

## Supporting Information

### Diversity of dye aggregates: Self-assembly of naphthalene-linked chlorophyll dyads dependent on substitution position

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## S1. General Experiments

All the reactions were performed in the dark under nitrogen or argon atmosphere and monitored by thin layer chromatography and UV-vis absorption spectroscopy. UV-vis absorption and CD spectra were measured in solutions with a 10 mm quartz cell at room temperature (rt) using a Hitachi U3500 spectrophotometer and a Jasco J-720W spectropolarimeter, respectively. FT-IR spectra were measured in solution using a liquid cell and a JASCO FT/IR-6700 spectrophotometer.  $^1\text{H}$  NMR spectra were recorded in  $\text{CDCl}_3$  using a JEOL ECA-600 [**D-1,5/1,7/2,6/2,7**] or Bruker Avance 500US spectrometer [**D-1,3/1,6**]:  $\text{CHCl}_3$  ( $\delta_{\text{H}} = 7.26$  ppm) was used as an internal standard. High-resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF II spectrometer [**D-1,5/1,7/2,6/2,7**] or Waters SELECT SERIES Cyclic IMS instrument [**D-1,3/1,6**]; atmospheric pressure chemical ionization (APCI) or electrospray ionization (ESI) and positive mode in an acetonitrile solution. AFM measurements were performed by a Bruker AXS Multimode 8 AFM system in tapping mode in air at rt on an HOPG substrate, and a Bruker silicon cantilever RTESP-300 was used. Energy-minimalization of dyads were carried out using Chem3D 26.0 (PerkinElmer) with the MM2 force field.

## S2. Spectral Data of Stearyl 3-Aminomethyl-Pyropheophorbide-*a*

UV-vis ( $\text{CHCl}_3$ )  $\lambda_{\text{max}} = 663$  ( $\epsilon = 5.5 \times 10^4$ ), 607 ( $1.0 \times 10^4$ ), 538 ( $1.1 \times 10^4$ ), 507 ( $1.2 \times 10^4$ ), 412 ( $1.0 \times 10^5$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta = 9.44$  (1H, s, 10-H), 9.27 (1H, s, 5-H), 8.51 (1H, s, 20-H), 5.24, 5.09 (each 1H, d,  $J = 19$  Hz,  $13^1\text{-CH}_2$ ), 5.01 (2H, s, 3- $\text{CH}_2$ ), 4.47 (1H, dq,  $J = 2, 7$  Hz, 18-H), 4.28 (1H, dt,  $J = 8, 2$  Hz, 17-H), 4.02–3.92 (2H, m,  $17^2\text{-CO}_2\text{CH}_2$ ), 3.66 (2H, q,  $J = 8$  Hz, 8- $\text{CH}_2$ ), 3.62 (3H, s, 12- $\text{CH}_3$ ), 3.36 (3H, s, 2- $\text{CH}_3$ ), 3.23 (3H, s, 7- $\text{CH}_3$ ), 2.71–2.65, 2.55–2.50, 2.33–2.22

(1H+1H+2H, m, 17-CH<sub>2</sub>CH<sub>2</sub>), 1.80 (3H, d, *J* = 7 Hz, 18-CH<sub>3</sub>), 1.68 (3H, t, *J* = 8 Hz, 8<sup>1</sup>-CH<sub>3</sub>), 1.49–1.43 (2H, m, 17<sup>2</sup>-CO<sub>2</sub>CCH<sub>2</sub>), 1.29–1.13 (30H, m, 17<sup>2</sup>-CO<sub>2</sub>C<sub>2</sub>(CH<sub>2</sub>)<sub>15</sub>), 0.87 (3H, t, *J* = 8 Hz, 17<sup>2</sup>-CO<sub>2</sub>C<sub>17</sub>CH<sub>3</sub>), 0.41, –1.73 (each 1H, NH×2) [The 3<sup>1</sup>-NH<sub>2</sub> could be invisible.]; HRMS (APCI) found: *m/z* = 790.5614, calcd for C<sub>50</sub>H<sub>72</sub>N<sub>5</sub>O<sub>3</sub>: [M+H]<sup>+</sup>, 790.5630.

### S3. Synthesis of Naphthalenedicarboxylic Acid Dichloride

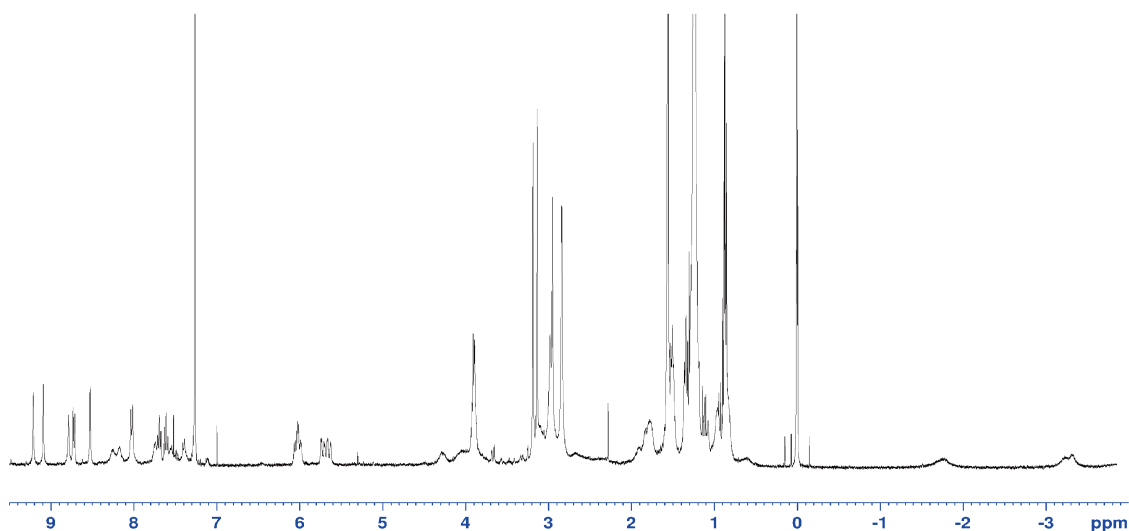
A mixture of naphthalenedicarboxylic acid (40.0 mg, 185 μmol), SOCl<sub>2</sub> (100 μL, 1.38 mmol), and a catalytic amount of DMF in dry tetrahydrofuran (THF, 4 mL) was refluxed for 3 h. After cooling down to rt, SOCl<sub>2</sub>, DMF, and THF were removed *in vacuo*. The residue was dissolved in dichloromethane (DCM) and an excess amount of hexane was added to give the corresponding naphthalenedicarboxylic acid dichloride as a pale yellow solid. The solid were collected by filtration, and a part of the obtained naphthalenedicarboxylic acid dichlorides were used directly in the following synthesis of Chl dyads without further purification.

### S4. Synthesis of Naphthalene-linked Chl Dyads

#### S4-1. Synthesis of **D-1,3**

To a dichloromethane (DCM) solution of stearyl 3-aminomethyl-pyropheophorbide-*a* (33.4 mg, 42.2 μmol) was added the 1,3-naphthalenedicarboxylic acid dichloride (4.9 mg, 19 μmol) and triethylamine (Et<sub>3</sub>N, 30.0 μL, 215 μmol) at 0 °C. After stirring for 1 day at rt, the reaction was quenched by addition of water, extracted by DCM, washed with water, and dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporating the solvent, the residue was purified by silica gel column chromatography (0.5–1.5% MeOH/DCM) to give **D-1,3** as a black solid (6.6 mg, 3.5 μmol) in 18% yield.

