Electronic Supplementary Information

Dimerization-Enhanced Aggregation of Chlorophyll into Helical Supramolecular Polymers

Ryo Kudo,[‡a] Ryuichi Kawai,[‡a] Sho Takamiya,[‡a] Sougata Datta,[b] Hiroki Hanayama,[c] Nobuyuki Hara,[d,e] Hitoshi Tamiaki,[d] and Shiki Yagai[*b,c]

a. Division of Advanced Science and Engineering, Graduate School of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan.
b. Institute for Advanced Academic Research (IAAR), Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan.
c. Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan.
d. Graduate School of Life Sciences, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan.
e. Department of Chemistry, College of Humanities & Sciences, Nihon University, Setagaya-ku, Tokyo 156-8550, Japan

E-mail: yagai@faculty.chiba-u.jp
Fax: +81-(0)43-290-3401
Tel: +81-(0)43-290-3169

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1. Materials and Methods

General. Column chromatography was performed using spherical neutral silica gel (particle size: 63–210 μm, Kanto Chemical Co. Inc.). All starting materials and reagents were purchased from commercial suppliers and used without further purification. The methylcyclohexane (MCH) and tetrahydrofuran (THF) for spectroscopic analyses were all spectral grade (Kanto Chemical Co. Inc.) and used without further purification. Gel permeation chromatography (GPC) was performed with recycling preparative liquid chromatograohy (LC-9225NEXT, Japan Analytical Industry) equipped with two GPC columns (JAIGEL-2HR Plus and JAIGEL-2.5HR Plus). ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ at 20 °C on a Bruker AVANCE III-400M NMR spectrometer or a Bruker AVANCE III-500M NMR spectrometers. ^{1}H NMR chemical shifts reported in parts per million (ppm, δ) were referenced to the chemical shifts of tetramethylsilane (TMS) at 0.00 ppm. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), qui (quintet), brs (broad singlet), dd (double doublet), dt (double triplet), dq (double quartet) and m (multiplet). ^{13}C NMR chemical shifts reported in δ (in ppm) were referenced to the chemical shifts of $CDCl_3$ at 77.16 ppm. High-resolution mass spectra (HRMS) were measured on an Exactive (Thermo Scientific) using atmospheric pressure chemical ionization (APCI) or electrospray ionization (APCI). Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was conducted on Bruker ultrafleXtreme mass spectrometer. Fourier transform infrared (FT-IR) spectra were measured on a JASCO FT-IR-4600 spectrometer using a 1.0 mm pathlength KBr cell. Molecular mechanics calculations were performed on MacroModel/Maestro version 12.2 (Schrödinger) with OPLS2005 force field without solvent.

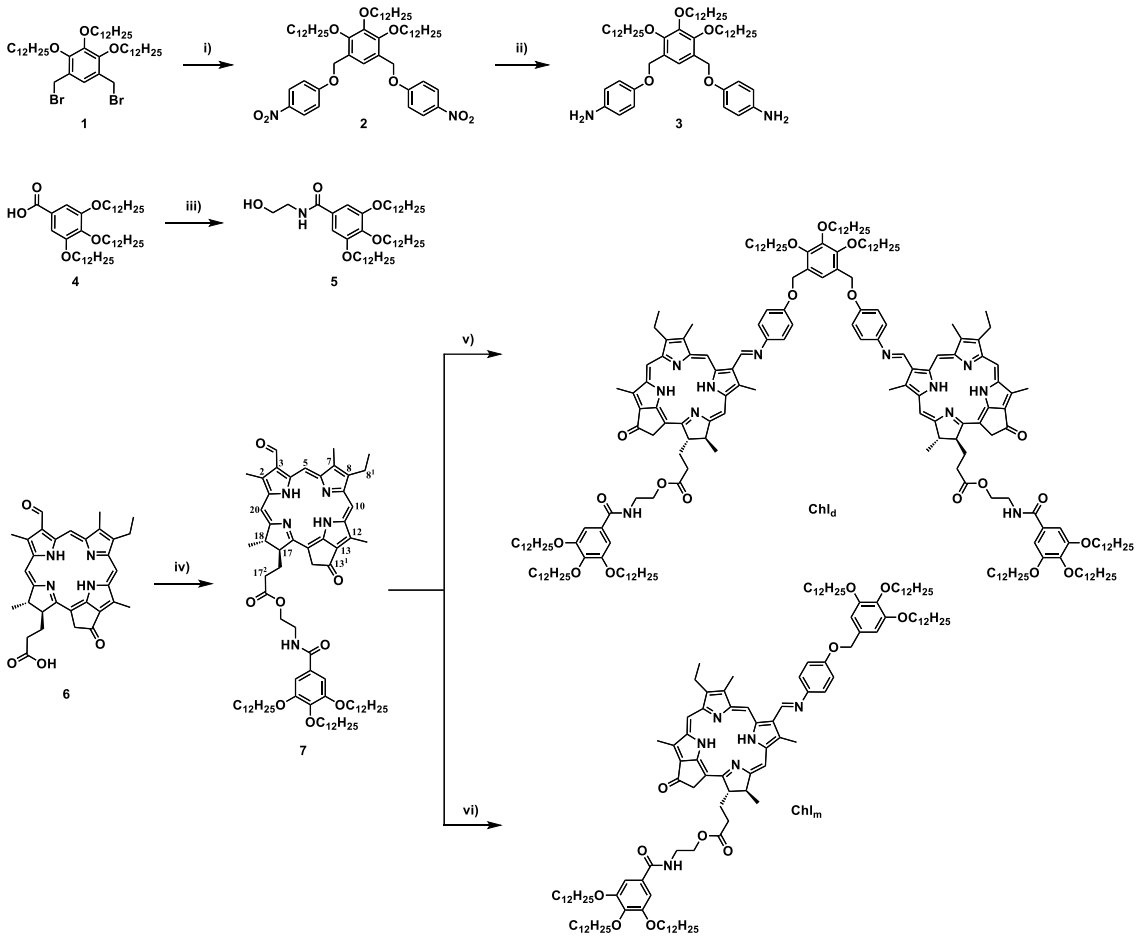
Ultraviolet/visible (UV/Vis) absorption and circular dichroism (CD) spectra. UV/Vis absorption spectra were recorded on a JASCO V760 spectrophotometer equipped with a JASCO ETCS-761 temperature-control unit. Circular dichroism (CD) spectra were recorded on a JASCO J820 spectropolarimeter equipped with a JASCO PTC-423L temperature-control unit. These spectra were recorded using a screw-capped quartz cuvette of 1.0 mm pathlength.

Atomic force microscopy (AFM). AFM images were obtained under ambient conditions using a Multimode 8 Nanoscope V (Bruker AXS) in Peak Force Tapping (ScanAsyst) mode. The scan rate was set to 0.996 Hz. Silicon cantilevers (SCANASYST-AIR) with a spring constant of 0.4 N/m and a frequency of 70 kHz (nominal value, Bruker, Japan) were used. The samples were prepared by spin-coating (3000 rpm, 1 min) approximately 10 μL of MCH solutions of assemblies onto freshly cleaved highly oriented pyrolytic graphite (HOPG, 0.5 cm × 0.5 cm) at room temperature. AFM images were processed using NanoScope Analysis 3.0 (Bruker).

2. Synthesis and Characterization

2-1. Synthesis of $\mathbf{Chl_d}$ and $\mathbf{Chl_m}$

$\mathbf{Chl_d}$ and $\mathbf{Chl_m}$ were synthesized by the following procedure as shown in Scheme S1. Synthesis of **1**,[S1] **4**,[S2] and **6**[S3] were reported previously.



Scheme S1. Synthesis of $\mathbf{Chl_d}$ and $\mathbf{Chl_m}$. Reagents and conditions: i) 4-nitrophenol, K_2CO_3, DMF, 70 °C; ii) zinc powder, CH_2Cl_2/AcOH, r.t.; iii) 2-aminoethanol, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl), *N,N′*-dimethyl-4-aminopyridine (DMAP), CH_2Cl_2, r.t.; iv) **5**, EDC·HCl, DMAP, CH_2Cl_2, r.t.; v) **3**, CH_2Cl_2/EtOH, 70 °C; vi) 4-((3,4,5-tris(dodecyloxy)benzyl)oxy)aniline, CH_2Cl_2/EtOH, 70 °C.

2: Compound **1** (535 mg, 0.655 mmol), 4-nitrophenol (228 mg, 1.64 mmol), and K_2CO_3 (272 mg, 1.96 mmol) were suspended in 8 mL of dry DMF, and the mixture was stirred for 5 h at 70 °C under N_2 atmosphere. After cooling to room temperature, the mixture was poured into cold water, and the solution was acidified with aqueous HCl (2 M) solution.

The resulting precipitates were collected by suction filtration and washed with water and then cold acetone. The residue was purified by column chromatography over silica gel (eluent: *n*-hexane/$CHCl_3$ = 30/70, v/v%) and further purified by recrystallization with acetone to give **2** as a white solid (311 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, see Chart S1): δ = 8.21, 7.03 (dd, J = 2.2, 9.3 Hz, each 4H, C_6H_4 × 2), 7.21 (s, 1H, C_6H), 5.11 (s, 4H, C_6H–CH_2 × 2), 4.09, 4.01 (t, J = 6.6 Hz, 4H + 2H, –OCH_2 × 3), 1.78–1.67 (m, 6H, –OCH_2CH_2 × 3), 1.47–1.22 (m, 54H, –$O(CH_2)_2(CH_2)_9CH_3$ × 3), 0.90–0.86 (m, 9H, –$O(CH_2)_{11}CH_3$ × 3). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C, see Chart S2): δ = 163.73, 152.47, 145.81, 141.61, 125.97, 124.56, 124.48, 114.65, 74.35, 73.81, 65.90, 31.96, 31.94, 30.37, 29.76, 29.71, 29.68, 29.65, 29.58, 29.51, 29.42, 29.39, 26.17, 22.72, 14.16. HRMS (APCI): *m/z* calcd. for $C_{56}H_{89}O_9N_2$, 933.6563 $[M+H]^+$, found 933.6555.

