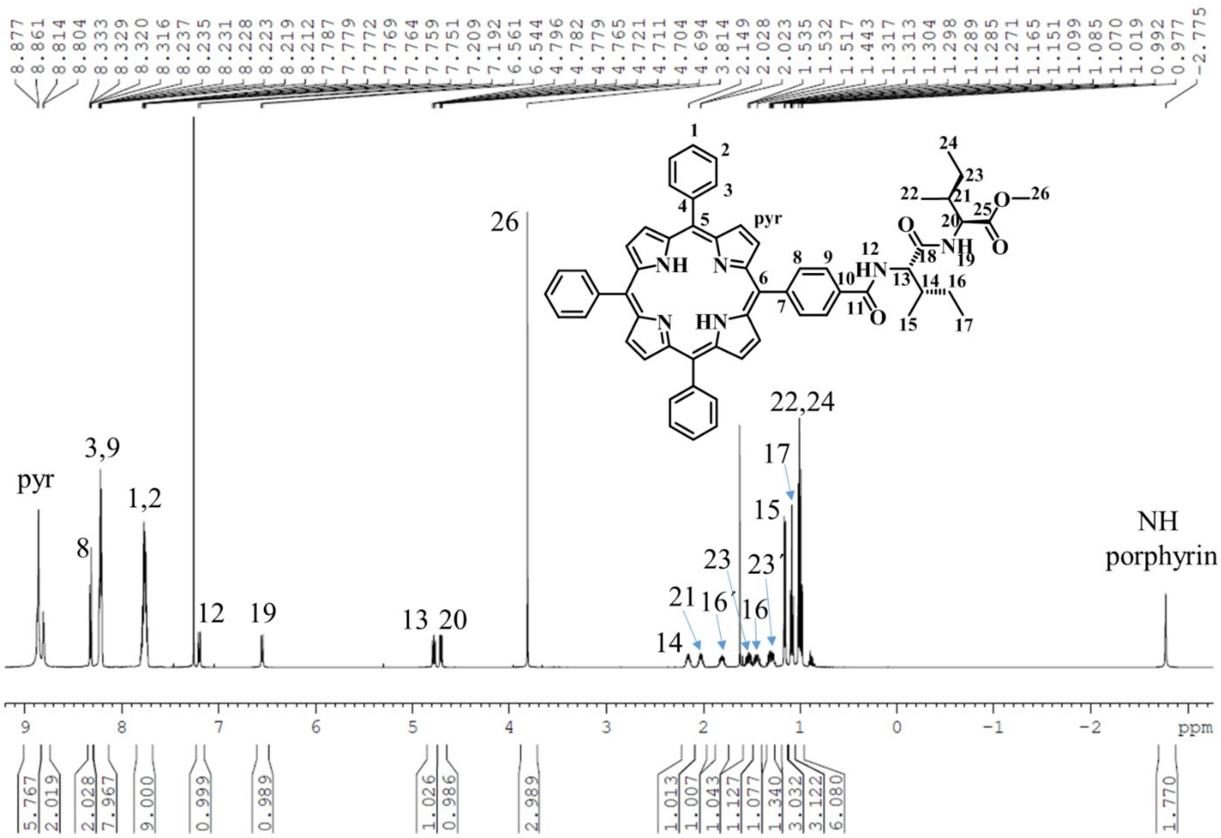


Fig. S11 ^{1}H NMR spectrum of **TPP-Ile-Ile-OMe** (500 MHz, CDCl$_3$).

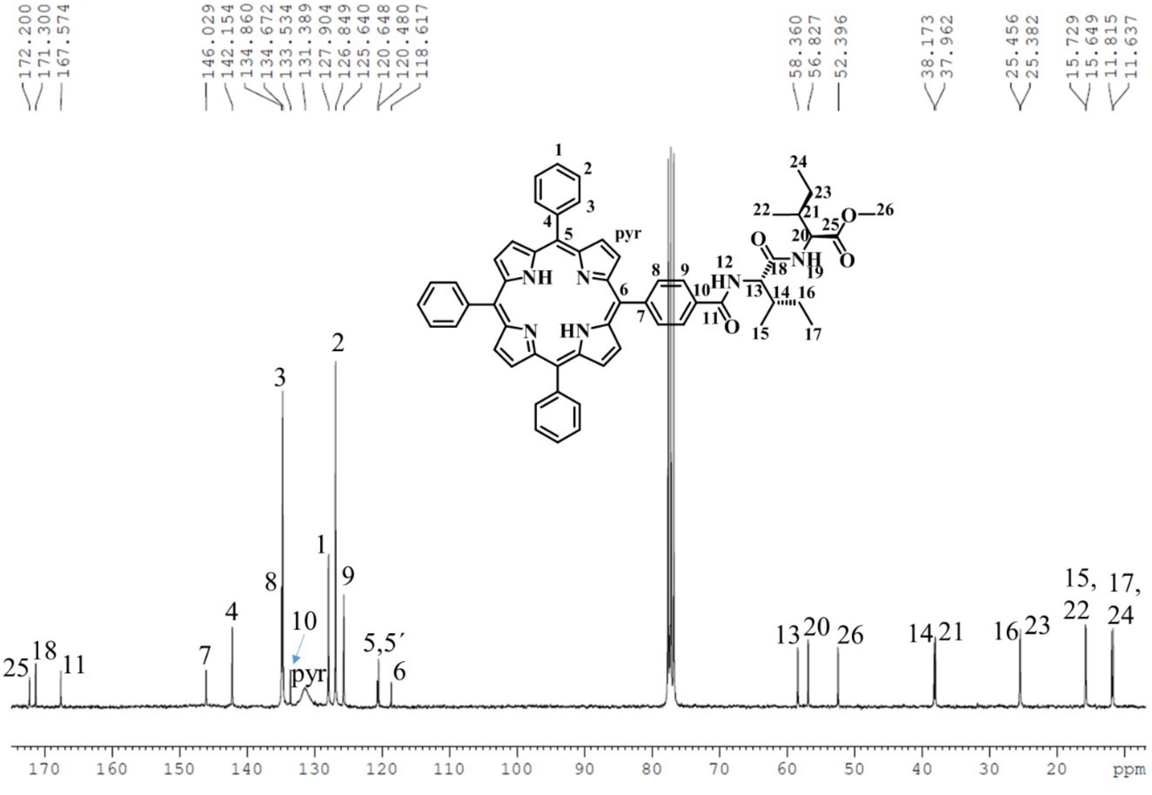


Fig. S12 ^{13}C NMR spectrum of **TPP-Ile-Ile-OMe** (75 MHz, CDCl$_3$).