UV-vis (CHCl<sub>3</sub>)  $\lambda_{\text{max}}/\text{nm} = 665$  ( $\epsilon = 1.2 \times 10^5$ ), 609 ( $1.8 \times 10^4$ ), 538 ( $2.0 \times 10^4$ ), 508 ( $2.2 \times 10^4$ ), 411 ( $2.2 \times 10^5$ ), 400 ( $1.8 \times 10^5$ ), 381 ( $1.3 \times 10^5$ ), 319 ( $5.1 \times 10^4$ ); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, 500 MHz)  $\delta/\text{ppm} = 9.21, 9.09$  (each 1H, s, 5-H $\times 2$ ), 8.79, 8.21 (each 1H, s, 10-H $\times 2$ ), 8.72 (1H, d,  $J = 8$  Hz, 8-H of naphthalene), 8.53 (1H, s, 4-H of naphthalene), 8.03, (1H, br, 5-H of naphthalene) 8.01 (1H, s, 2-H of naphthalene), 7.74, 7.48 (each 1H, br, 3<sup>1</sup>-NH $\times 2$ ), 7.69 (1H, t,  $J = 8$  Hz, 7-H of naphthalene), 7.61 (1H, t,  $J = 8$  Hz, 6-H of naphthalene), 7.55, 7.38 (each 1H, s, 20-H $\times 2$ ), 6.05, 6.00, 5.72, 5.64 (each 1H, dd,  $J = 14, 6$  Hz, 3-CH<sub>2</sub> $\times 2$ ), 4.28–3.94 (4H, m, 17-H $\times 2$ , 18-H $\times 2$ ) 3.90 (4H, m, 17<sup>2</sup>-COOCH<sub>2</sub> $\times 2$ ), 3.18, 3.14 (each 3H, s, 2-CH<sub>3</sub> $\times 2$ ), 3.11–3.00 (4H, br, 8-CH<sub>2</sub> $\times 2$ ), 2.98, 2.84 (each 3H, s, 12-CH<sub>3</sub> $\times 2$ ), 2.95, 2.84 (each 3H, s, 7-CH<sub>3</sub> $\times 2$ ), 2.75–1.70 (8H, m, 17-CH<sub>2</sub>CH<sub>2</sub> $\times 2$ ), 1.51, 1.49 (each 3H, d,  $J = 7$  Hz, 18-CH<sub>3</sub>), 1.34 (6H, t,  $J = 7$  Hz, 8<sup>1</sup>-CH<sub>3</sub> $\times 2$ ), 1.29–1.17 (64H, m, 17<sup>2</sup>-COOC(CH<sub>2</sub>)<sub>16</sub> $\times 2$ ), 0.87 (6H, t,  $J = 7$  Hz, 17<sup>2</sup>-COOC<sub>17</sub>CH<sub>3</sub> $\times 2$ ), -1.74, -3.31 (each 2H, br-s, NH $\times 4$ ) [The 13<sup>1</sup>-CH<sub>2</sub> peaks were not found.]; HRMS (ESI) found:  $m/z = 1760.1393$ , calcd for C<sub>112</sub>H<sub>146</sub>N<sub>10</sub>O<sub>8</sub>: M<sup>+</sup>, 1760.1354.

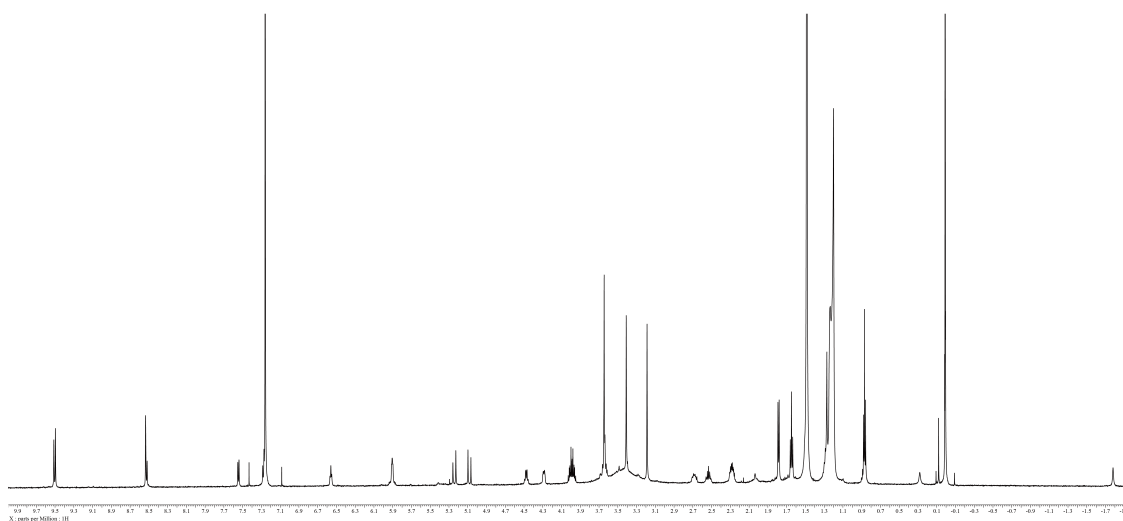


**Figure S1.** <sup>1</sup>H NMR spectrum of **D-1,3** in CDCl<sub>3</sub>.

#### S4-2. Synthesis of **D-1,5**

**D-1,5** was obtained by the same procedure of **D-1,3** synthesis (Section 3-1) using stearyl 3-aminomethyl-pyropheophorbide-*a* (32.2 mg, 40.8  $\mu\text{mol}$ ), 1,5-naphthalenedicarboxylic acid dichloride (5.0 mg, 20  $\mu\text{mol}$ ),  $\text{Et}_3\text{N}$  (28.3  $\mu\text{L}$ , 203  $\mu\text{mol}$ ), and DCM (10 mL). Yield: 26% (9.1 mg, 5.2  $\mu\text{mol}$ ).

UV-vis ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}/\text{nm} = 666$  ( $\epsilon = 1.0 \times 10^5$ ), 609 ( $1.5 \times 10^4$ ), 538 ( $1.7 \times 10^4$ ), 508 ( $1.9 \times 10^4$ ), 412 ( $1.9 \times 10^5$ ), 400 ( $1.5 \times 10^5$ ), 381 ( $1.1 \times 10^5$ ), 319 ( $4.4 \times 10^4$ );  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 50  $^\circ\text{C}$ , 600 MHz)  $\delta/\text{ppm} = 9.51$  (2H, s, 5-H $\times 2$ ), 9.46 (2H, s, 10-H $\times 2$ ), 8.54 (2H, s, 20-H $\times 2$ ), 8.53 (2H, d,  $J = 8$  Hz, 2,6-H of naphthalene), 7.54 (2H, d,  $J = 8$  Hz, 4,8-H of naphthalene), 7.27 (2H, t,  $J = 8$  Hz, 3,7-H of naphthalene), 6.56 (2H, br, 3 $^1$ -NH $\times 2$ ), 5.91 (4H, br, 3-CH $_2 \times 2$ ), 5.24, 5.08 (each 2H, d,  $J = 19$  Hz, 13 $^1$ -CH $_2 \times 2$ ), 4.48 (2H, br-q,  $J = 8$  Hz, 18-H $\times 2$ ), 4.29 (2H, br-d,  $J = 8$  Hz, 17-H $\times 2$ ), 4.03–3.95 (4H, m, 17 $^2$ -COOCH $_2 \times 2$ ), 3.65 (6H, s, 12-CH $_3 \times 2$ ), 3.64 (4H, q,  $J = 8$  Hz, 8-CH $_2 \times 2$ ), 3.41 (6H, s, 2-CH $_3 \times 2$ ), 3.19 (6H, s, 7-CH $_3 \times 2$ ), 2.72–2.65, 2.58–2.50, 2.33–2.25 (2H+2H+4H, m, 17-CH $_2\text{CH}_2 \times 2$ ), 1.79 (6H, d,  $J = 8$  Hz, 18-CH $_3 \times 2$ ), 1.65 (6H, t,  $J = 8$  Hz, 8 $^1$ -CH $_3 \times 2$ ), 1.29–1.19 (64H, m, 17 $^2$ -COOC(CH $_2$ ) $_{16} \times 2$ ), 0.87 (6H, t,  $J = 7$  Hz, 17 $^2$ -COOC $_{17}$ CH $_3 \times 2$ ), 0.28, -1.78 (each 2H, br-s, NH $\times 4$ ); HRMS (ESI) found:  $m/z = 1761.1435$ , calcd for  $\text{C}_{112}\text{H}_{147}\text{N}_{10}\text{O}_8$ :  $[\text{M}+\text{H}]^+$ , 1761.1432.