3: To a solution of compound **2** (147 mg, 0.158 mmol) in a mixture of dry CH_2Cl_2 (12 mL) and AcOH (4 mL) at room temperature, zinc powder (317 mg, 4.85 mmol) was added portion-wise, and the reaction mixture was stirred vigorously for 3 h at room temperature under N_2 atmosphere. The oxide film covering zinc was removed by sonicating in an aqueous HCl (2 M) solution before use. The mixture was filtrated through a short pad of Celite® and the cake was washed with CH_2Cl_2. The filtrate was washed with saturated $NaHCO_3$ solution. The organic layer was dried over Na_2SO_4, filtrated, and evaporated *in vacuo*. The residue was purified by column chromatography over silica gel (eluent: $CHCl_3$/EtOAc = 95/5→60/40, v/v%) to give **3** as dark brown oil (106 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, see Chart S3): δ = 7.28 (s, 1H, C_6H), 6.81, 6.64 (dd, J = 2.3, 8.8 Hz, each 4H, C_6H_4 × 2), 4.93 (s, 4H, C_6H–CH_2 × 2), 4.04–3.98 (m, 6H, –O$CH_2(CH_2)_{10}CH_3$ × 3), 3.42 (brs, 4H, –NH_2 × 2), 1.78–1.68 (m, 6H, –$OCH_2CH_2(CH_2)_9CH_3$ × 3), 1.46–1.25 (m, 54H, –$O(CH_2)_2(CH_2)_9CH_3$ × 3), 0.90–0.86 (m, 9H, –$O(CH_2)_{11}CH_3$ × 3). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C, see Chart S4): δ = 152.21, 151.61, 145.68, 140.00, 126.35, 124.59, 116.38, 115.92, 74.28, 73.68, 65.89, 31.97, 30.41, 29.75, 29.71, 29.69, 29.61, 29.57, 29.42, 26.16, 22.74, 14.17. HRMS (APCI): *m/z* calcd for $C_{56}H_{93}O_5N_2$, 873.7079 $[M+H]^+$, found 873.7076.

5: Compound **4** (523 mg, 0.774 mmol), 2-aminoethanol (118 mg, 1.94 mmol), and DMAP (94 mg, 0.77 mmol) were dissolved in 6 mL of dry CH_2Cl_2 and sonicated for 5 min. To this mixture, EDC·HCl (208 mg, 1.08 mmol) was added portion-wise, and the mixture was stirred for 15 h at room temperature. The reaction mixture was diluted with $CHCl_3$ and washed with cold aqueous HCl (2 M) solution and then brine. The organic layer was dried over Na_2SO_4, filtrated, and evaporated *in vacuo*. The residue was purified by column chromatography over silica gel (eluent: $CHCl_3$/EtOAc = 97/3→90/10, v/v%) to give **5** as a pale-yellow solid (364 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, see Chart S5): δ = 6.97 (s, 2H, C_6H_2), 6.48 (t, J = 5.6 Hz, 1H, –CONH–), 4.03–3.97 (m, 6H, –O$CH_2(CH_2)_{10}CH_3$ × 3), 3.84 (t, J = 4.8 Hz, 2H, –CONHCH_2–), 3.64–3.60 (m, 2H, –$CONHCH_2CH_2$–), 2.57 (brs, 1H, –OH), 1.84–1.70 (m, 6H, –$OCH_2CH_2(CH_2)_9CH_3$ × 3), 1.48–1.23 (m, 54H, –$O(CH_2)_2(CH_2)_9CH_3$ × 3), 0.90–0.86 (m, 9H, –$O(CH_2)_{11}CH_3$ × 3).

^{13}C NMR (100 MHz, $CDCl_3$, 20 °C, see Chart S6): δ = 168.65, 153.04, 141.11, 128.93, 105.64, 73.51, 69.27, 62.21, 42.99, 31.95, 30.34, 29.78, 29.77, 29.74, 29.72, 29.69, 29.62, 29.46, 29.42, 29.40, 29.38, 26.12, 22.72, 14.13. HRMS (APCI): *m/z* calcd for $C_{45}H_{84}O_5N$, 718.6344 $[M+H]^+$, found 718.6340.

7: Using a procedure similar to that for **5**, compound **7** was obtained as a black solid in 67% yield (258 mg) from compound **5** (237 mg, 0.330 mmol), compound **6** (166 mg, 309 mmol), DMAP (27 mg, 0.22 mmol), and EDC·HCl (97 mg, 0.51 mmol) in 15 mL of dry CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, see Chart S7): δ = 11.54 (s, 1H, 3-C*H*O), 10.30 (s, 1H, 5-*H*), 9.59 (s, 1H, 10-*H*), 8.81 (s, 1H, 20-*H*), 6.87 (s, 2H, C_6H_2), 6.36 (t, *J* = 5.6 Hz, 1H, –CON*H*–), 5.33, 5.17 (d, *J* = 20 Hz, each 1H, 13^1-CH_2), 4.54 (dq, *J* = 1.8, 7.2 Hz, 1H, 18-*H*), 4.37 (dt, *J* = 7.8, 2.1 Hz, 1H, 17-*H*), 4.29–4.18 (m, 2H, 17^2-COOCH_2), 3.87–3.82 (m, 6H, –OCH_2(CH$_2$)$_{10}$CH$_3$ × 3), 3.76 (s, 3H, 2-CH_3), 3.71 (q, 2H, *J* = 7.6 Hz, 8-CH_2), 3.70 (s, 3H, 12-CH_3), 3.59 (q, *J* = 5.4 Hz, 2H, –CONHCH_2–), 3.31 (s, 3H, 7-CH_3), 2.75–2.56, 2.39–2.29 (m, each 2H, 17-CH_2CH_2), 1.82 (d, *J* = 7.3 Hz, 3H, 18-CH_3), 1.71 (t, *J* = 7.6 Hz, 3H, 8^1-CH_3), 1.68–1.55 (m, 6H, –OCH$_2$CH_2(CH$_2$)$_9$CH$_3$ × 3), 1.42–1.18 (m, 54H, –O(CH$_2$)$_2$(CH_2)$_9$CH$_3$ × 3), 0.89–0.84 (m, 9H, –O(CH$_2$)$_{11}$CH_3 × 3), −0.12, −2.06 (s, each 1H, pyrrole-N*H* × 2). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C, see Chart S8): δ = 195.99, 188.26, 173.44, 169.75, 167.56, 161.50, 155.16, 153.00, 152.34, 148.50, 144.90, 141.14, 140.72, 139.69, 138.30, 137.71, 134.02, 131.66, 130.03, 129.30, 129.00, 106.98, 105.61, 103.31, 99.90, 94.81, 73.40, 69.22, 63.42, 52.19, 49.56, 48.25, 39.61, 31.96, 31.93, 31.05, 30.26, 29.77, 29.74, 29.72, 29.68, 29.66, 29.61, 29.58, 29.42, 29.37, 29.34, 29.23, 26.04, 25.98, 23.36, 22.73, 22.71, 19.39, 17.37, 14.15, 12.10, 11.29, 11.20. HRMS (APCI): *m/z* calcd for $C_{77}H_{114}O_8N_5$, 1236.8662 $[M+H]^+$, found 1236.8648.

Chl$_d$: Compounds **3** (47 mg, 0.054 mmol) and compound **7** (202 mg, 0.163 mmol) were dissolved in a mixture of 5 mL of dry CH_2Cl_2 and 5 mL of dry EtOH at 70 °C and stirred for 24 h under N_2 atmosphere. After cooling to room temperature, solvent was evaporated *in vacuo*. The residue was purified by GPC (eluent: $CHCl_3$) to give **Chl$_d$** as a black solid (155 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, see Chart S9): δ = 10.43 (s, 2H, 3-C*H*O × 2), 9.78 (s, 2H, 5-*H* × 2), 9.26 (s, 2H, 10-*H* × 2), 8.26 (s, 2H, 20-*H* × 2), 7.68, 7.20 (dd, *J* = 8.9, 2.1 Hz, each 4H, C_6H_4 × 2), 7.42 (s, 1H, C_6H), 6.95 (s, 4H, C_6H_2 × 2), 6.69 (t, *J* = 5.6 Hz, 2H, –CON*H*– × 2), 5.26 (s, 4H, C_6H–CH_2 × 2), 5.21, 5.02 (d, *J* = 20 Hz, each 2H, 13^1-CH_2 × 2), 4.31–4.27 (m, 4H, 17-*H* × 2, 18-*H* × 2), 4.20–4.10, 3.88–3.84 (m, 22H, 17^2-COOCH_2 × 2, –OCH_2(CH$_2$)$_{10}$CH$_3$ × 9), 3.64 (q, *J* = 5.5 Hz, 4H, –CONHCH_2– × 2), 3.59 (s, 6H, 12-CH_3 × 2), 3.57–3.52 (m, 4H, 8-CH_2 × 2), 3.47 (s, 6H, 2-CH_3 × 2), 3.19 (s, 6H, 7-CH_3 × 2), 2.67–2.49, 2.36–2.29, 2.17–2.14 (m, 4H + 2H + 2H, 17-CH_2CH_2 × 2), 1.87–1.81 (m, 6H, 8^1-CH_3 × 2), 1.68 (d, *J* = 7.1 Hz, 6H, 18-CH_3 × 2), 1.65–1.49 (m, 18H, –OCH$_2$CH_2(CH$_2$)$_9$CH$_3$ × 9), 1.39–1.16 (m, 162H, –O(CH$_2$)$_2$(CH_2)$_9$CH$_3$ × 9), 0.90–0.77 (m, 27H, –O(CH$_2$)$_{11}$CH_3 × 9), −0.10, −2.27 (s, each 2H, pyrrole-N*H* × 4). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C, see Chart S10): δ = 196.21, 173.45, 170.23, 167.66, 160.24, 158.09, 155.58, 153.00, 152.18, 151.73, 151.20, 149.08, 148.60, 145.89, 145.74, 144.56, 141.07, 139.84, 138.25, 136.85, 135.12, 130.93, 130.47,

129.04, 128.39, 125.94, 123.95, 122.60, 115.76, 105.95, 105.67, 103.42, 100.36, 93.07, 74.34, 73.85, 73.40, 69.19, 65.77, 63.50, 51.71, 49.69, 48.11, 39.68, 31.99, 31.96, 31.93, 31.21, 30.57, 30.52, 30.27, 29.80, 29.76, 29.74, 29.71, 29.68, 29.65, 29.61, 29.58, 29.45, 29.42, 29.37, 29.34, 29.26, 26.30, 26.04, 26.00, 22.95, 22.75, 22.72, 22.71, 22.68, 19.35, 17.38, 14.15, 14.10, 11.97, 11.44, 11.17. HRMS (ESI): *m/z* calcd for $C_{210}H_{314}O_{19}N_{12}Na$, 3331.3865 $[M+Na]^+$, found 3331.3889.