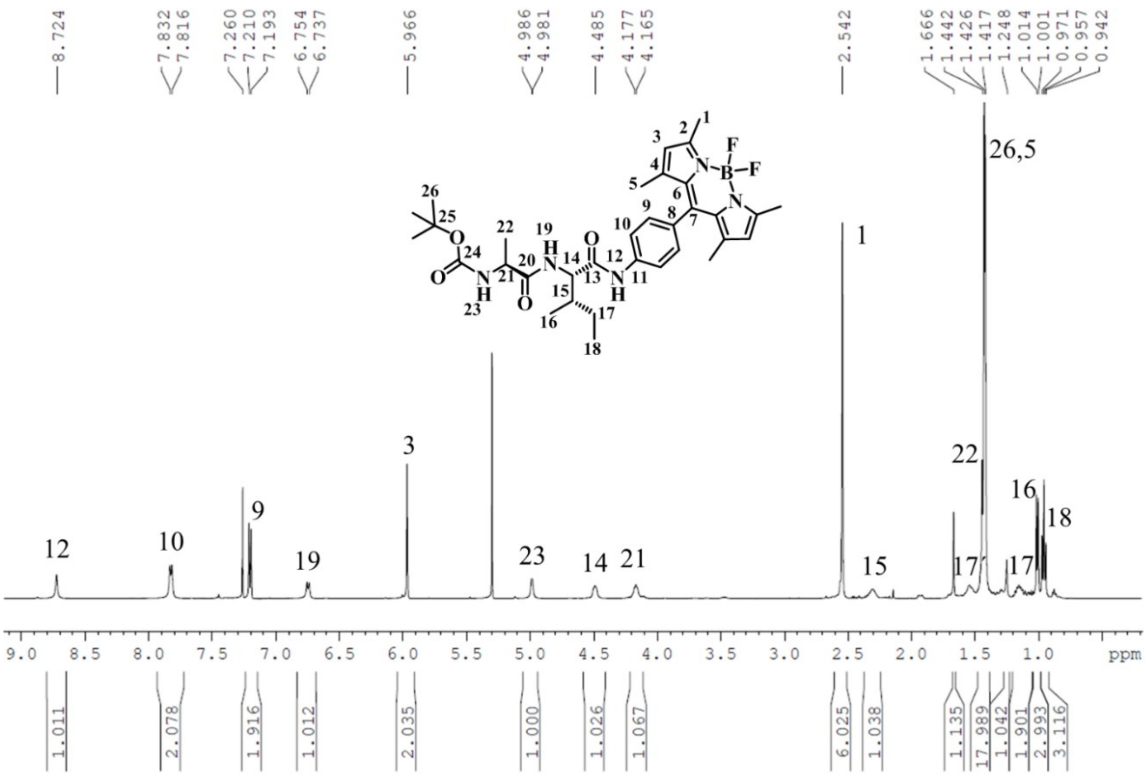


Fig. S13 ^{1}H NMR spectrum of **Boc-Ala-Ile-BDP** (500 MHz, $CDCl_3$).

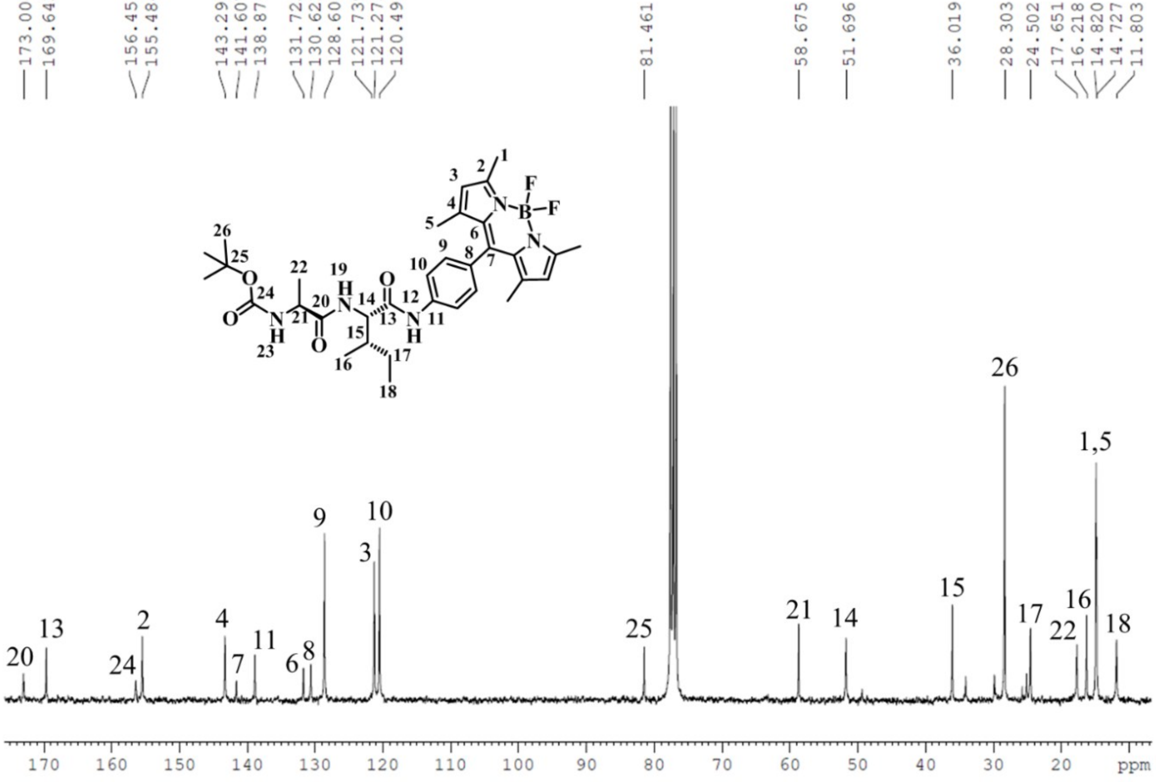


Fig. S14 ^{13}C NMR spectrum of **Boc-Ala-Ile-BDP** (75 MHz, $CDCl_3$).