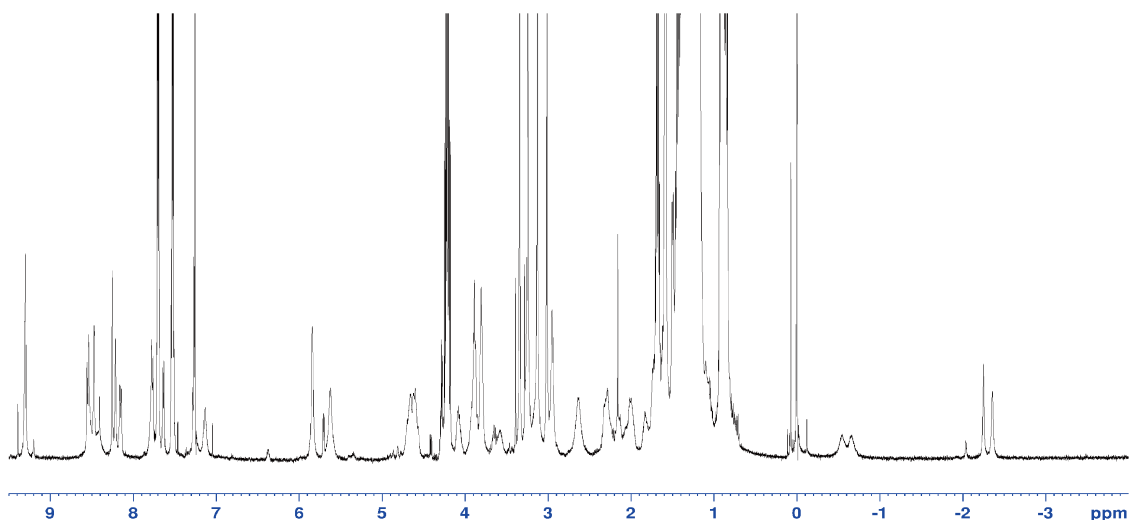


**Figure S2.**  $^1\text{H NMR}$  spectrum of **D-1,5** in  $\text{CDCl}_3$ .

### S4-3. Synthesis of **D-1,6**

**D-1,6** was obtained by the same procedure of **D-1,3** synthesis (Section 3-1) using stearyl 3-aminomethyl-pyropheophorbide-*a* (31.6 mg, 40.0  $\mu\text{mol}$ ), 1,6-naphthalenedicarboxylic acid dichloride (4.9 mg, 19  $\mu\text{mol}$ ),  $\text{Et}_3\text{N}$  (30.0  $\mu\text{L}$ , 215  $\mu\text{mol}$ ), and DCM (10 mL). Yield: 57% (19.2 mg, 11.0  $\mu\text{mol}$ ).

UV-vis ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}/\text{nm} = 665$  ( $\epsilon = 1.1 \times 10^5$ ), 609 ( $1.7 \times 10^4$ ), 538 ( $1.9 \times 10^4$ ), 508 ( $2.1 \times 10^4$ ), 411 ( $2.1 \times 10^5$ ), 400 ( $1.7 \times 10^5$ ), 381 ( $1.2 \times 10^5$ ), 319 ( $1.8 \times 10^4$ );  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 50  $^\circ\text{C}$ , 500 MHz)  $\delta/\text{ppm} = 9.30$  (2H, s, 5-H $\times 2$  of Chl-1,6), 8.56 (1H, d,  $J = 9$  Hz, 8-H of naphthalene), 8.54, (1H, s, 10-H of Chl-6), 8.48 (1H, s, 10-H of Chl-1), 8.41 (1H, s, 5-H of naphthalene), 8.26 (1H, s, 20-H of Chl-1), 8.22 (1H, s, 20-H of Chl-6), 8.16 (1H, d,  $J = 9$  Hz, 7-H of naphthalene), 7.78 (1H, br, 3 $^1$ -NH of Chl-6), 7.77 (1H, d,  $J = 9$  Hz, 4-H of naphthalene), 7.64 (1H, d,  $J = 7$  Hz, 2-H of naphthalene) 7.27 (1H, t,  $J = 8$  Hz, 3-H of naphthalene), 7.14 (1H, br, 3 $^1$ -NH of Chl-1), 5.84, (2H, br, 3- $\text{CH}_2$  of Chl-6), 5.63, (2H, d,  $J = 5$  Hz, 3- $\text{CH}_2$  of Chl-1), 4.75–4.55 (4H, m, 13 $^1$ - $\text{CH}_2 \times 2$  of Chl-1,6), 4.28 (1H, m, 18-H), 4.26–4.17 (11H, m, 8- $\text{CH}_2 \times 2$ , 17-H $\times 2$ , and 17 $^2$ - $\text{COOCH}_2 \times 2$  of Chl-1,6, 18-H), 3.84, 3.80 (each 3H, s, 12- $\text{CH}_3 \times 2$  of Chl-1,6), 3.34 (3H, s, 2- $\text{CH}_3$  of Chl-6), 3.24 (3H, s, 2- $\text{CH}_3$  of Chl-1), 3.13, 3.02 (each 3H, s, 7- $\text{CH}_3 \times 2$  of Chl-1,6), 2.63, 2.30, 2.16, 2.00 (each 2H, m, 17- $\text{CH}_2\text{CH}_2 \times 2$  of Chl-1,6) 1.68 (6H, t,  $J = 6$  Hz, 8 $^1$ - $\text{CH}_3 \times 2$  of Chl-1,6), 1.50 (6H, d,  $J = 8$  Hz, 18- $\text{CH}_3 \times 2$  of Chl-1,6), 1.45–1.15 (64H, m, 17 $^2$ - $\text{COOC}(\text{CH}_2)_{16} \times 2$  of Chl-1,6), 0.87 (6H, t,  $J = 7$  Hz, 17 $^2$ - $\text{COOC}_{17}\text{CH}_3 \times 2$  of Chl-1,6), -0.46, -0.54, -2.24, -2.35 (each 1H, br-s, NH $\times 4$  of Chl-1,6) [Chl-1 and Chl-6 were connected to the 1- and 6-positions of a naphthalene linker, respectively.]; HRMS (ESI) found:  $m/z = 879.5679$ , calcd for  $\text{C}_{112}\text{H}_{146}\text{N}_{10}\text{O}_8$ :  $\text{M}^{2+}$ , 879.5657.



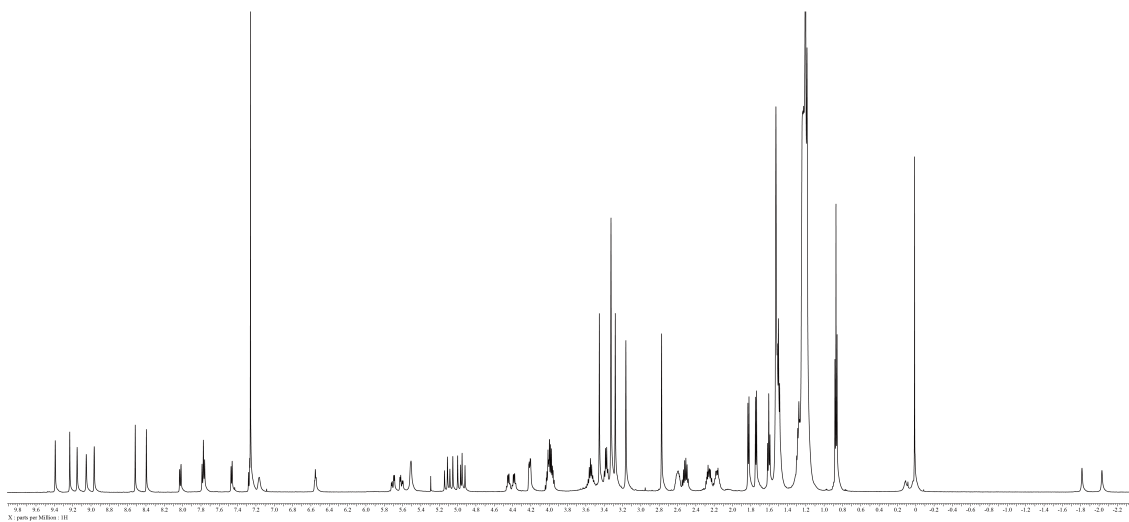
**Figure S3.**  $^1\text{H}$  NMR spectrum of **D-1,6** in  $\text{CDCl}_3$ .