Chl$_m$: Using a procedure similar to that for **Chl**, the reference monad **Chl$_m$** was obtained as a black solid in 73% yield (71 mg) from reaction of 4-((3,4,5-tris(dodecyloxy)benzyl)oxy)aniline (46 mg, 0.059 mmol) and **Chl-7** (61 mg, 0.049 mmol) in a mixture of 10 mL of dry CH_2Cl_2 and 12 mL of dry EtOH. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, see Chart S11): δ = 10.56 (s, 1H, 3-C*H*), 9.78 (s, 1H, 5-*H*), 9.46 (s, 1H, 10-*H*), 8.63 (s, 1H, 20-*H*), 7.65, 7.21 (d, *J* = 8.8 Hz, each 2H, C_6H_4), 6.89 (s, 2H, C_6H_2), 6.72 (s, 2H, C_6H_2), 6.44 (t, *J* = 5.5 Hz, 1H, –CON*H*–), 5.27, 5.10 (d, *J* = 20 Hz, each 1H, 13^1-CH_2), 5.09 (s, 2H, C_6H_4-OCH_2), 4.48 (dq, *J* = 7.1, 1.8 Hz, 1H, 17-*H*), 4.30 (dt, *J* = 8.8, 3.1 Hz, 1H, 18-*H*), 4.28–4.18 (m, 2H, 17^2-COOCH_2), 4.04, 3.99 (t + t, *J* = 6.5 Hz, 4H + 2H, $CH_2C_6H_2(OCH_2)_3$), 3.85 (t, *J* = 6.2 Hz, 6H, –NHCO$C_6H_2(OCH_2)_3$), 3.67 (q, *J* = 8.0 Hz, 2H, 8-CH_2), 3.62, 3.61 (s, each 3H, 2-CH_3, 12-CH_3), 3.58 (q, *J* = 5.4 Hz, 2H, –CONHCH_2–), 3.26 (s, 3H, 7-CH_3), 2.71–2.55, 2.36–2.29 (m, each 2H, 17-CH_2CH_2), 1.88–1.75, 1.70–1.59 (m, 18H, 8^1-CH_3, 18-CH_3, –OCH$_2$CH_2(CH$_2$)$_9$CH$_3$ × 6), 1.54–1.17 (m, 108H, –O(CH$_2$)$_2$(CH_2)$_9$CH$_3$ × 6), 0.90–0.84 (m, 18H, –O(CH$_2$)$_{11}$CH_3 × 6), 0.31, −1.79 (s, each 1H, pyrrole-N*H* × 2). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C, see Chart S12): δ = 196.18, 173.53, 170.63, 167.54, 160.50, 158.08, 155.80, 153.41, 152.99, 152.44, 151.54, 148.79, 145.86, 144.90, 141.08, 140.15, 138.57, 138.03, 137.14, 135.27, 131.78, 131.09, 130.83, 128.99, 128.83, 122.56, 115.66, 106.35, 106.20, 105.55, 103.84, 100.55, 93.61, 73.50, 73.40, 70.87, 69.19, 63.39, 51.79, 49.88, 48.16, 39.62, 31.98, 31.95, 31.93, 31.00, 30.40, 30.27, 29.81, 29.79, 29.77, 29.75, 29.74, 29.70, 29.66, 29.61, 29.59, 29.58, 29.49, 29.47, 29.44, 29.40, 29.37, 29.34, 29.23, 26.19, 26.17, 26.04, 25.99, 23.18, 22.74, 22.72, 22.70, 19.48, 17.45, 14.15, 12.08, 11.62, 11.26. HRMS (APCI): *m/z* calcd for $C_{126}H_{197}O_{11}N_6$, 1970.5035 $[M+H]^+$, found 1970.5035.

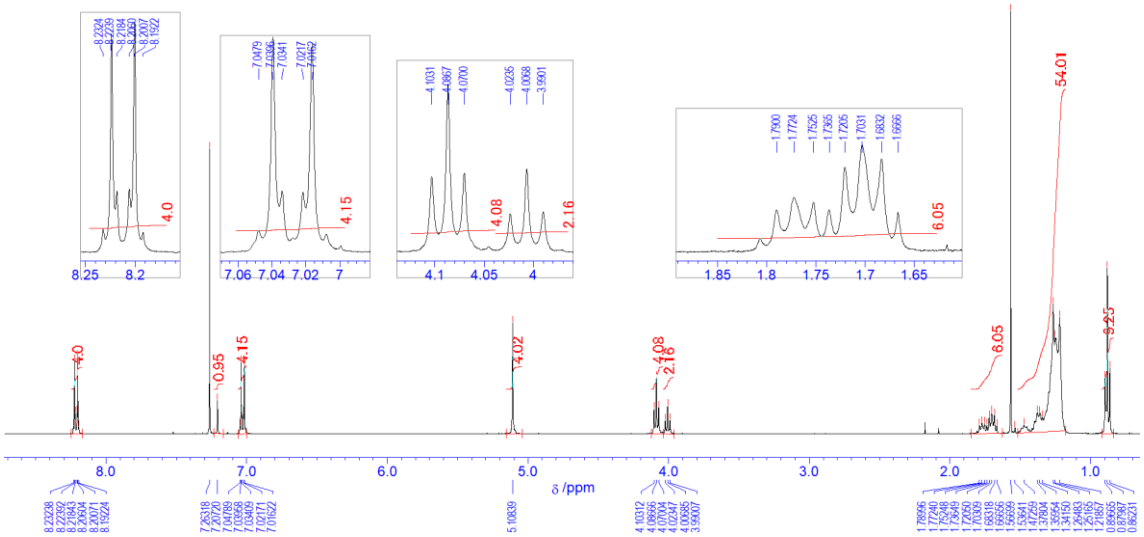


Chart S1. ^{1}H NMR spectrum of **2**.

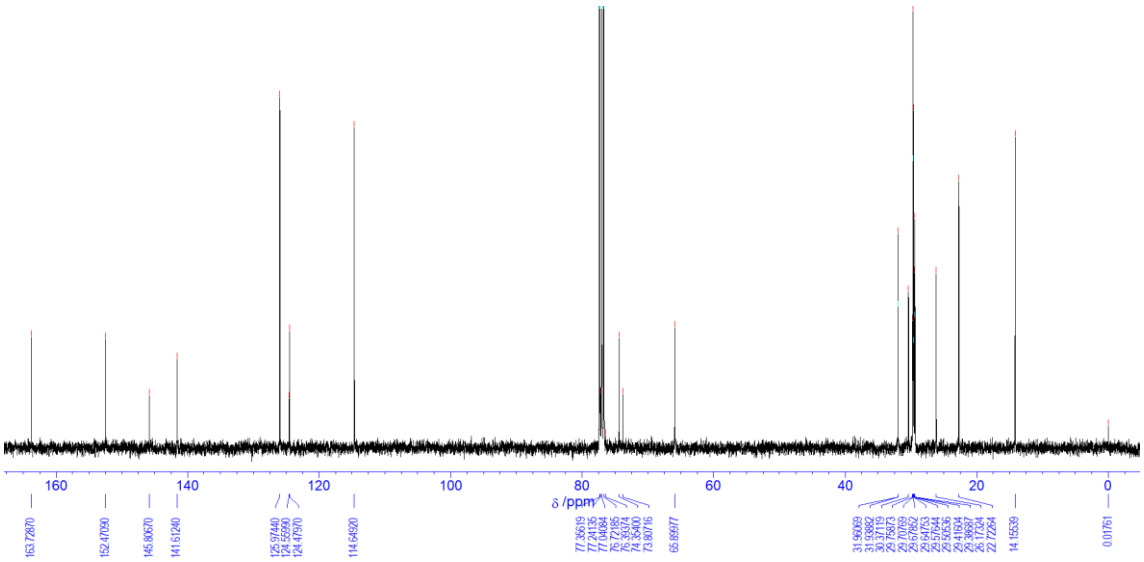


Chart S2. ^{13}C NMR spectrum of **2**.

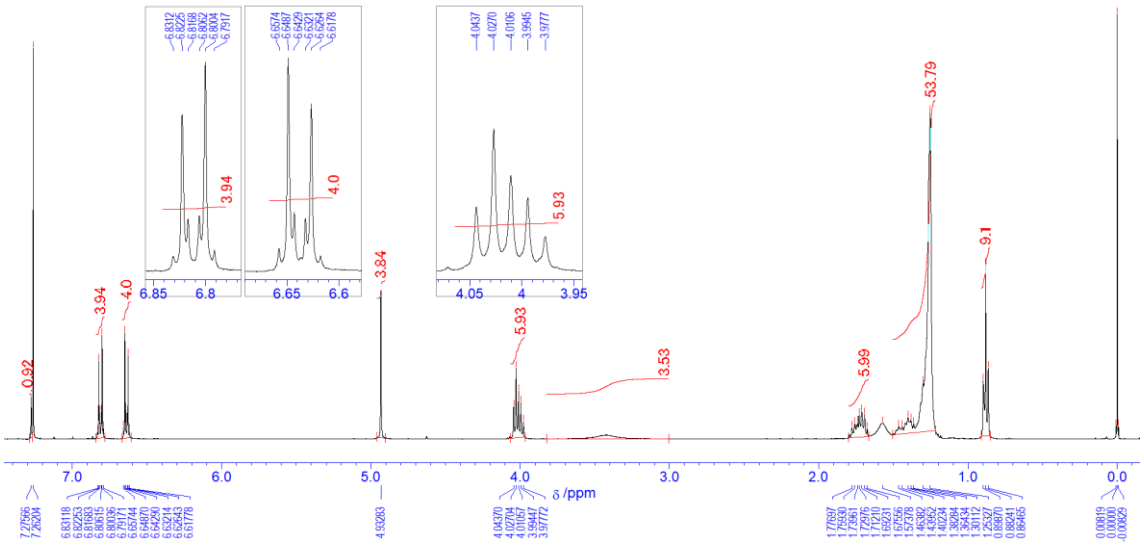


Chart S3. ^{1}H NMR spectrum of **3**.

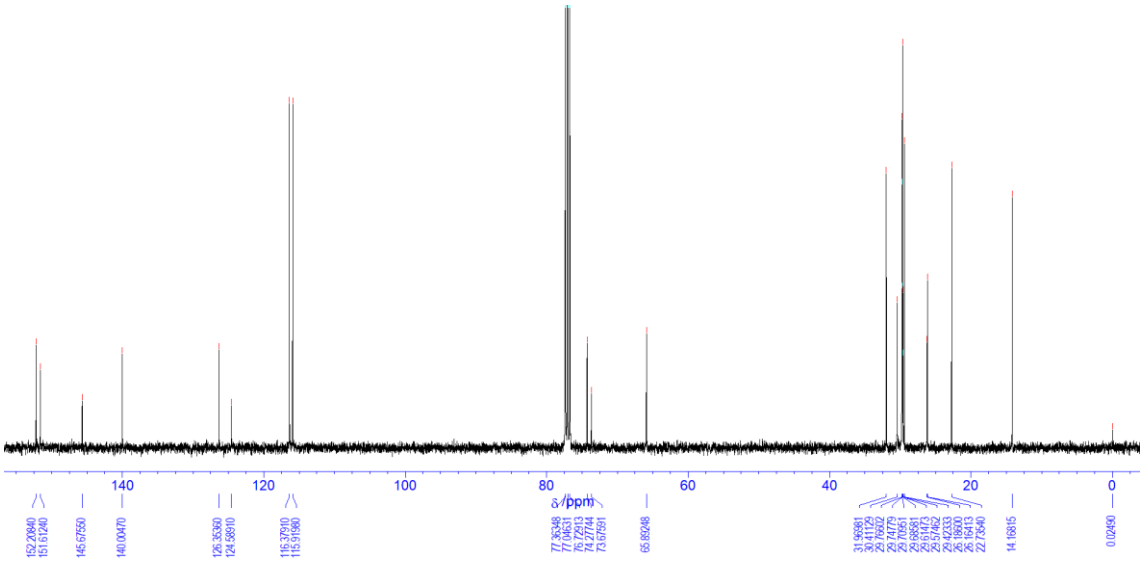


Chart S4. ^{13}C NMR spectrum of **3**.