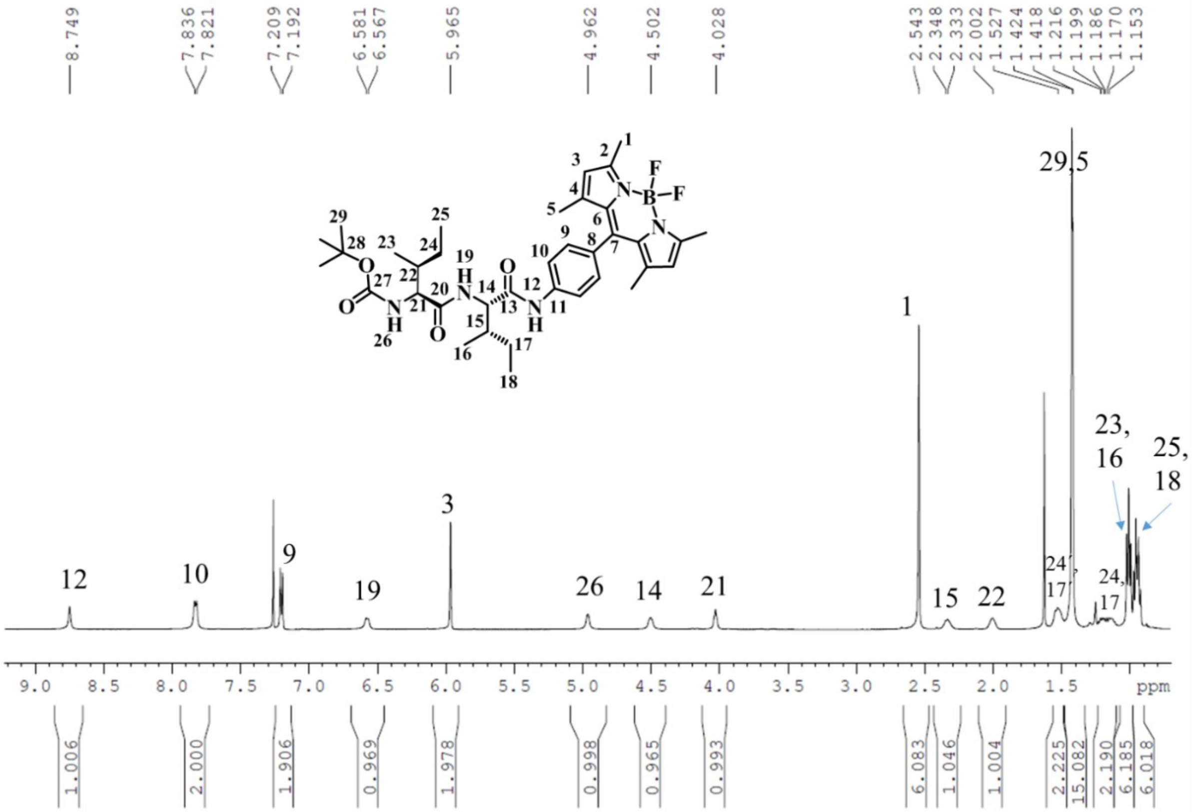


Fig. S15 ^{1}H NMR spectrum of **Boc-Ile-Ile-BDP** (500 MHz, $CDCl_3$).

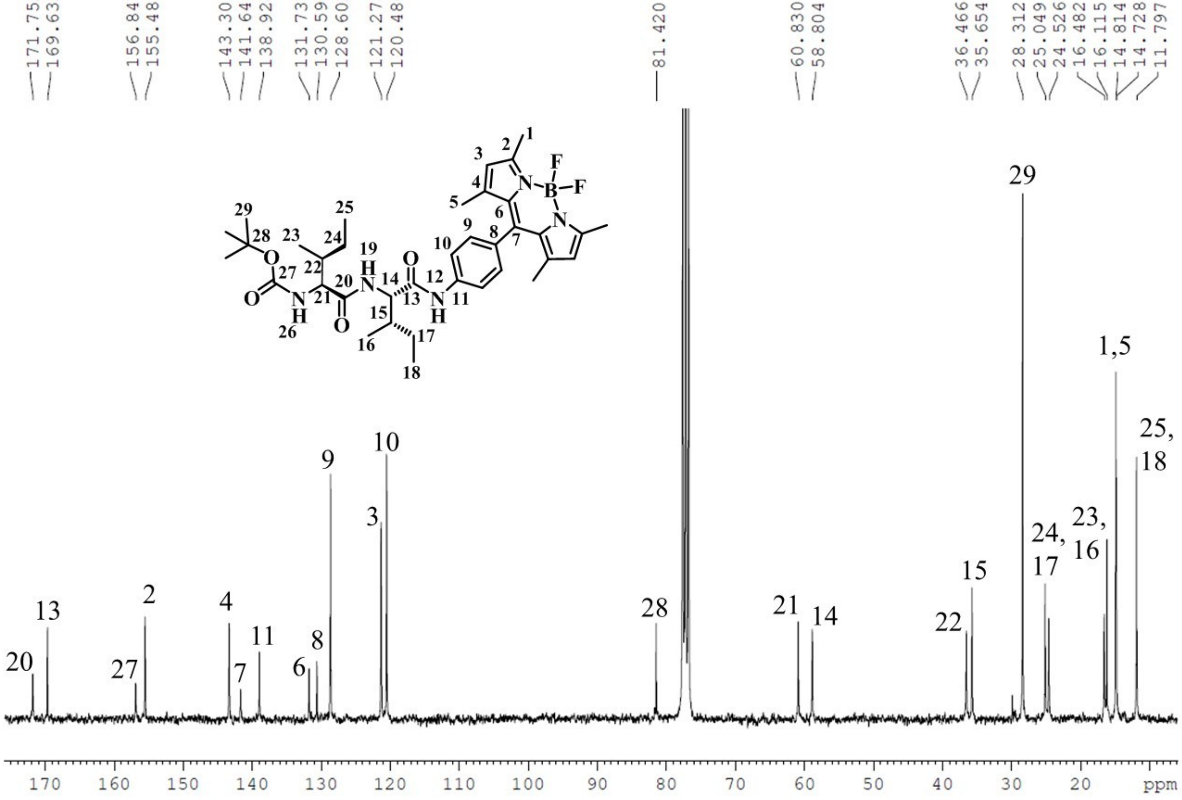


Fig. S16 ^{13}C NMR spectrum of **Boc-Ile-Ile-BDP** (75 MHz, $CDCl_3$).

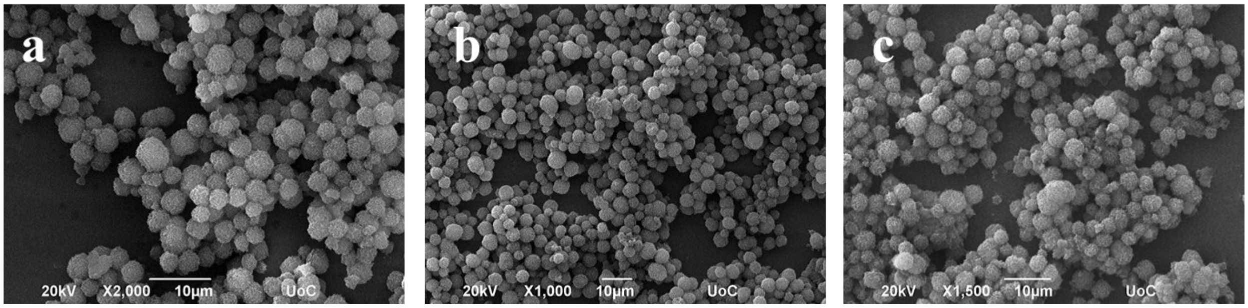


Fig. S17 SEM images of **Boc-Ile-Ile-TPP** in HFIP-MeOH 2:8 a) after 1h, b) after 24h and c) after 1 week.