#### *S4-4. Synthesis of D-1,7*

**D-1,7** was obtained by the same procedure of **D-1,3** synthesis (Section 3-1) using stearyl 3-aminomethyl-pyropheophorbide-*a* (31.6 mg, 40.0  $\mu\text{mol}$ ), 1,7-naphthalenedicarboxylic acid dichloride (4.7 mg, 19  $\mu\text{mol}$ ),  $\text{Et}_3\text{N}$  (28.3  $\mu\text{L}$ , 203  $\mu\text{mol}$ ), and DCM (10 mL). Yield: 28% (9.3 mg, 5.3  $\mu\text{mol}$ ).

UV-vis ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}/\text{nm} = 665$  ( $\epsilon = 1.1 \times 10^5$ ), 608 ( $1.7 \times 10^4$ ), 537 ( $1.9 \times 10^4$ ), 507 ( $2.1 \times 10^4$ ), 411 ( $2.1 \times 10^5$ ), 399 ( $1.8 \times 10^5$ ), 381 ( $1.3 \times 10^5$ ), 319 ( $4.8 \times 10^4$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta/\text{ppm} = 9.39$  (1H, s, 5-H of Chl-7), 9.23 (1H, s, 10-H of Chl-7), 9.15 (1H, s, 10-H of Chl-1), 9.05 (1H, s, 5-H of Chl-1), 8.97 (1H, s, 8-H of naphthalene), 8.52 (1H, s, 20-H of Chl-7), 8.40 (1H, s, 20-H of Chl-1), 8.02 (1H, d,  $J = 9$  Hz, 6-H of naphthalene), 7.78 (1H, d,  $J = 9$  Hz, 5-H of naphthalene), 7.76 (1H, d,  $J = 8$  Hz, 4-H of naphthalene), 7.47 (1H, d,  $J = 7$  Hz, 2-H of naphthalene), 7.27 (1H, br-t,  $J = 8$  Hz, 3-H of naphthalene), 7.16 (1H, br,  $3^1\text{-NH}$  of Chl-7), 6.55 (1H, br,  $3^1\text{-NH}$  of Chl-1), 5.71, 5.61 (each 1H, dd,  $J = 15, 5$  Hz, 3- $\text{CH}_2$  of Chl-7), 5.51 (2H, br, 3- $\text{CH}_2$  of Chl-1), 5.13, 5.07, 4.98, 4.94 (each 1H, d,  $J = 19$  Hz,  $13^1\text{-CH}_2 \times 4$  of Chl-1,7), 4.45 (1H,

br-q,  $J = 7$  Hz, 18-H of Chl-7), 4.38 (1H, br-q,  $J = 8$  Hz, 18-H of Chl-1), 4.24–4.16 (2H, m, 17-H $\times$ 2 of Chl-1,7), 4.05–3.94 (4H, m, 17<sup>2</sup>-COOCH<sub>2</sub> $\times$ 2 of Chl-1,7), 3.57, 3.53 (each 1H, dq,  $J = 15$ , 8 Hz, 8-CH<sub>2</sub> of Chl-1), 3.45 (3H, s, 12-CH<sub>3</sub> of Chl-7), 3.38 (2H, q,  $J = 8$  Hz, 8-CH<sub>2</sub> of Chl-7), 3.27 (6H, s, 2-CH<sub>3</sub> of Chl-7, 12-CH<sub>3</sub> of Chl-1), 3.28 (3H, s, 7-CH<sub>3</sub> of Chl-7), 3.16 (3H, s, 2-CH<sub>3</sub> of Chl-1), 2.77 (3H, s, 7-CH<sub>3</sub> of Chl-1), 2.65–2.56, 2.55–2.46, 2.31–2.22, 2.21–2.12 (each 2H, m, 17-CH<sub>2</sub>CH<sub>2</sub> $\times$ 2 of Chl-1,7), 1.83 (3H, d,  $J = 7$  Hz, 18-CH<sub>3</sub> of Chl-7), 1.74 (3H, d,  $J = 8$  Hz, 18-CH<sub>3</sub> of Chl-1), 1.60 (3H, t,  $J = 8$  Hz, 8<sup>1</sup>-CH<sub>3</sub> of Chl-1), 1.50 (3H, t,  $J = 8$  Hz, 8<sup>1</sup>-CH<sub>3</sub> of Chl-1), 1.32–1.12 (64H, m, 17<sup>2</sup>-COOC<sub>2</sub>(CH<sub>2</sub>)<sub>16</sub> $\times$ 2 of Chl-1,7), 0.87 (6H, t,  $J = 7$  Hz, 17<sup>2</sup>-COOC<sub>17</sub>CH<sub>3</sub> $\times$ 2 of Chl-1,7), 0.12, 0.03, -1.81, -2.03 (each 1H, br-s, NH $\times$ 4 of Chl-1,7) [Chl-1 and Chl-7 were connected to the 1- and 7-positions of a naphthalene linker, respectively.]; HRMS (ESI) found:  $m/z = 1761.1431$ , calcd for C<sub>112</sub>H<sub>147</sub>N<sub>10</sub>O<sub>8</sub>: [M+H]<sup>+</sup>, 1761.1432.



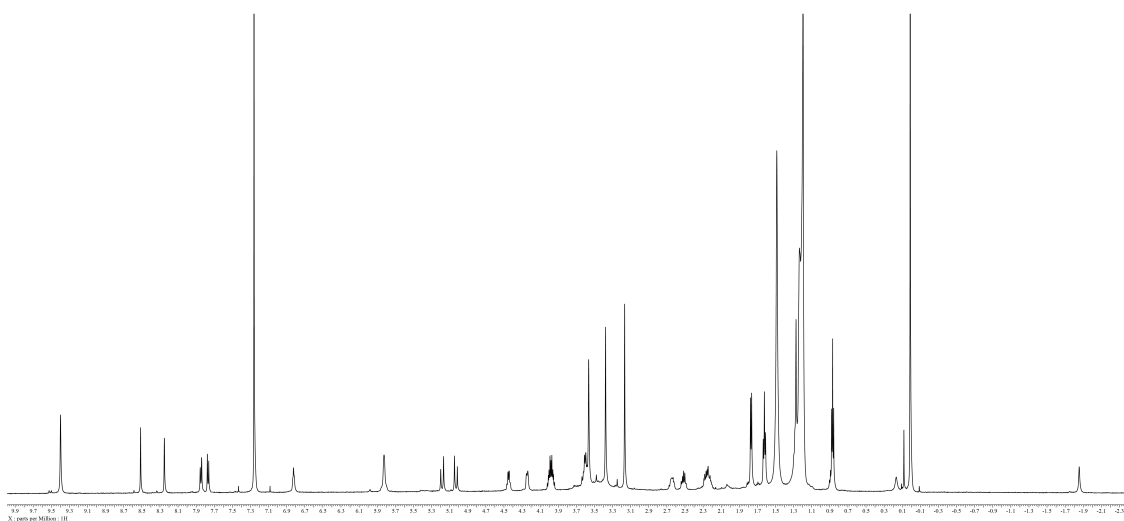
**Figure S4.** <sup>1</sup>H NMR spectrum of **D-1,7** in CDCl<sub>3</sub>.

#### S4-5. Synthesis of **D-2,6**

**D-2,6** was obtained by the same procedure of **D-1,3** synthesis (Section 3-1) using stearyl 3-aminomethyl-pyropheophorbide-*a* (30.0 mg, 38.0 μmol), 2,6-naphthalenedicarboxylic acid

dichloride (4.7 mg, 19  $\mu\text{mol}$ ),  $\text{Et}_3\text{N}$  (26.4  $\mu\text{L}$ , 189  $\mu\text{mol}$ ), and DCM (10 mL). Yield: 30% (9.7 mg, 5.5  $\mu\text{mol}$ ).