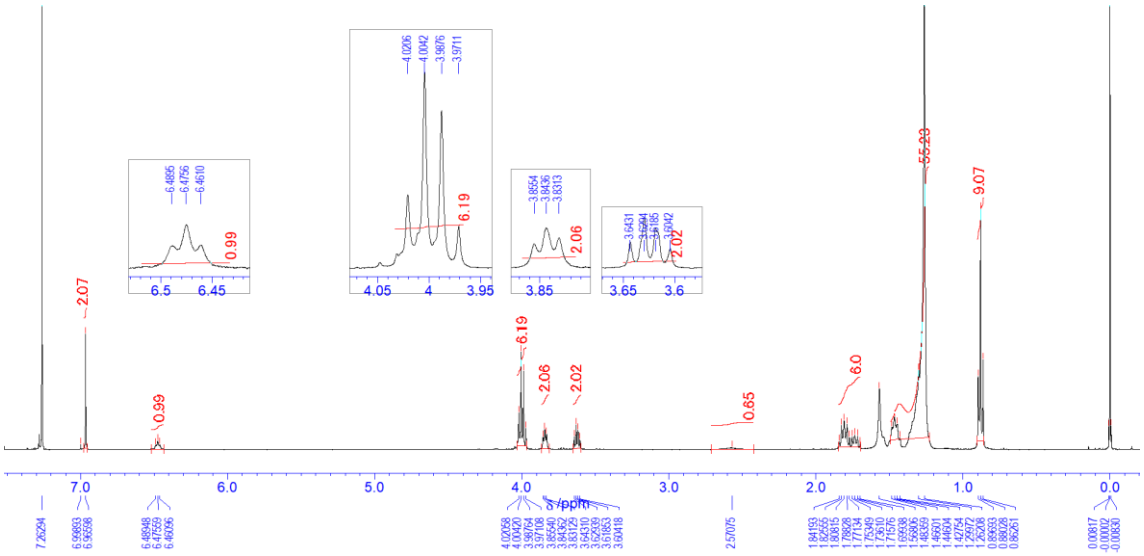


Chart S5. ^{1}H NMR spectrum of **5**.

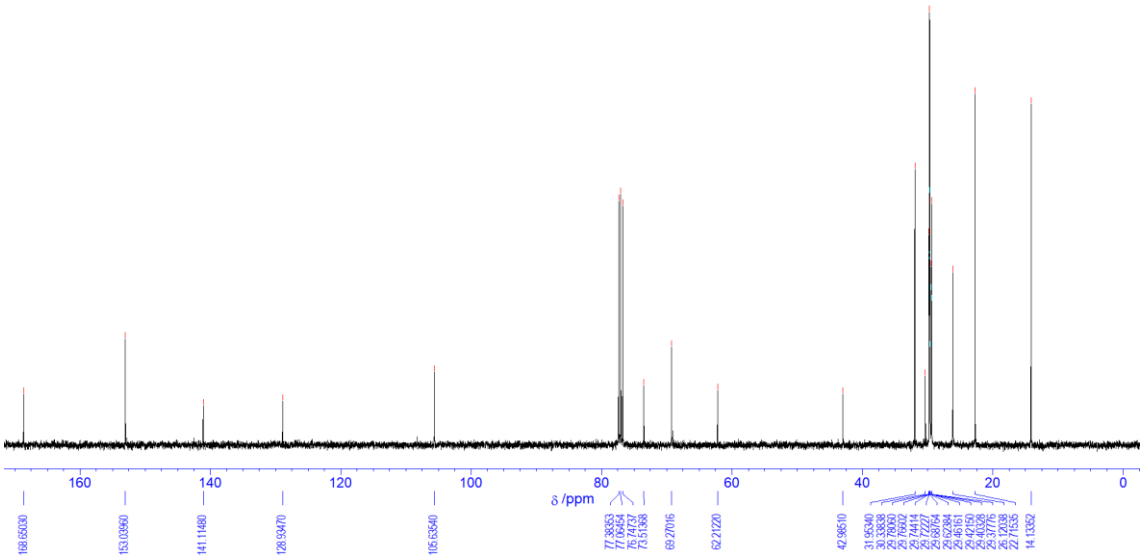


Chart S6. ^{13}C NMR spectrum of **5**.

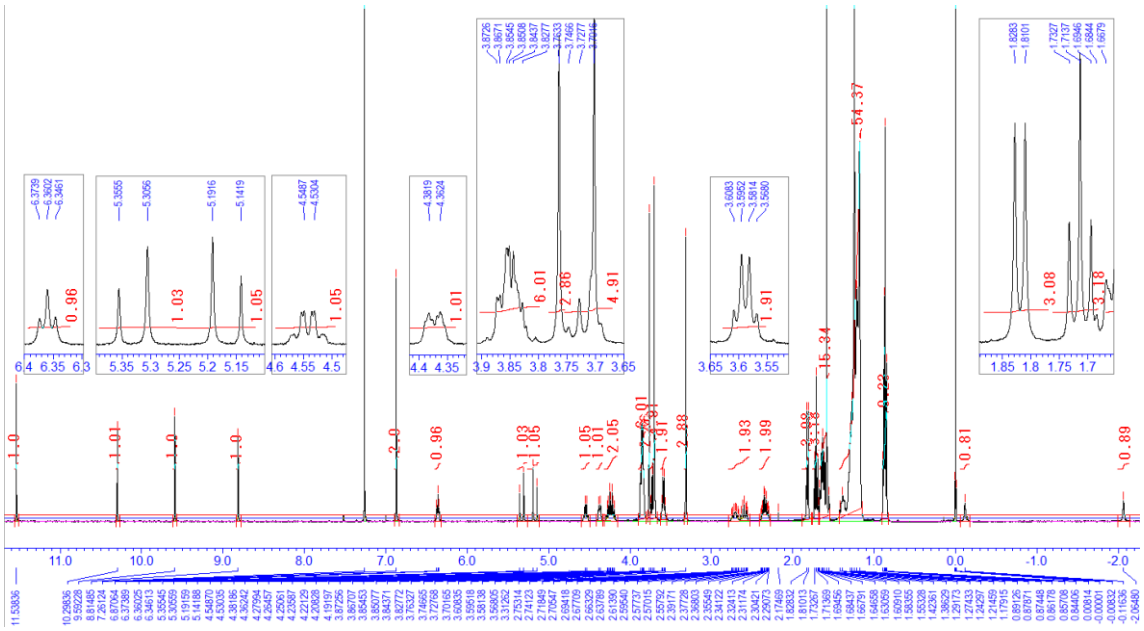


Chart S7. ^{1}H NMR spectrum of **7**.

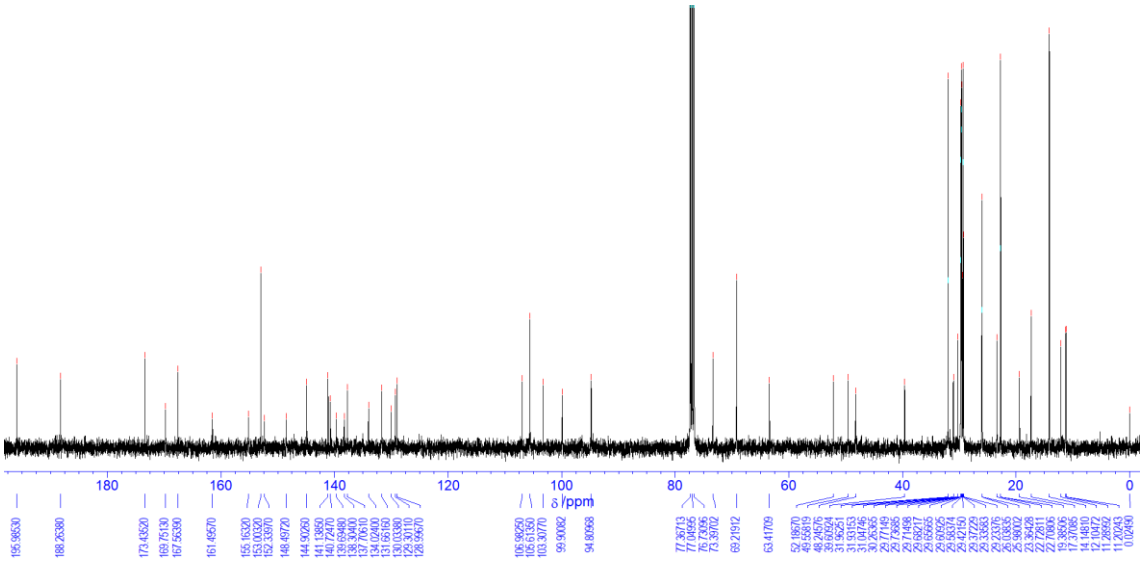


Chart S8. ^{13}C NMR spectrum of **7**.