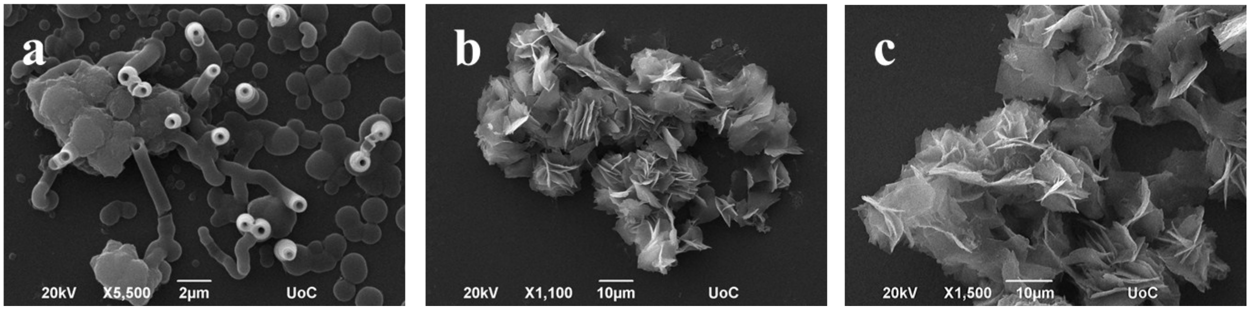


Fig. S18 SEM images of **Boc-Ile-Ile-TPP** in HFIP-EtOH 2:8 a) after 1h, b) after 24h and c) after 1 week.

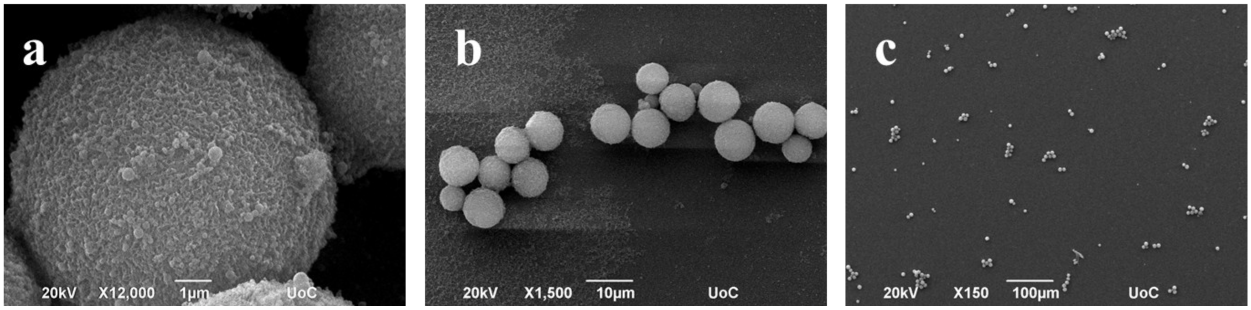


Fig. S19 SEM images of **Boc-Ile-Ile-TPP** in HFIP-H_2O 2:8 after 24h.

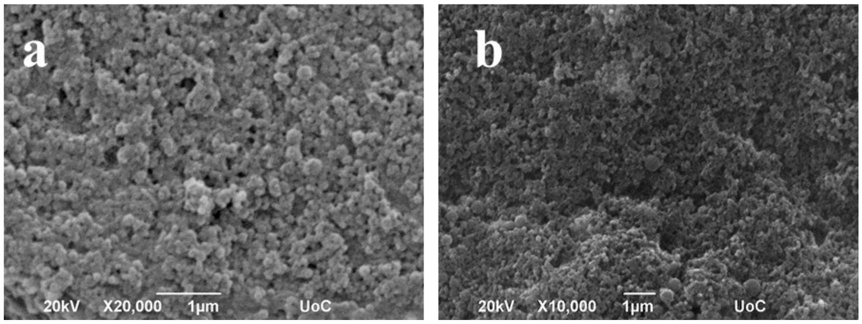


Fig. S20 SEM images of **Boc-Ala-Ile-TPP** in HFIP-H_2O 2:8, b) **Z-Ala-Ile-TPP** in HFIP- H_2O 2:8.

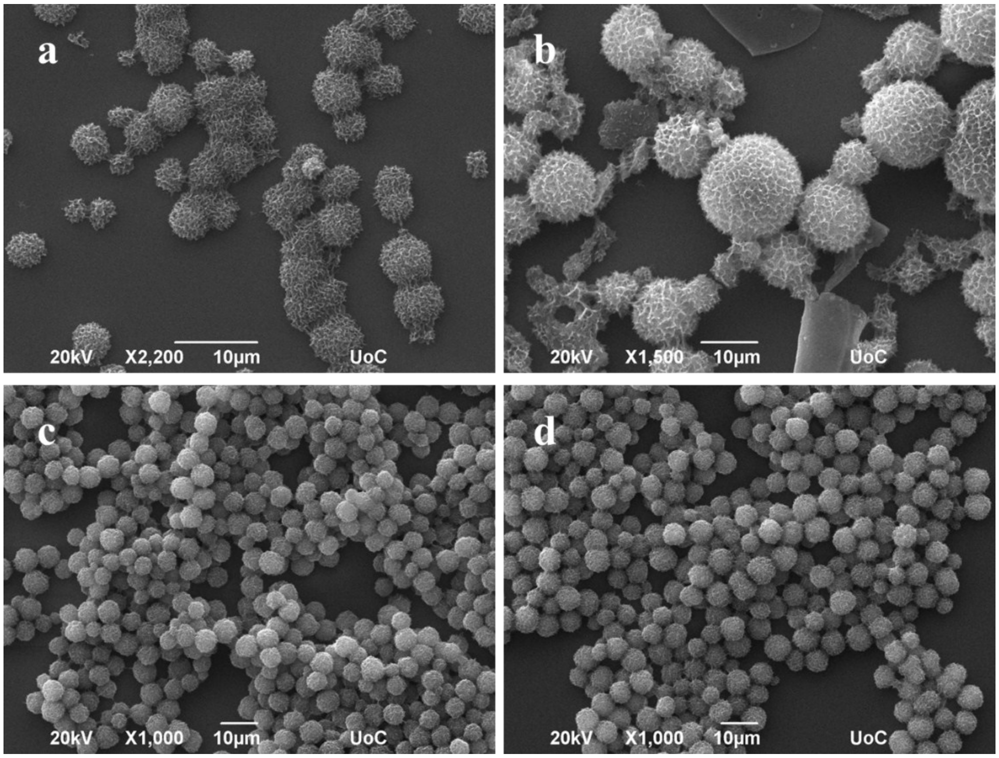


Fig. S21 SEM images of **Z-Ala-Ile-TPP** in a) HFIP-MeOH 2:8 after 60min, b) HFIP-MeOH 2:8 after 24h, c) HFIP-EtOH 2:8 after 60min, d) HFIP-EtOH 2:8 after 24h.