UV-vis ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}/\text{nm} = 666$  ( $\epsilon = 1.0 \times 10^5$ ), 609 ( $1.5 \times 10^4$ ), 538 ( $1.7 \times 10^4$ ), 508 ( $1.9 \times 10^4$ ), 412 ( $1.9 \times 10^5$ ), 400 ( $1.5 \times 10^5$ ), 381 ( $1.1 \times 10^5$ ), 319 ( $4.2 \times 10^4$ );  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 50  $^\circ\text{C}$ , 600 MHz)  $\delta/\text{ppm} = 9.40$  (4H, s, 5,10-H $\times 2$ ), 8.51 (2H, s, 20-H $\times 2$ ), 8.25 (2H, s, 1,5-H of naphthalene), 7.84 (2H, d,  $J = 9$  Hz, 3,7-H of naphthalene), 7.76 (2H, d,  $J = 9$  Hz, 4,8-H of naphthalene), 6.83 (2H, br, 3 $^1$ -NH $\times 2$ ), 5.82 (4H, s, 3-CH $_2 \times 2$ ), 5.18, 5.03 (each 2H, d,  $J = 19$  Hz, 13 $^1$ -CH $_2 \times 2$ ), 4.45 (2H, br-q,  $J = 7$  Hz, 18-H $\times 2$ ), 4.24 (2H, br-d,  $J = 9$  Hz, 17-H $\times 2$ ), 4.02–3.94 (4H, m, 17 $^2$ -COOCH $_2 \times 2$ ), 3.60 (4H, q,  $J = 8$  Hz, 8-CH $_2 \times 2$ ), 3.56 (6H, s, 12-CH $_3 \times 2$ ), 3.38 (6H, s, 2-CH $_3 \times 2$ ), 3.18 (6H, s, 7-CH $_3 \times 2$ ), 2.67–2.61, 2.54–2.48, 2.29–2.20 (2H+2H+4H, m, 17-CH $_2\text{CH}_2 \times 2$ ), 1.77 (6H, d,  $J = 7$  Hz, 18-CH $_3 \times 2$ ), 1.62 (6H, t,  $J = 8$  Hz, 8 $^1$ -CH $_3 \times 2$ ), 1.30–1.26 (4H, m, 17 $^2$ -COOCCH $_2 \times 2$ ), 1.25–1.17 (60H, m, 17 $^2$ -COOC $_2(\text{CH}_2)_{15} \times 2$ ), 0.87 (6H, t,  $J = 7$  Hz, 17 $^2$ -COOC $_{17}\text{CH}_3 \times 2$ ), 0.16, -1.86 (each 2H, br-s, NH $\times 4$ ); HRMS (ESI) found:  $m/z = 1761.1429$  and 881.0749, calcd for  $\text{C}_{112}\text{H}_{147}\text{N}_{10}\text{O}_8$ :  $[\text{M}+\text{H}]^+$ , 1761.1432 and for  $\text{C}_{112}\text{H}_{148}\text{N}_{10}\text{O}_8$ :  $[\text{M}+2\text{H}]^{2+}$ , 881.0752.

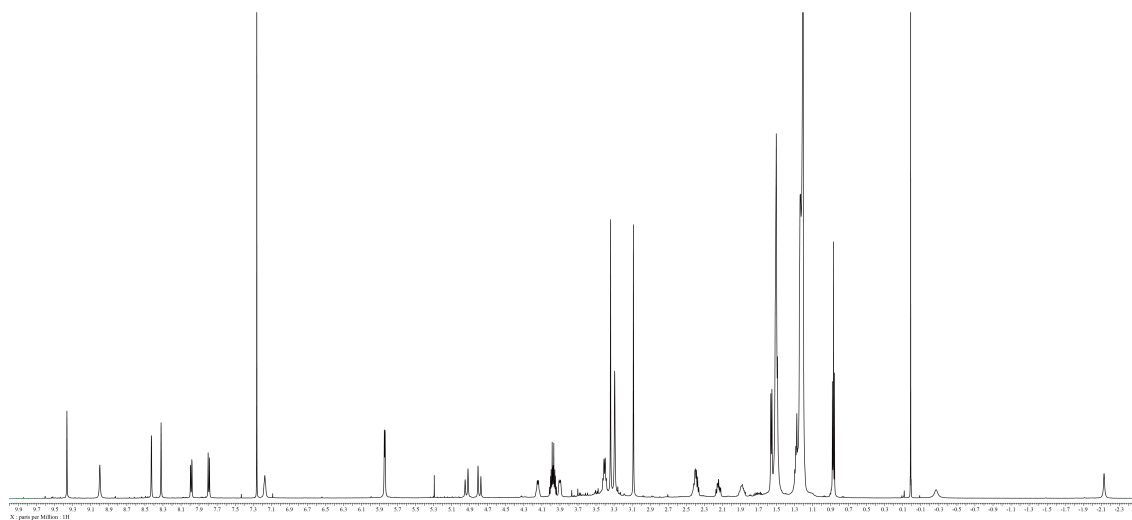


**Figure S5.**  $^1\text{H NMR}$  spectrum of **D-2,6** in  $\text{CDCl}_3$ .

#### S4-6. Synthesis of **D-2,7**

**D-2,7** was obtained by the same procedure of **D-1,3** synthesis (Section 3-1) using stearyl 3-aminomethyl-pyropheophorbide-*a* (30.0 mg, 38.0  $\mu\text{mol}$ ), 2,7-naphthalenedicarboxylic acid dichloride (4.7 mg, 19  $\mu\text{mol}$ ),  $\text{Et}_3\text{N}$  (26.4  $\mu\text{L}$ , 189  $\mu\text{mol}$ ), and DCM (10 mL). Yield: 62% (20.3 mg, 11.5  $\mu\text{mol}$ ).