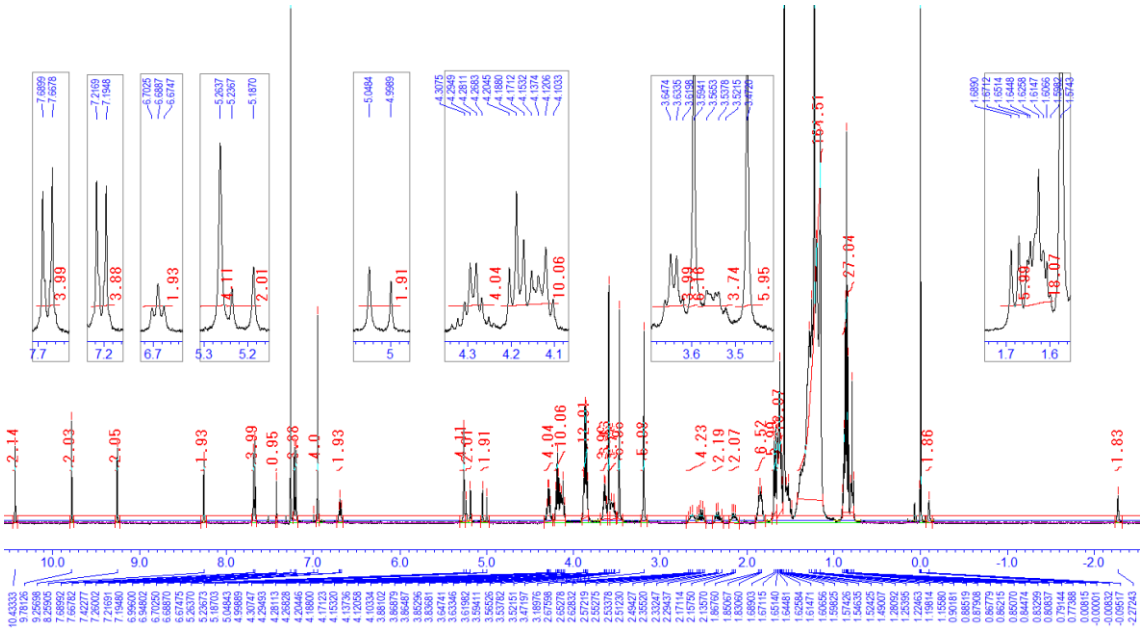


Chart S9. ^{1}H NMR spectrum of **Chl$_{d}$**.

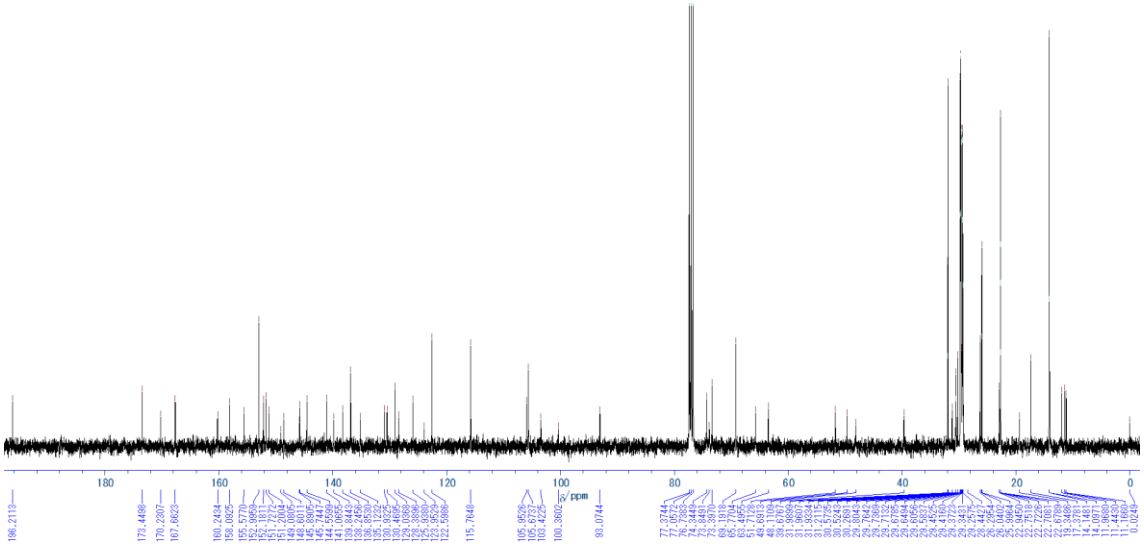


Chart S10. ^{13}C NMR spectrum of **Chl$_{d}$**.

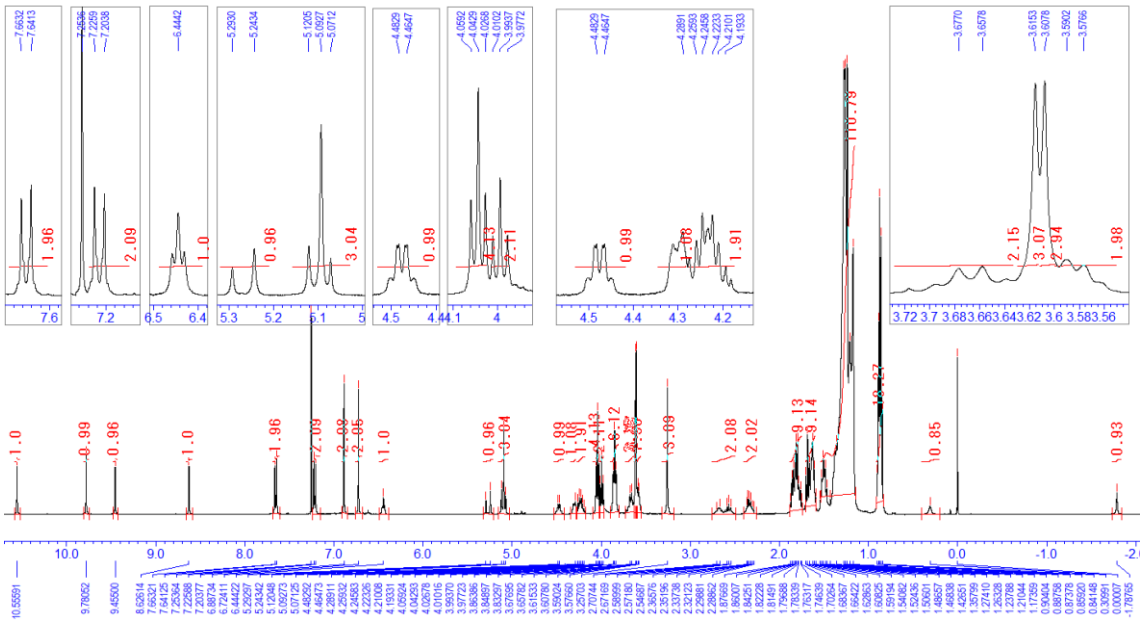


Chart S11. ^{1}H NMR spectrum of **Chl$_{m}$**.

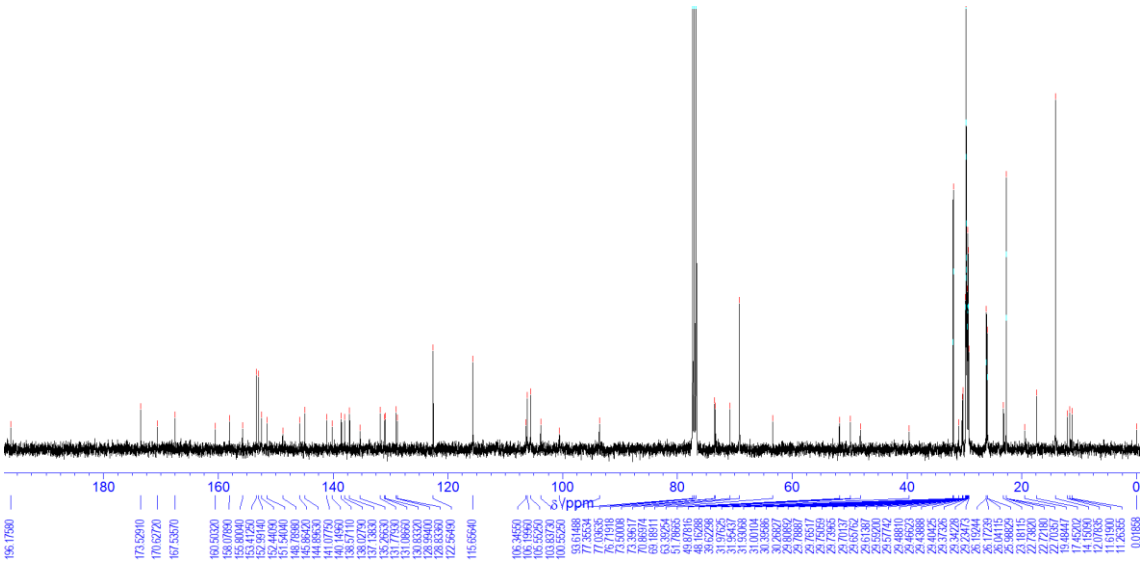
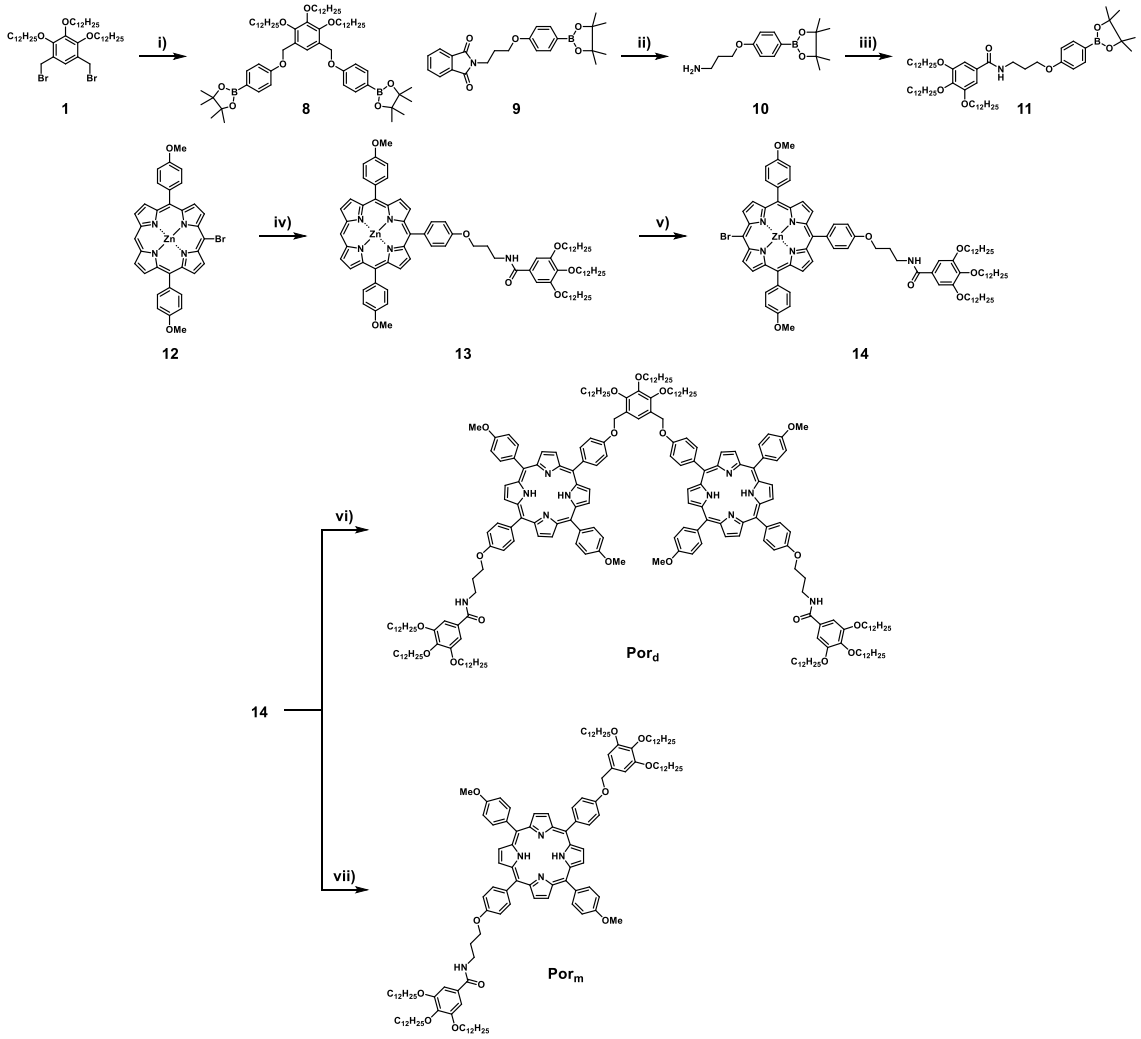


Chart S12. ^{13}C NMR spectrum of **Chl$_{m}$**.