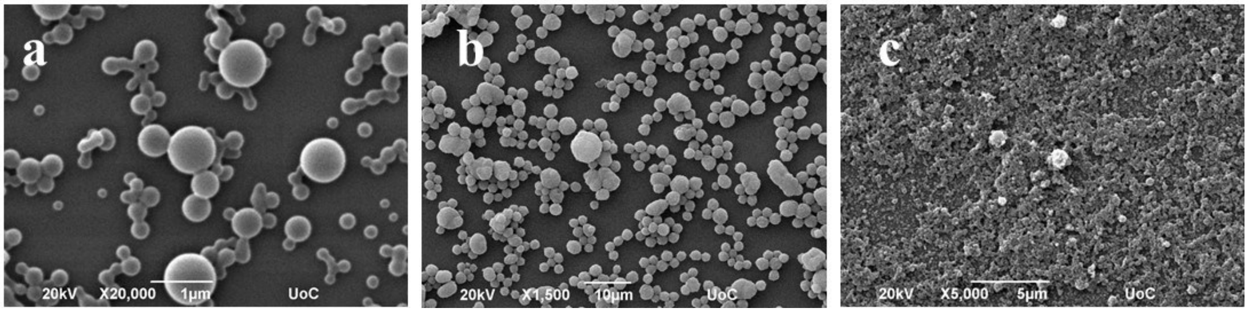


Fig.S22 SEM images of **Fmoc-Ala-Ile-TPP** in a) HFIP- MeOH 2:8, b) HFIP- EtOH 2:8, c) HFIP-H_2O 2:8.

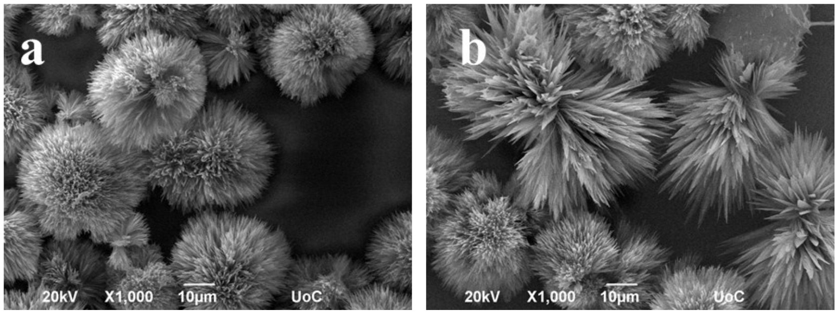


Fig.S23 SEM images of **Fmoc-Ile-Ile-TPP** in a) HFIP- MeOH 2:8, b) HFIP- EtOH 2:8.

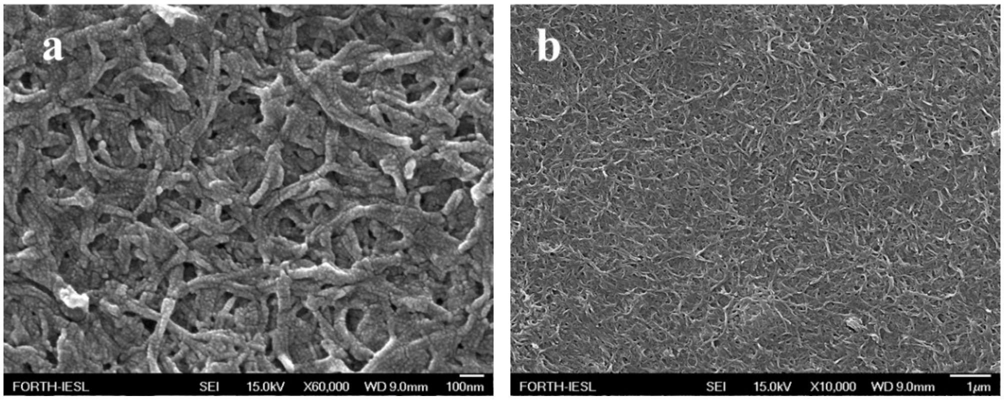


Fig.S24 FESEM image of the formed hydrogel using **Fmoc-Ile-Ile-TPP** in HFIP-H_2O 2:8 1 mM after 24 hours.

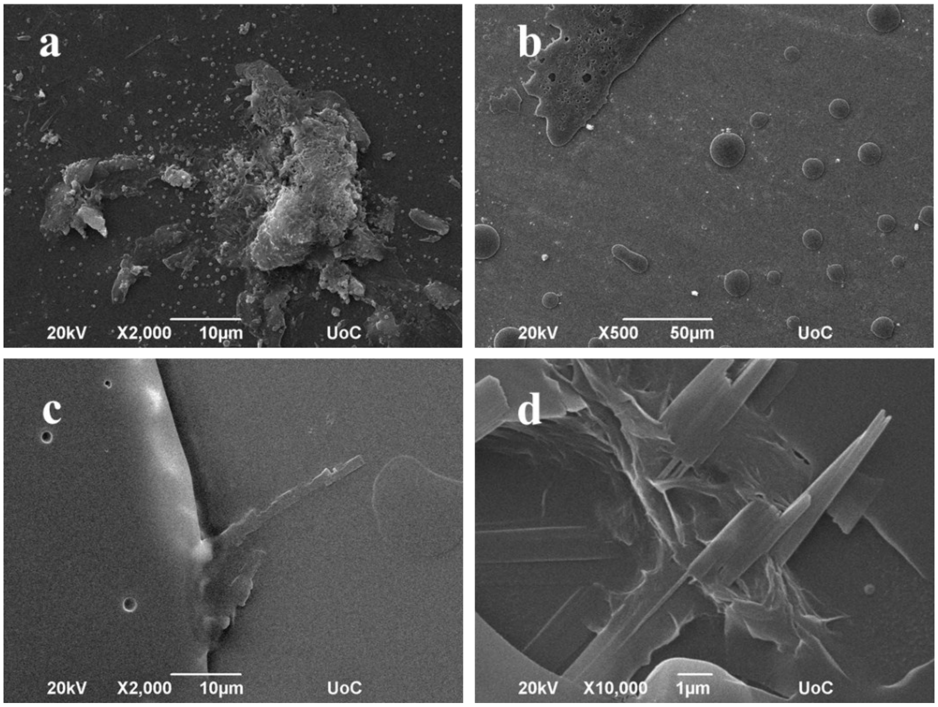


Fig. S25 SEM images of a) **Boc-Ile-Ile-BDP** in HFIP-EtOH 2:8, b) **Boc-Ile-Ile-BDP** in HFIP-MeOH 2:8, c) **Boc-Ala-Ile-BDP** in HFIP-EtOH 2:8, d) **Boc-Ala-Ile-BDP** in HFIP-MeOH 2:8.