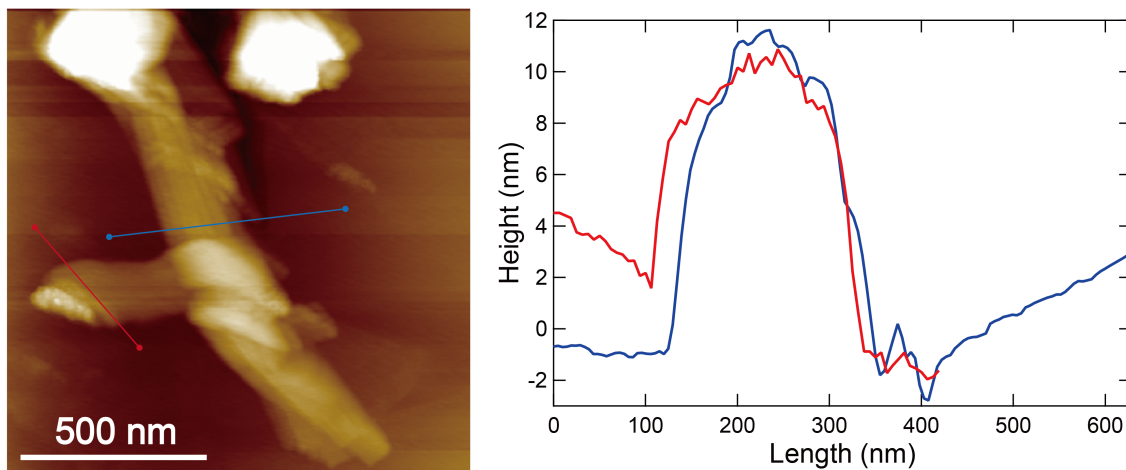
UV-vis ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}/\text{nm} = 665$  ( $\epsilon = 1.0 \times 10^5$ ), 608 ( $1.5 \times 10^4$ ), 537 ( $1.7 \times 10^4$ ), 506 ( $1.9 \times 10^4$ ), 411 ( $1.9 \times 10^5$ ), 398 ( $1.5 \times 10^5$ ), 382 ( $1.1 \times 10^5$ ), 320 ( $4.0 \times 10^4$ );  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 600 MHz)  $\delta/\text{ppm} = 9.37$  (2H, s, 5-H $\times 2$ ), 9.00 (2H, s, 1,8-H of naphthalene), 8.43 (2H, s, 10-H $\times 2$ ), 8.32 (2H, s, 20-H $\times 2$ ), 8.00 (2H, d,  $J = 8$  Hz, 3,6-H of naphthalene), 7.79 (2H, d,  $J = 8$  Hz, 4,5-H of naphthalene), 7.18 (2H, br, 3<sup>1</sup>-NH $\times 2$ ), 5.84 (4H, d,  $J = 5$  Hz, 3-CH $_2 \times 2$ ), 4.93, 4.79 (each 2H, d,  $J = 19$  Hz, 13<sup>1</sup>-CH $_2 \times 2$ ), 4.15 (2H, br-q,  $J = 7$  Hz, 18-H $\times 2$ ), 4.02–3.94 (4H, m, 17<sup>2</sup>-COOCH $_2 \times 2$ ), 3.90 (2H, br-d,  $J = 8$  Hz, 17-H $\times 2$ ), 3.41 (4H, q,  $J = 8$  Hz, 8-CH $_2 \times 2$ ), 3.34 (6H, s, 2-CH $_3 \times 2$ ), 3.29 (6H, s, 7-CH $_3 \times 2$ ), 3.09 (6H, s, 12-CH $_3 \times 2$ ), 2.46–2.32, 2.19–2.10, 1.94–1.83 (4H+2H+2H, each m, 17-CH $_2\text{CH}_2 \times 2$ ), 1.56 (6H, d,  $J = 7$  Hz, 18-CH $_3 \times 2$ ), 1.29–1.19 (10H, m, 8<sup>1</sup>-CH $_3 \times 2$ , 17<sup>2</sup>-COOCCH $_2 \times 2$ ), 1.29–1.17 (60H, m, 17<sup>2</sup>-COOC $_2(\text{CH}_2)_{15} \times 2$ ), 0.87 (6H, t,  $J = 7$  Hz, 17<sup>2</sup>-COOC $_{17}\text{CH}_3 \times 2$ ), -0.27, -2.13 (each 2H, br-s, NH $\times 4$ ); HRMS (ESI) found:  $m/z = 1761.1432$ , calcd for  $\text{C}_{112}\text{H}_{147}\text{N}_{10}\text{O}_8$ :  $[\text{M}+\text{H}]^+$ , 1761.1432.



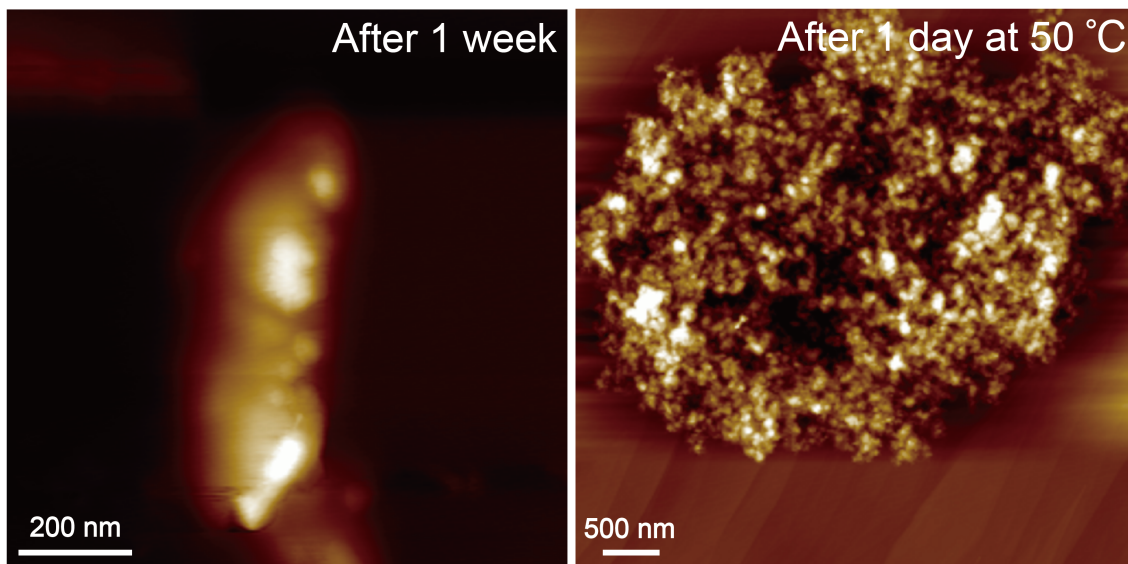
**Figure S6.**  $^1\text{H}$  NMR spectrum of **D-2,7** in  $\text{CDCl}_3$ .

## S5. Additional Experimental Data

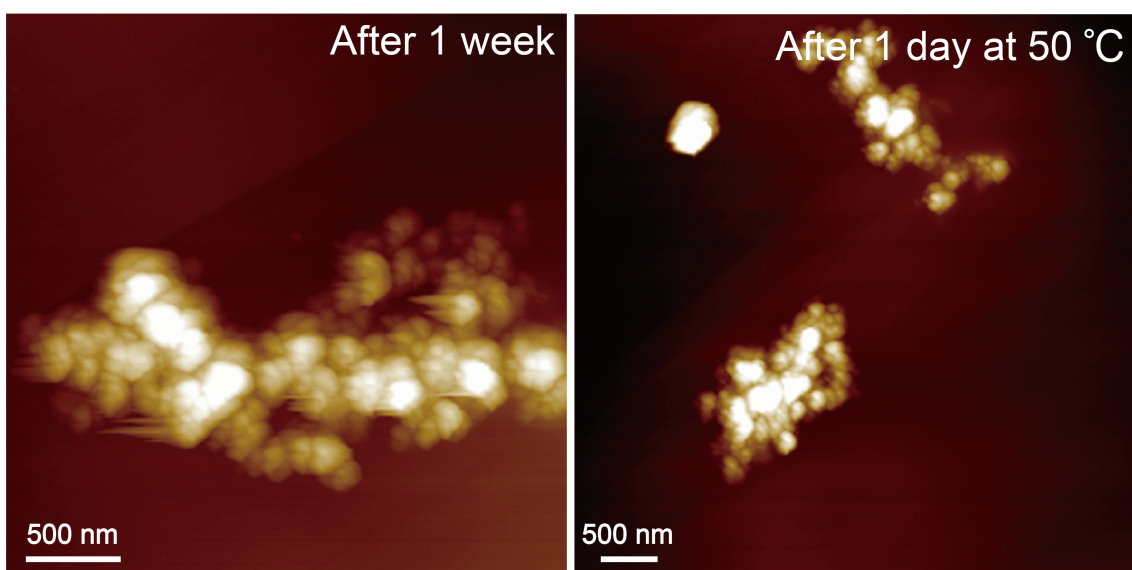
### S5-1. AFM Images



**Figure S7.** AFM image of **D-1,6** aggregates after standing the dispersion for 1 day on an HOPG substrate (left) and height profiles of **D-1,6** aggregates.

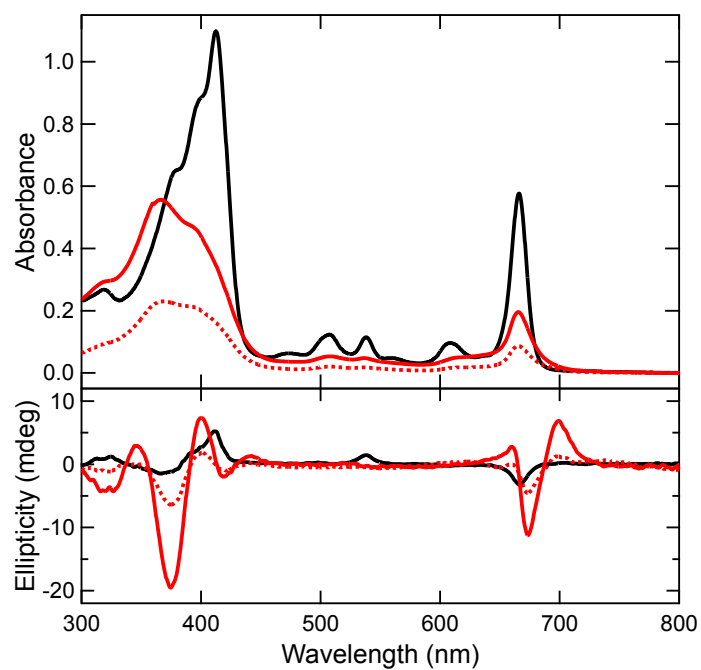


**Figure S8.** AFM images of **D-1,5** aggregates after standing the dispersion for 1 week at rt (left) and 1 day at 50 °C on an HOPG substrate (right).