2-2. Synthesis of $\mathbf{Por_d}$ and $\mathbf{Por_m}$

$\mathbf{Por_d}$ and $\mathbf{Por_m}$ were synthesized by the following procedure as shown in Scheme S2. Synthesis of compounds **1**,[S1] **9**,[S4] and **12**[S5] were reported previously.



Scheme S2. Synthesis of $\mathbf{Por_d}$ and $\mathbf{Por_m}$. Reagents and conditions: i) 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol, K_2CO_3, DMF, 80 °C; ii) hydrazine monohydrate, THF, reflux; iii) 3,4,5-tris(dodecyloxy)benzoic acid, EDC·HCl, DMAP, CH_2Cl_2, 25 °C; iv) **11**, $Pd(PPh_3)_4$, K_3PO_4, THF/water, 60 °C; v) *N*-bromosuccinimide (NBS), pyridine, $CHCl_3$; vi) **8**, $Pd(PPh_3)_4$, K_3PO_4, THF/water, 60 °C; vii) 4-((3,4,5-tris(dodecyloxy)benzyl)oxy)phenylboronic acid pinacol ester, $Pd(PPh_3)_4$, K_3PO_4, THF/water, 60 °C.

8: Compound **1** (565 mg, 0.412 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (275 mg, 1.25 mmol), and K_2CO_3 (290 mg, 2.10 mmol) were dissolved in 10 mL of dry DMF, and the mixture was stirred for 12 h at 75 °C. The reaction mixture was then diluted with EtOAc and washed with H_2O and brine. The organic layer separated was dried over Na_2SO_4 and then evaporated to dryness under a reduced pressure. The crude product was purified by column chromatography over silica gel (eluent: EtOAc:*n*-hexane = 1:24) to give compound **8** as a white solid (253 mg, 56% yield). ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, see Chart S13): δ = 7.75, 6.97 (d, J = 8.7 Hz, each 4H, C_6H_4 × 2), 7.27 (s, 1H, C_6H), 5.03 (s, 4H, C_6H–CH_2 × 2), 4.06–3.98 (m, 6H, –$OCH_2(CH_2)_{10}CH_3$ × 3), 1.76–1.68 (m, 6H, –$OCH_2CH_2(CH_2)_9CH_3$ × 3), 1.39–1.23 (m, 78H, –$O(CH_2)_2(CH_2)_9CH_3$ × 3, –$B(OC(CH_3)_2)_2$ × 2), 0.88 (t, J = 7.0 Hz, 9H, –$O(CH_2)_{11}CH_3$ × 3). ^{13}C NMR (126 MHz, $CDCl_3$, 20 °C, see Chart S14): δ = 161.49, 151.98, 145.76, 136.52, 125.73, 124.75, 114.08, 83.53, 74.33, 73.70, 64.99, 31.97, 30.41, 30.39, 29.77, 29.71, 29.69, 29.65, 29.61, 29.54, 29.42, 29.40, 26.18, 26.16, 24.88, 22.73, 14.17. HRMS (ESI): *m*/*z* calcd for $C_{68}H_{113}O_9B_2$ $[M+H]^+$ 1095.8565, found 1095.8546.

10: Compound **9** (319 mg, 0.783 mmol) and hydrazine monohydrate (0.15 mL, 3.01 mmol) were dissolved in 5 mL of dry THF and the mixture was refluxed for 2 h. The reaction mixture was then diluted with EtOAc and washed with H_2O and brine. The organic layer separated was dried over Na_2SO_4 and then evaporated to dryness under a reduced pressure to give compound **10** as a pale-yellow oily liquid (157 mg, 72 % yield). ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, see Chart S15): δ = 7.74, 6.89 (d, J = 8.7 Hz, each 2H, C_6H_4), 4.08 (t, J = 6.2 Hz, 2H, –OCH_2), 2.91 (t, J = 6.8 Hz, 2H, –$O(CH_2)_2CH_2$), 1.93 (qui, J = 6.4 Hz, 2H, –OCH_2CH_2), 1.33 (s, 12H, –$B(OC(CH_3)_2)_2$). ^{13}C NMR (126 MHz, $CDCl_3$, 20 °C, see Chart S16): δ = 161.56, 136.52, 113.82, 83.54, 65.63, 39.23, 33.01, 24.87. HRMS (ESI): *m*/*z* calcd for $C_{15}H_{24}BNO_3$ $[M+H]^+$ 278.1922, found 278.1919.

11: Compound **10** (414 mg, 1.49 mmol), 3,4,5-tris(dodecyloxy)benzoic acid (1.22 g, 1.80 mmol), and DMAP (67 mg, 0.548 mmol) were dissolved in 10 mL of dry CH_2Cl_2. To this mixture, EDC·HCl (853 mg, 4.45 mmol) was added portion-wise and the mixture was stirred for 11 h at room temperature. The reaction mixture was neutralized with aqueous HCl (2 M), then diluted with CH_2Cl_2 and washed with H_2O and then brine. The organic layer was separated, dried over Na_2SO_4, and then evaporated to dryness under a reduced pressure. The crude product was purified by column chromatography over silica gel (eluent: EtOAc:*n*-hexane = 1:4) to give compound **11** as a white solid (881 mg, 63% yield). ^{1}H NMR, ^{13}C NMR, and MS measurements were consistent with those reported.[S6]

13: Compound **11** (202 mg, 0.304 mmol), **12** (356 mg, 0.381 mmol), K_3PO_4 (198 mg, 0.933 mmol), and $Pd(PPh_3)_4$ (34 mg, 0.0294 mmol) were dissolved in a mixture of degassed THF (100 mL) and degassed water (25 mL), and the mixture was stirred for 8h at 60 °C under N_2 atmosphere. After cooling to room temperature, the reaction mixture was passed through a small pad of Celite®. The filtrate was diluted with EtOAc and washed with H_2O and brine. The organic layer was separated, dried over Na_2SO_4 and then evaporated to dryness under a reduced pressure. The crude product was purified by column chromatography over silica gel (eluent: EtOAc:*n*-hexane = 1:3) and further purified by GPC (eluent: $CHCl_3$) to give **13** as a purple solid (21 mg, 5% yield). ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, see Chart S17): δ = 10.24 (s, 1H, *meso-H*), 9.40, (d, J = 4.5 Hz, 2H, β-pyrrole), 9.13 (d, J = 4.5 Hz, 2H, β-pyrrole), 9.02 (d, J = 4.6 Hz, 2H, β-pyrrole), 8.98 (d, J = 4.6 Hz, 2H, β-pyrrole), 8.15 (d, J = 8.5 Hz, 4H, C_6H_4), 8.13, 7.28 (d+d, J = 8.6 Hz, 2H + 2H, C_6H_4), 7.32 (d, J = 8.5 Hz, 4H, C_6H_4), 6.95 (s, 2H, C_6H_2), 6.64 (t, J = 5.1 Hz, 1H, –CON*H*–), 4.41 (t, J = 5.6 Hz, 2H, –CONHCH$_2$CH$_2$C*H*$_2$O–), 4.12 (s, 6H, –OC*H*$_3$ × 2), 4.04–3.97 (m, 6H, –OC*H*$_2$(CH$_2$)$_{10}$CH$_3$ × 3), 3.70 (q, 2H, –CONHC*H*$_2$CH$_2$CH$_2$O–), 2.27 (qui, J = 5.9 Hz, 2H, –CONHCH$_2$C*H*$_2$CH$_2$O–), 1.80–1.71 (m, 6H, –OCH$_2$C*H*$_2$(CH$_2$)$_9$CH$_3$ × 3), 1.45–1.40 (m, 6H, –O(CH$_2$)$_2$C*H*$_2$(CH$_2$)$_8$CH$_3$ × 3), 1.26–1.11 (m, 48H, O(CH$_2$)$_3$(C*H*$_2$)$_8$CH$_3$ × 3), 0.88–0.81 (m, 9H, O(CH$_2$)$_{11}$C*H*$_3$ × 3). ^{13}C NMR (126 MHz, $CDCl_3$, 20 °C, see Chart S18): δ = 167.15, 159.18, 158.10, 152.74, 150.44, 150.42, 149.89, 149.82, 140.89, 136.09, 135.55, 135.34, 132.46, 131.77, 131.55, 128.41, 120.71, 120.10, 112.45, 112.08, 105.61, 104.95, 77.62, 73.48, 69.21, 67.03, 55.59, 37.86, 31.96, 31.91, 30.38, 29.79, 29.72, 29.68, 29.66, 29.64, 29.45, 29.42, 29.40, 29.35, 28.76, 26.15, 22.72, 22.69, 14.14. HRMS (ESI): *m*/*z* calcd for $C_{86}H_{112}N_5O_7Zn$ $[M+H]^+$ 1390.7848, found 1390.7827.