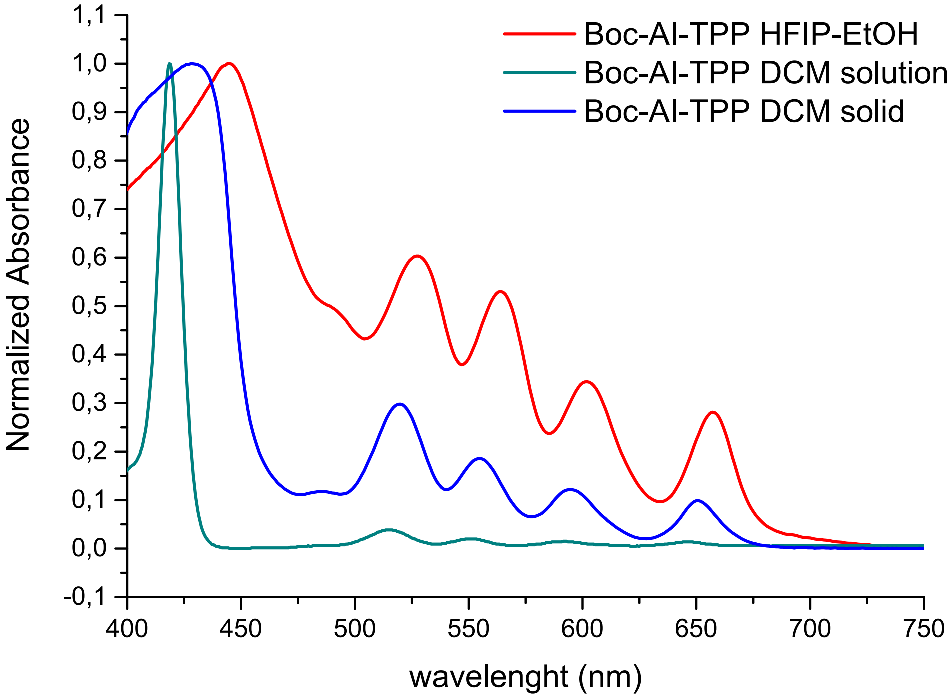


Fig. S26 Normalized absorption spectra of porphyrin **Boc-AI-TPP** in solution (gray line), in amorphous solid state (blue line) and in self-assembled state.

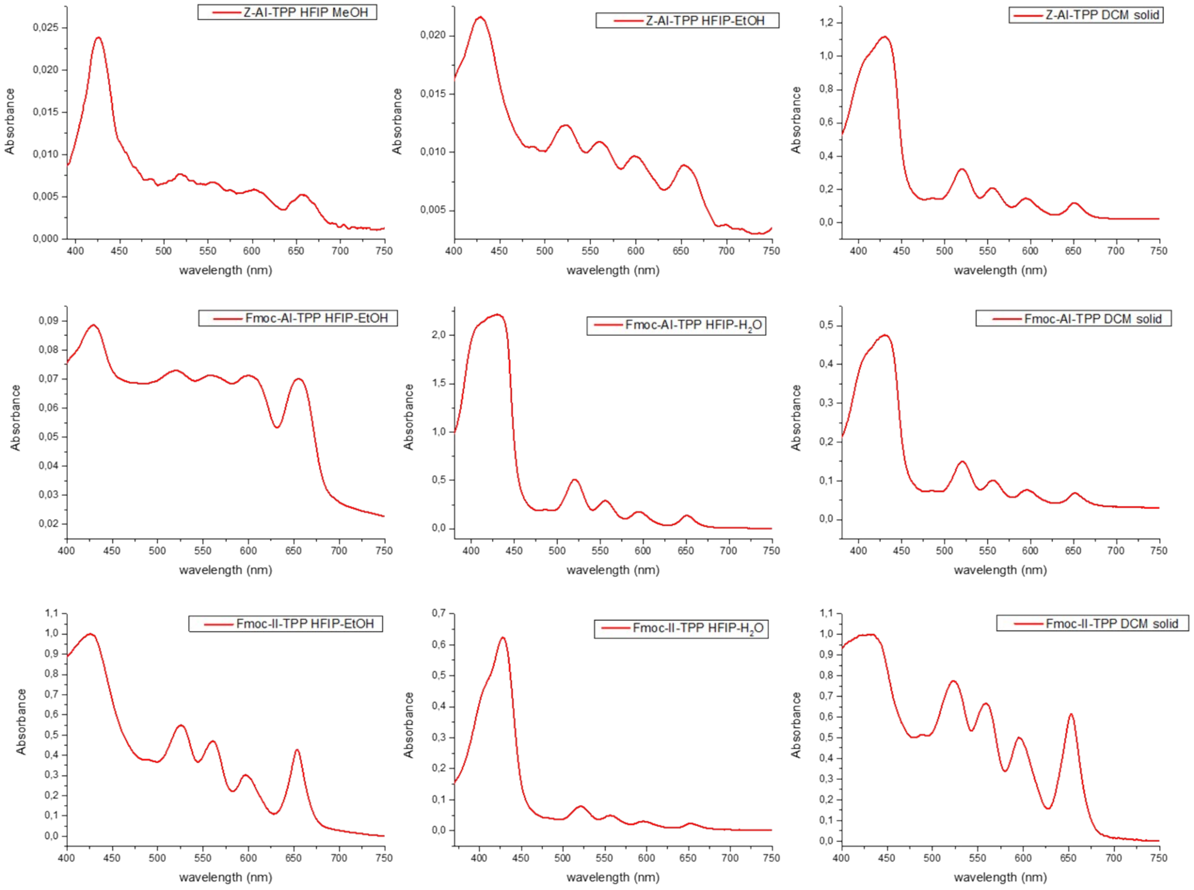


Fig. S27 UV-Vis spectra of porphyrin hybrids in solution, solid and self-assembled states.