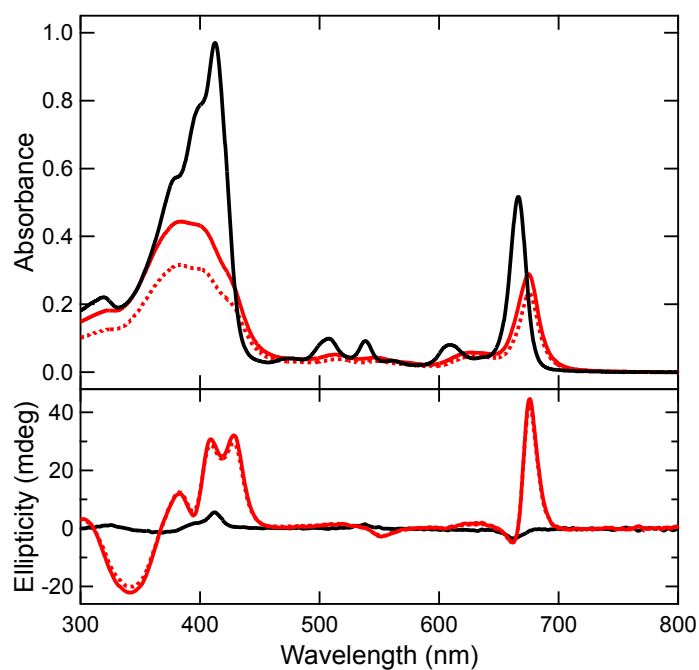


**Figure S9.** AFM images of **D-2,6** aggregates after standing the dispersion for 1 week at rt (left) and 1 day at 50 °C on an HOPG substrate (right).

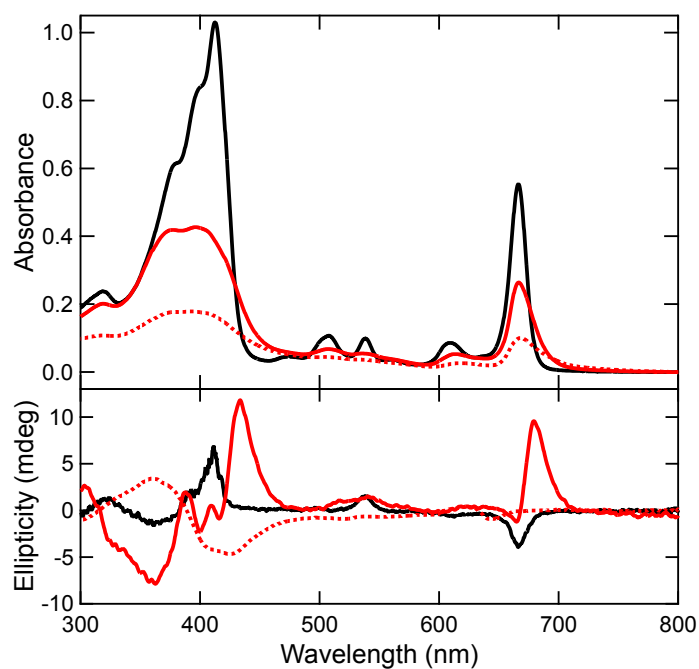
*S5-2. UV-vis absorption and CD spectra*



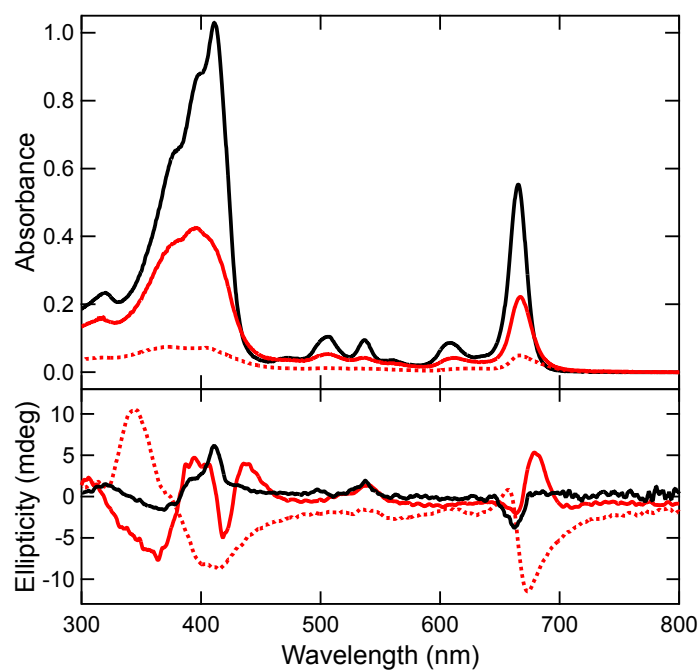
**Figure S10.** UV-vis absorption (upper) and CD spectra (lower) of **D-1,3** in  $\text{CHCl}_3$  (black) and 5%  $\text{CHCl}_3$ -hexane (red) just after preparation (solid lines) and after standing the dispersion for 1 day (dotted lines).



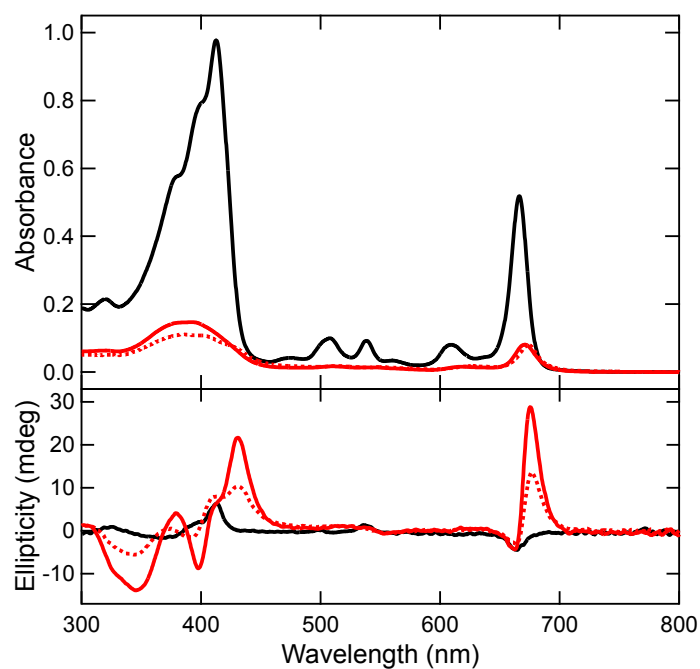
**Figure S11.** UV-vis absorption (upper) and CD spectra (lower) of **D-1,5** in CHCl<sub>3</sub> (black) and 5%CHCl<sub>3</sub>-hexane (red) just after preparation (solid lines) and after standing the dispersion for 1 day (dotted lines).