14: Compound **13** (20 mg, 14.4 μmol) and pyridine (0.1 mL) were dissolved in 7 mL of $CHCl_3$ and the solution was cooled to 0 °C in an ice bath. To this mixture, NBS (2.8 mg, 15.7 μmol) was added portion-wise and the mixture was stirred for 1.5 h at 0 °C. The ice bath was removed and the mixture was stirred at room temperature for 30 min. The reaction mixture was neutralized with acetone (10 mL) and then evaporated to dryness under a reduced pressure. The crude product was purified by recrystallization in EtOH to give pure **14** as a purple solid (5 mg, 24% yield). ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, see Chart S19): δ = 9.73, 9.00 (d, J = 4.7 Hz, 2H, β-pyrrole), 9.00 (d, J = 4.7 Hz, 2H, β-pyrrole), 8.93–8.90 (m, 4H, β-pyrrole), 8.11–8.09 (m, 6H, C_6H_4), 7.30 (d, J = 8.5 Hz, 4H, C_6H_4), 7.24 (d, J = 8.5 Hz, 2H, C_6H_4), 6.50 (brs, 2H, C_6H_2), 6.30 (brs, 1H, –CON*H*–),

4.25 (brs, 2H, –CONHCH$_2$CH$_2$C*H*$_2$O–), 4.11 (s, 6H, –OC*H*$_3$ × 2), 4.01–3.91 (m, 6H, –OC*H*$_2$(CH$_2$)$_{10}$CH$_3$ × 3), 3.17 (brs, 2H, –CONHC*H*$_2$CH$_2$CH$_2$O–), 2.02 (brs, 2H, –CONHCH$_2$C*H*$_2$CH$_2$O–), 1.81–1.72 (m, 6H, –OCH$_2$C*H*$_2$(CH$_2$)$_9$CH$_3$ × 3), 1.45–1.41 (m, 6H, –O(CH$_2$)$_2$C*H*$_2$(CH$_2$)$_8$CH$_3$ × 3), 1.28–1.14 (m, 48H, –O(CH$_2$)$_3$(C*H*$_2$)$_8$CH$_3$ × 3), 0.87–0.82 (m, 9H, –O(CH$_2$)$_{11}$C*H*$_3$ × 3). ^{13}C NMR (126 MHz, CDCl$_3$, 20 °C, see Chart S20): δ = 167.13, 159.22, 158.10, 152.48, 150.86, 150.72, 150.65, 149.64, 140.83, 135.81, 135.52, 135.23, 132.97, 132.55, 132.18, 132.07, 127.23, 121.10, 121.03, 112.55, 112.04, 104.28, 104.20, 77.61, 73.49, 69.06, 66.65, 55.58, 37.19, 31.97, 31.93, 30.04, 29.81, 29.74, 29.72, 29.68, 29.50, 29.43, 29.41, 29.38, 28.47, 26.17, 22.73, 22.71, 14.15. HRMS (ESI): *m*/*z* calcd for C$_{86}$H$_{110}$N$_5$O$_7$BrNaZn [M+Na]$^+$ 1490.6772, found 1490.6791.

Por$_d$: Using a procedure similar to that for compound **13**, **Por$_d$** was obtained as a purple solid in 4% yield (3 mg) from compound **8** (25 mg, 22.8 μmol), **14** (72 mg, 48.9 μmol), K$_3$PO$_4$ (32 mg, 151 μmol), and Pd(PPh$_3$)$_4$ (15 mg, 13.0 μmol) in a mixture of 20 mL of degassed THF and 5 mL of degassed water. ^{1}H NMR (500 MHz, CDCl$_3$, 20 °C, see Chart S21): δ = 8.91–8.84 (m, 16H, β-pyrrole), 8.18 (d, *J* = 8.5 Hz, 4H, C$_6$*H*$_4$), 8.13 (d, *J* = 8.5 Hz, 4H, C$_6$*H*$_4$), 8.08 (d, *J* = 8.6 Hz, 8H, C$_6$*H*$_4$ × 2), 7.72 (s, 1H, C$_6$*H*), 7.46 (d, *J* = 8.6 Hz, 4H, C$_6$*H*$_4$), 7.30 (d, *J* = 8.5 Hz, 4H, C$_6$*H*$_4$), 7.22 (d, *J* = 8.6 Hz, 8H, C$_6$*H*$_4$ × 2), 7.07 (s, 4H, C$_6$*H*$_2$ × 2), 6.71 (t, *J* = 5.5 Hz, 2H, –CON*H*– × 2), 5.43 (s, 4H, C$_6$H–C*H*$_2$ × 2), 4.43 (d, *J* = 5.4 Hz, 4H, –CONHCH$_2$CH$_2$C*H*$_2$O– × 2), 4.28 (t, *J* = 6.5 Hz, 4H, –OC*H*$_2$(CH$_2$)$_{10}$CH$_3$ × 2), 4.17–3.98 (m, 26H, –OC*H*$_2$(CH$_2$)$_{10}$CH$_3$ × 7, OC*H*$_3$ × 4), 3.85 (q, *J* = 5.7 Hz, 4H, –CONHC*H*$_2$CH$_2$CH$_2$O– × 2), 2.33 (qui, *J* = 5.9 Hz, 4H, –CONHCH$_2$C*H*$_2$CH$_2$O– × 2), 1.90–1.71 (m, 18H, –OCH$_2$C*H*$_2$(CH$_2$)$_9$CH$_3$ × 9), 1.44(m, 18H, –O(CH$_2$)$_2$C*H*$_2$(CH$_2$)$_8$CH$_3$ × 9), 1.25–1.15 (m, 144H, –O(CH$_2$)$_3$(C*H*$_2$)$_8$CH$_3$ × 9), 0.88–0.73 (m, 27H, –O(CH$_2$)$_{11}$C*H*$_3$ × 9), −2.75 (s, 4H, pyrrole-N*H* × 4). ^{13}C NMR (126 MHz, CDCl$_3$, 20 °C, see Chart S22): δ = 167.55, 159.34, 158.87, 158.39, 153.20, 152.21, 141.19, 135.69, 135.58, 135.18, 134.79, 134.60, 129.72, 126.11, 119.93, 119.93, 119.79, 119.38, 113.07, 112.67, 112.15, 105.71, 77.61, 74.54, 73.54, 69.45, 67.27, 65.69, 55.58, 55.51, 38.63, 31.97, 31.94, 31.89, 31.85, 30.61, 30.53, 30.34, 29.79, 29.75, 29.73, 29.69, 29.64, 29.60, 29.41, 29.40, 29.32, 29.22, 26.36, 26.28, 26.11, 22.73, 22.70, 22.67, 22.62, 14.16, 14.12, 14.06. MS (MALDI): *m*/*z* calcd for C$_{228}$H$_{313}$N$_{10}$O$_{19}$ [M+H]$^+$ 3495.383, found 3495.357.

Por$_m$: Using a procedure similar to that for compound **13**, **Por$_m$** was obtained as a purple solid in 34% yield (14 mg) from 4-((3,4,5-tris(dodecyloxy)benzyl)oxy)phenylboronic acid pinacol ester (19 mg, 22.0 μmol), compound **14** (29 mg, 19.7 μmol), K$_3$PO$_4$ (32 mg,

151 μmol), and $Pd(PPh_3)_4$ (9 mg, 7.79 μmol) in a mixture of 7 mL of degassed THF and 3 mL of degassed water. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, see Chart S23): δ = 8.87–8.84 (m, 8H, β–pyrrole), 8.14–8.12 (m, 8H, β–pyrrole), 7.37, 7.29 (d, J = 8.5 Hz, each 2H, C_6H_4), 7.07 (s, 2H, C_6H_2), 6.82 (s, 2H, C_6H_2), 6.71 (t, J = 5.6 Hz, 1H, –CONH–), 5.24 (s, 2H, C_6H_2–CH_2), 4.43 (t, J = 5.6 Hz, 2H, –$NHCH_2CH_2CH_2O$–), 4.16 (s, 6H, –OCH_3 × 2), 4.09–3.98 (m, 12H, –$OCH_2(CH_2)_{10}CH_3$ × 6), 3.85 (q, J = 6.1 Hz, 2H, –$NHCH_2CH_2CH_2O$–), 2.33 (qui, J = 6.1 Hz, 2H, –$NHCH_2CH_2CH_2O$–), 1.88–1.73 (m, 12H, –$OCH_2CH_2(CH_2)_9CH_3$ × 6), 1.53–1.44 (m, 12H, –$O(CH_2)_2CH_2(CH_2)_8CH_3$ × 6), 1.27–1.15 (m, 96H, –$O(CH_2)_3(CH_2)_8CH_3$ × 6), 0.90–0.81 (m, 18H, –$O(CH_2)_{11}CH_3$ × 6), −2.76 (s, 2H, pyrrole-NH × 2). ^{13}C NMR (126 MHz, $CDCl_3$, 20 °C, see Chart S24): δ = 167.52, 159.37, 158.66, 158.37, 153.43, 153.18, 141.17, 138.09, 135.66, 135.63, 135.58, 135.12, 134.92, 134.60, 131.81, 129.69, 119.78, 119.73, 119.42, 113.04, 112.65, 112.18, 106.43, 105.70, 77.59, 77.27, 77.01, 76.76, 73.51, 70.82, 69.43, 69.21, 67.26, 55.57, 38.62, 31.96, 31.93, 31.86, 30.40, 30.32, 29.79, 29.78, 29.73, 29.67, 29.61, 29.57, 29.47, 29.42, 29.38, 29.29, 29.19, 26.18, 26.16, 26.09, 22.70, 22.68, 22.65, 14.13, 14.10. HRMS (APCI): m/z calcd for $C_{135}H_{196}N_5O_{11}$ $[M+H]^+$ 2063.4926, found 2063.4941.

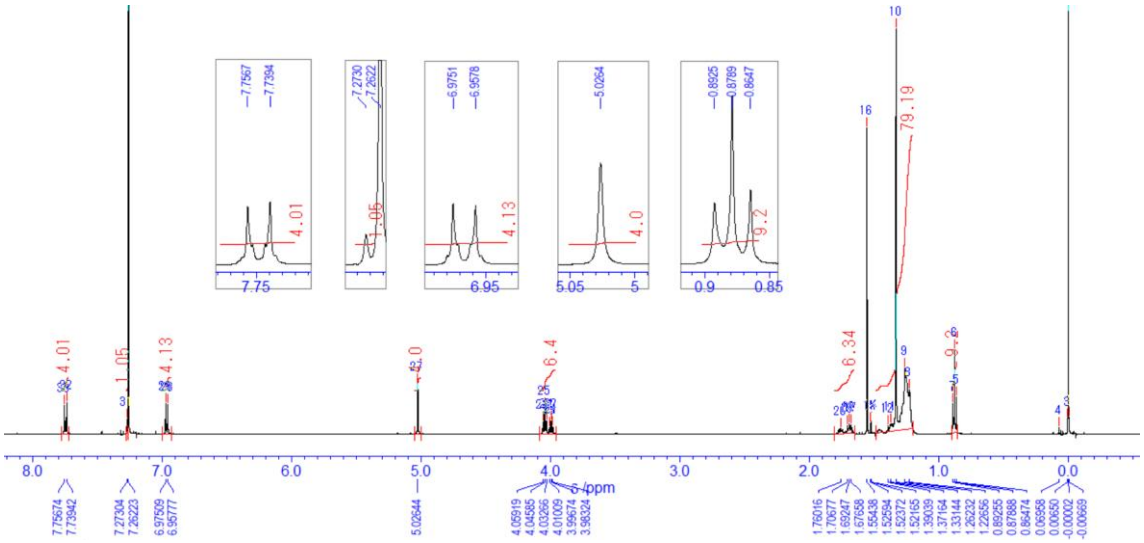


Chart S13 ^{1}H NMR spectrum of **8**.