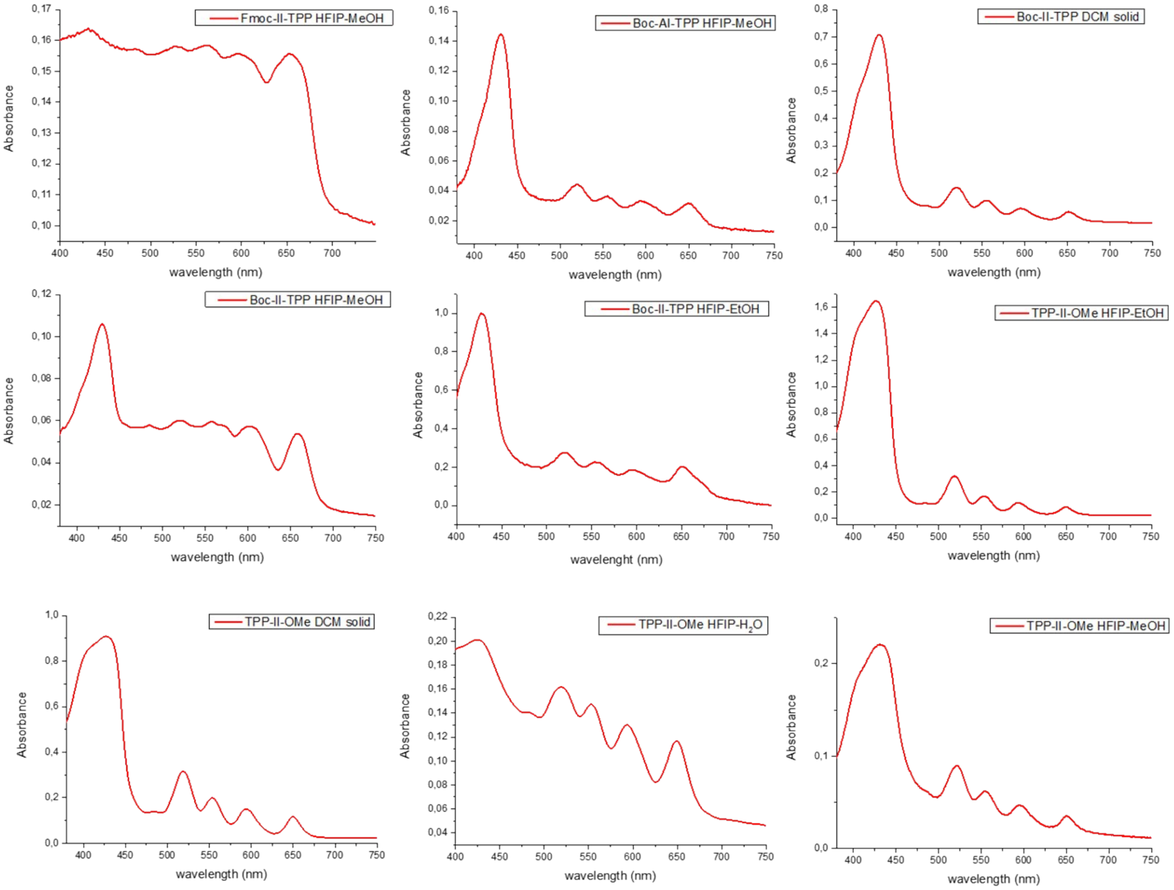


Fig. S28 UV-Vis spectra of porphyrin hybrids in solution, solid and self-assembled states.

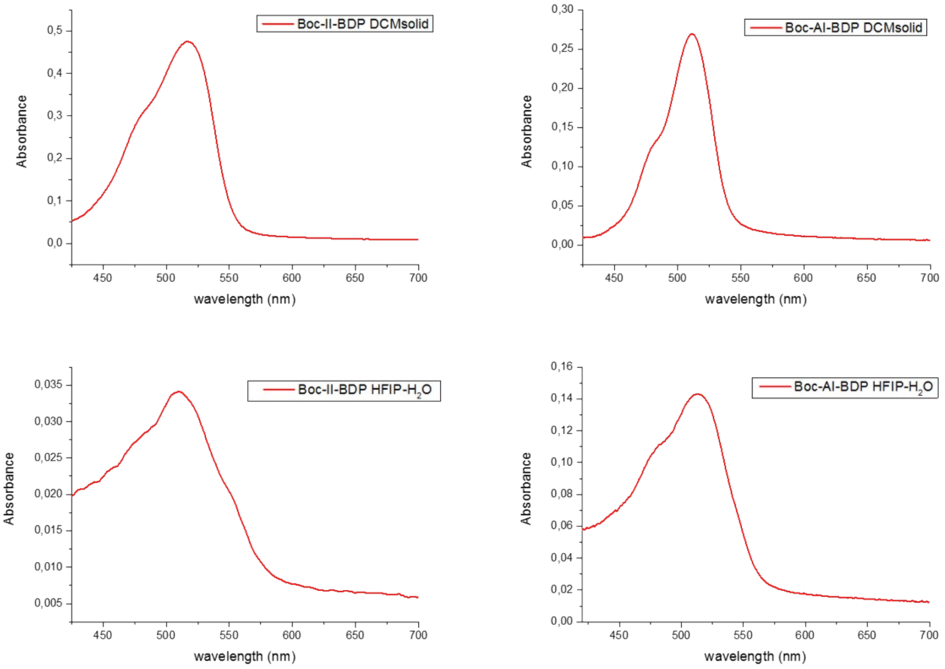


Fig. S29 UV-Vis spectra of BODIPY hybrids in solution, solid and self-assembled states.

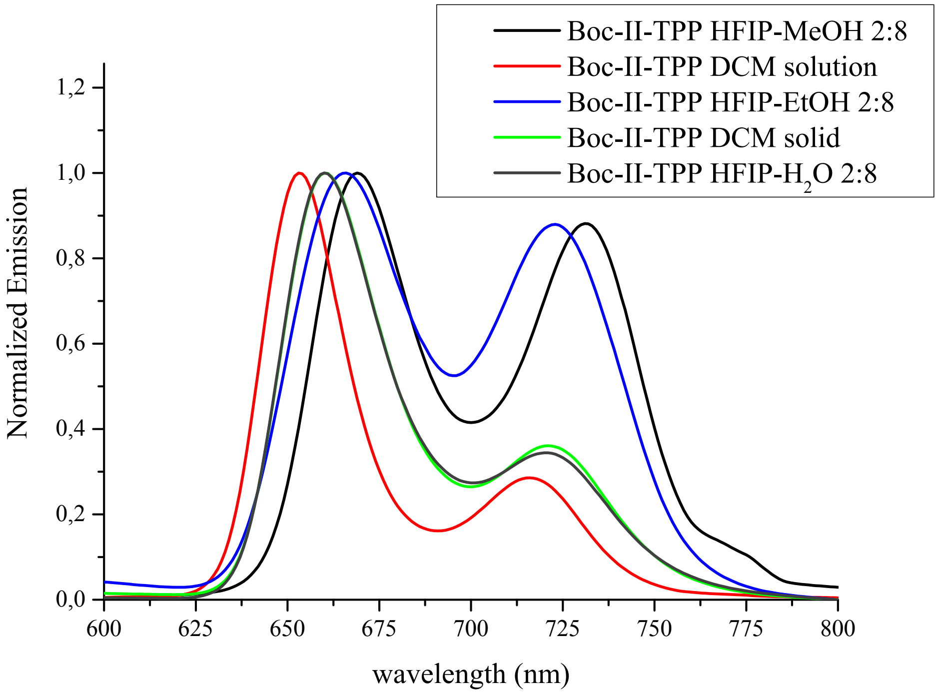


Fig. S30 Fluorescence spectra of **Boc-Ile-Ile-TPP** in solution, solid and self-assembled states.