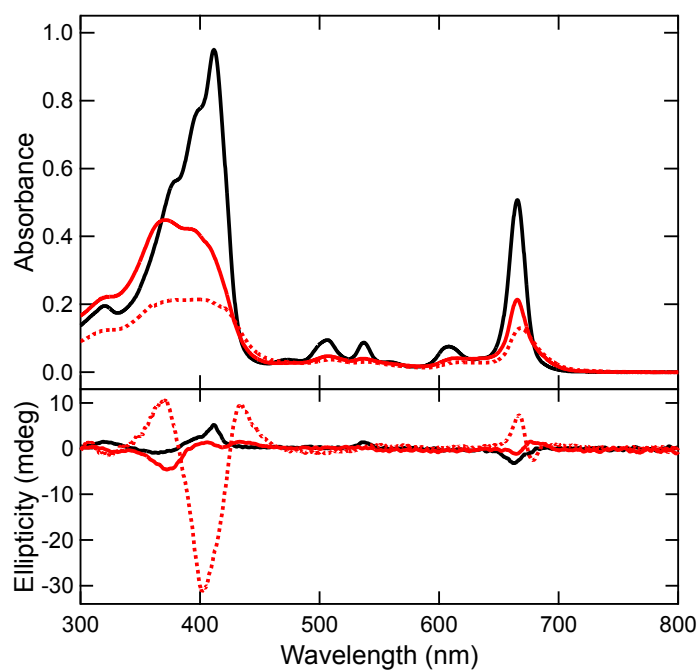
**Figure S12.** UV-vis absorption (upper) and CD spectra (lower) of **D-1,6** in CHCl<sub>3</sub> (black) and 5%CHCl<sub>3</sub>-hexane (red) just after preparation (solid lines) and after standing the dispersion for 1 day (dotted lines).



**Figure S13.** UV-vis absorption (upper) and CD spectra (lower) of **D-1,7** in CHCl<sub>3</sub> (black) and 5%CHCl<sub>3</sub>-hexane (red) just after preparation (solid lines) and after standing the dispersion for 1 day (dotted lines).

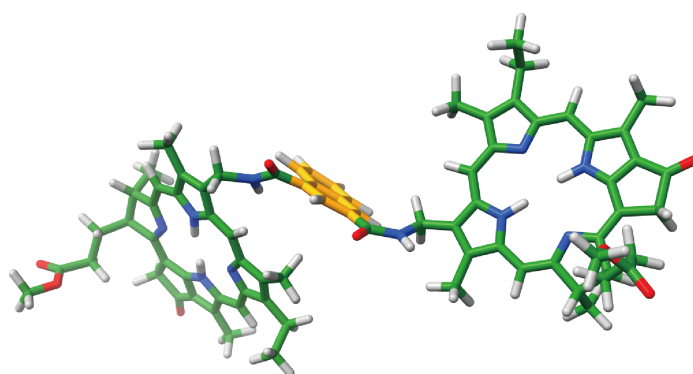


**Figure S14.** UV-vis absorption (upper) and CD spectra (lower) of **D-2,6** in CHCl<sub>3</sub> (black) and 5%CHCl<sub>3</sub>-hexane (red) just after preparation (solid lines) and after standing the dispersion for 1 day (dotted lines).

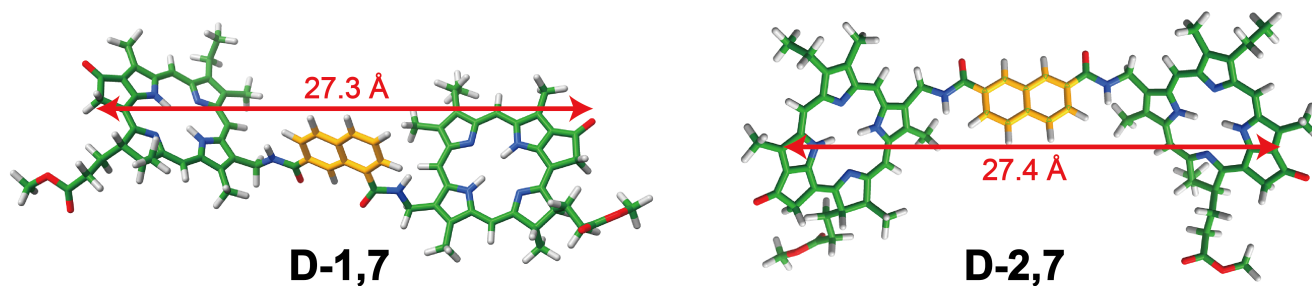


**Figure S15.** UV-vis absorption (upper) and CD spectra (lower) of **D-2,7** in CHCl<sub>3</sub> (black) and 5%CHCl<sub>3</sub>-hexane (red) just after preparation (solid lines) and after standing the dispersion for 1 day (dotted lines).

### S5-3. Molecular models

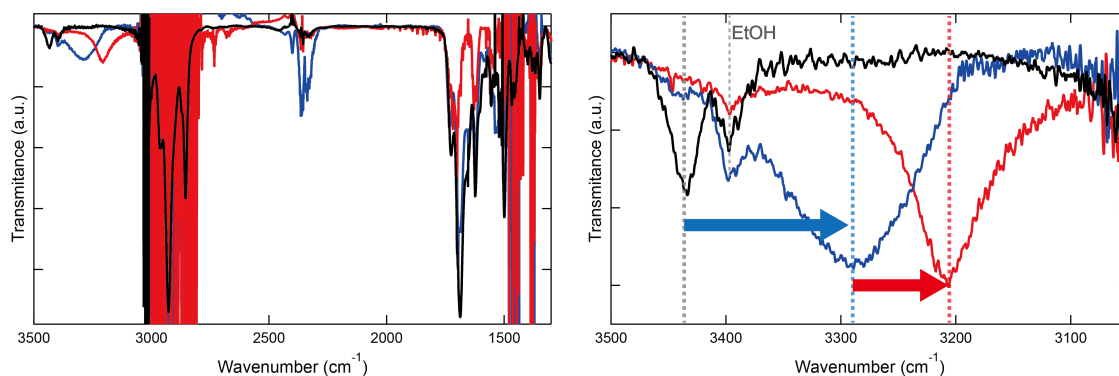


**Figure S16.** Energy-minimized molecular structure of a simplified **D-1,3** model by MM2 calculation. The stearyl esters at the 17<sup>2</sup>-position of the chlorophyll moieties were replaced by the methyl esters for the purposes of the calculation.

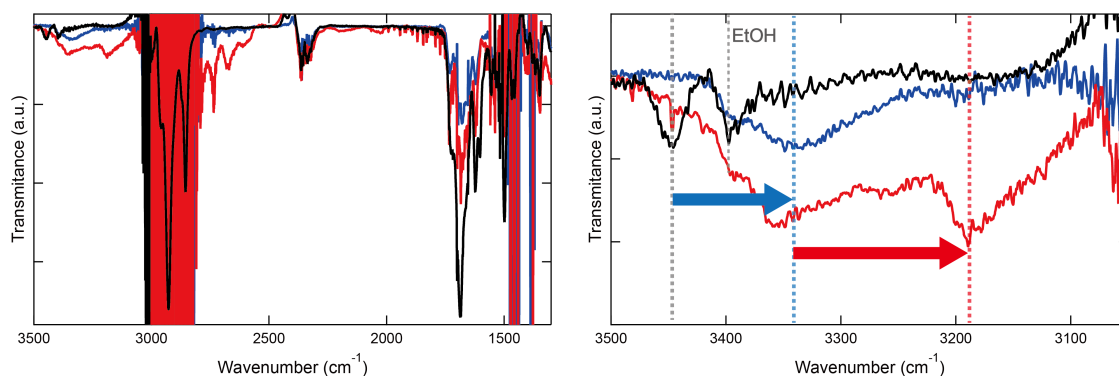


**Figure S17.** Energy-minimized molecular structures of simplified **D-1,7** (left) and **D-2,7** models (right) by MM2 calculation. The stearyl esters at the 17<sup>2</sup>-position of the chlorophyll moieties were replaced by the methyl esters for the purposes of the calculation.

#### S5-4. FT-IR spectra



**Figure S18.** FT-IR spectra of **D-1,7** in  $\text{CHCl}_3$  (black) and 5%  $\text{CHCl}_3$ –hexane just after preparation (blue) and after standing the dispersion for 1 day (red).



**Figure S19.** FT-IR spectra of **D-2,7** in  $\text{CHCl}_3$  (black) and 5%  $\text{CHCl}_3$ –hexane just after preparation (blue) and after standing the dispersion for 1 day (red).