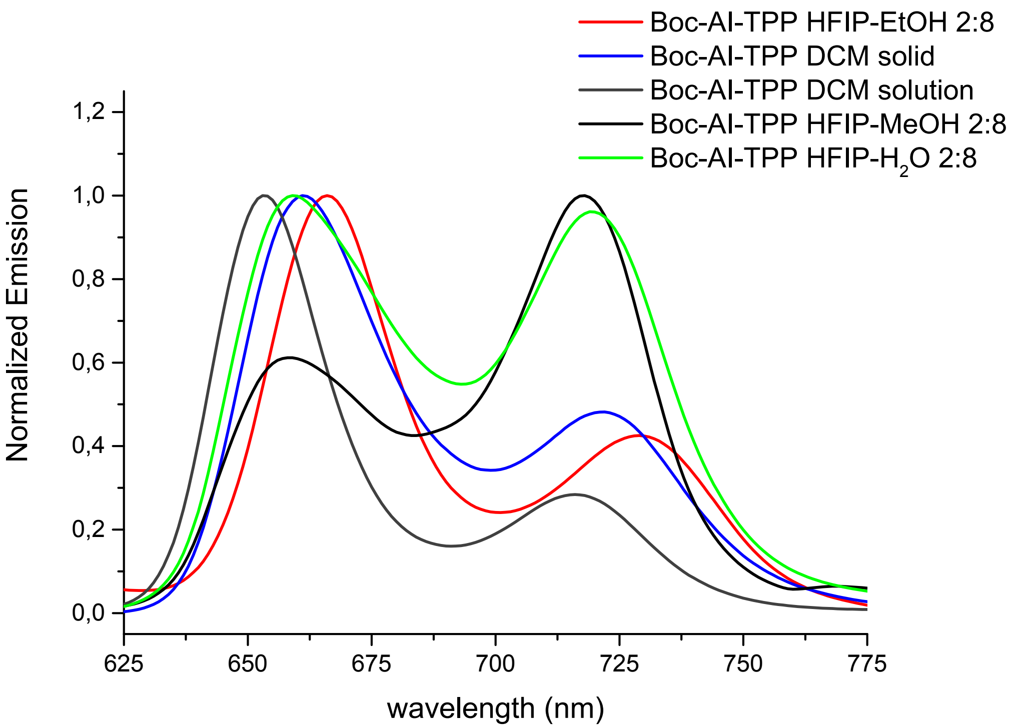


Fig. S31 Fluorescence spectra of **Boc-Ala-Ile-TPP** in solution, solid and self-assembled states.

Table S1 UV-Vis absorption bands of porphyrin and BODIPY conjugates in solution and in self-assembled state deposited from various solvent systems.

Compound	Solvent system	Solution λ_{abs} (nm)	Solid / Self-assembly λ_{abs} (nm)
Boc-Ile-Ile-TPP	DCM	418.5, 514.5, 551, 593, 646	430, 520, 555, 595, 651
	HFIP/EtOH (2:8)		427, 521, 555, 595, 651
	HFIP/MeOH (2:8)		430, 521, 559, 602, 658
	HFIP/H_2O (2:8)		437, 519, 555, 595, 651
Boc-Ala-Ile-TPP	DCM	418.5, 514.5, 551, 592, 646	428, 520, 555, 595, 651
	HFIP/EtOH (2:8)		445, 527, 564, 602, 657
	HFIP/MeOH (2:8)		431, 520, 555, 594, 652
Fmoc-Ile-Ile-TPP	DCM	418.5, 515, 551, 591, 646	430, 523, 559, 595, 653
	HFIP/EtOH (2:8)		426, 525, 561, 597, 654
	HFIP/MeOH (2:8)		430, 528, 557, 596, 653
	HFIP/H_2O (2:8)		428, 521, 556, 596, 652
Fmoc-Ala-Ile-TPP	DCM	418.5, 515, 551, 591, 647	430, 520, 556, 595, 652
	HFIP/EtOH (2:8)		428, 521, 563, 597, 656
	HFIP/MeOH (2:8)		431, 518, 554, 607, 656
	HFIP/H_2O (2:8)		430, 520, 556, 595, 651
Z-Ala-Ile-TPP	DCM	418.5, 514.5, 551, 590, 646	430, 520, 555, 595, 651
	HFIP/EtOH (2:8)		429, 522, 559, 598, 652
	HFIP/MeOH (2:8)		426, 519, 556, 601, 656
TPP-Ile-Ile-OMe	DCM	418, 515, 550, 590, 646	427, 519, 553, 594, 650
	HFIP/EtOH (2:8)		426, 519, 553, 594, 649
	HFIP/MeOH (2:8)		430, 521, 555, 595, 650
	HFIP/H_2O (2:8)		424, 519, 553, 593, 649
Boc-Ile-Ile-BDP	DCM	501	517
	HFIP/H_2O (2:8)		510
Boc-Ala-Ile-BDP	DCM	501	511
	HFIP/H_2O (2:8)		512

Table S2 Emission spectra peaks of porphyrin and BODIPY conjugates in solution and in self-assembled state deposited from various solvent systems.

Compound	Solvent system	Solution λ_{em} (nm)	Solid / Self-assembly λ_{em} (nm)
Boc-Ile-Ile-TPP	DCM	653, 716	660, 721
	HFIP/EtOH (2:8)		666, 723
	HFIP/MeOH (2:8)		669, 731
	HFIP/H_2O (2:8)		660, 720
Boc-Ala-Ile-TPP	DCM	653, 716	661, 722
	HFIP/EtOH (2:8)		666, 729
	HFIP/MeOH (2:8)		658, 718
	HFIP/H_2O (2:8)		659, 719
Fmoc-Ile-Ile-TPP	DCM	653, 716	661, 721
	HFIP/EtOH (2:8)		661, 723
	HFIP/MeOH (2:8)		667, 726
	HFIP/H_2O (2:8)		661, 722
Fmoc-Ala-Ile-TPP	DCM	654, 716	661, 720
	HFIP/EtOH (2:8)		665, 718
	HFIP/MeOH (2:8)		667, 727
	HFIP/H_2O (2:8)		660, 720
Z-Ala-Ile-TPP	DCM	653, 716	660, 722
	HFIP/EtOH (2:8)		663, 726
	HFIP/MeOH (2:8)		670, 731
	HFIP/H_2O (2:8)		667, 730
TPP-Ile-Ile-OMe	DCM	652, 715	659, 719
	HFIP/EtOH (2:8)		656, 719
	HFIP/MeOH (2:8)		665, 721
	HFIP/H_2O (2:8)		660, 720
Boc-Ile-Ile-BDP	DCM	518	547, 654, 718
	HFIP/H_2O (2:8)		546, 593
Boc-Ala-Ile-BDP	DCM	516	538, 650, 715
	HFIP/H_2O (2:8)		542