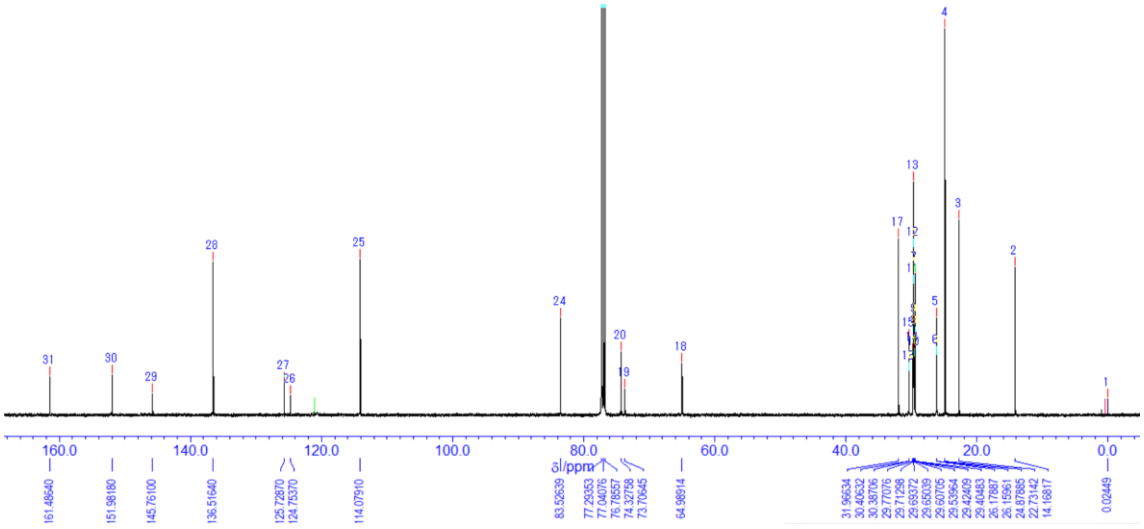


Chart S14 ^{13}C NMR spectrum of **8**.

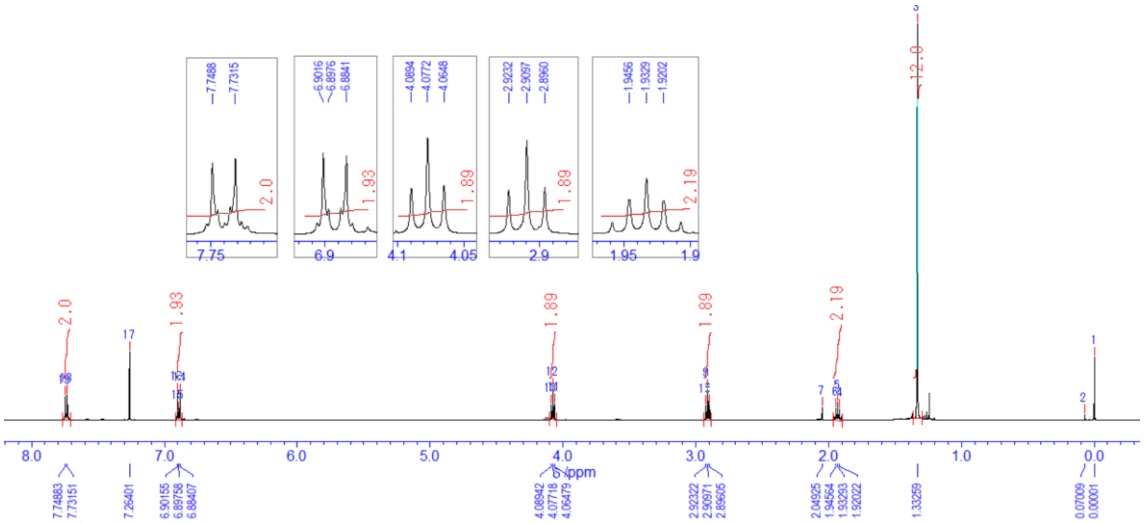


Chart S15 ^{1}H NMR spectrum of **10**.

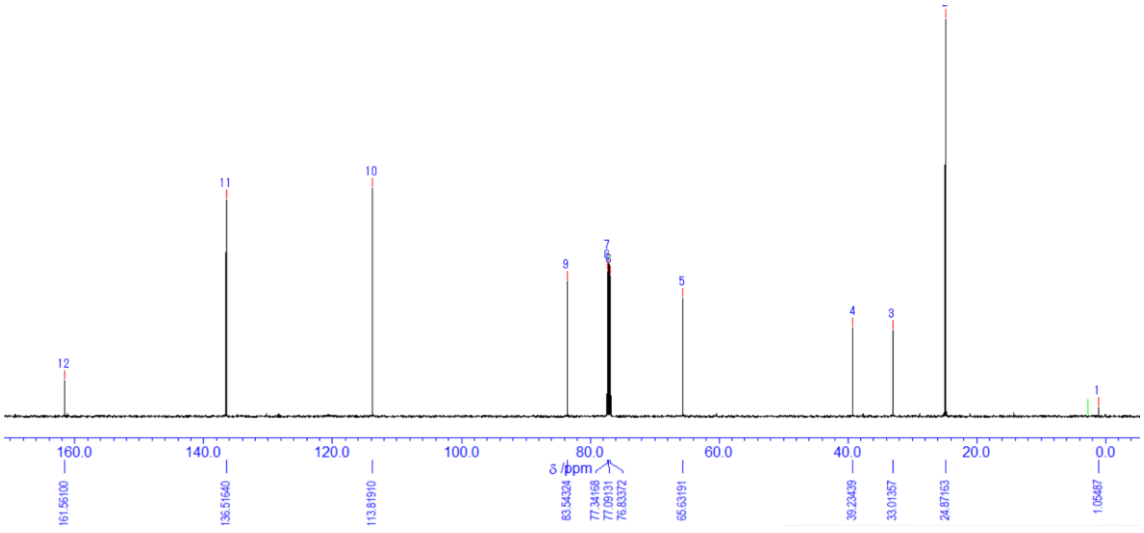


Chart S16 ^{13}C NMR spectrum of **10**.

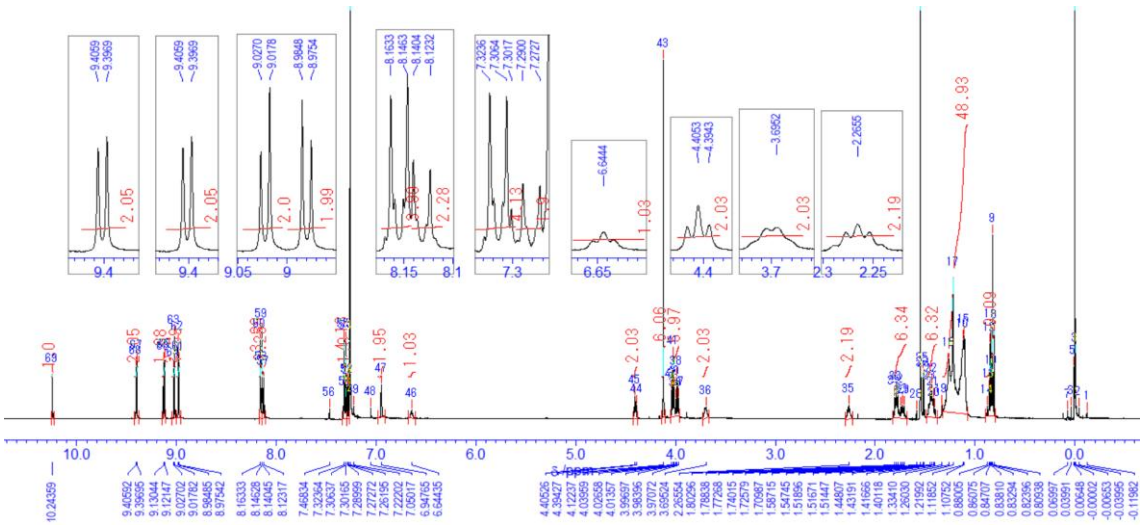


Chart S17 ^{1}H NMR spectrum of **13**.

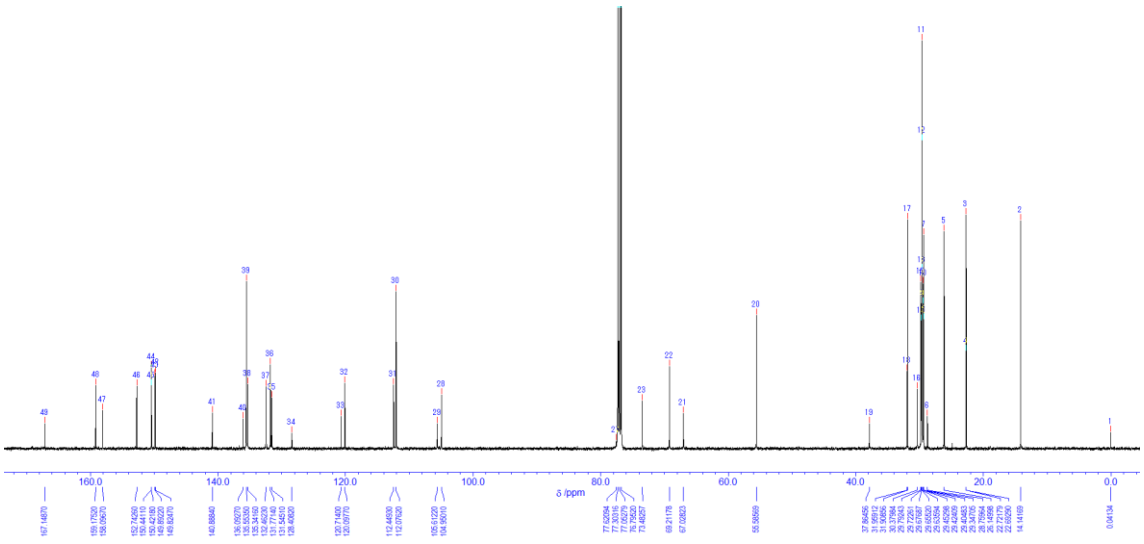


Chart S18 ^{13}C NMR spectrum of **13**.

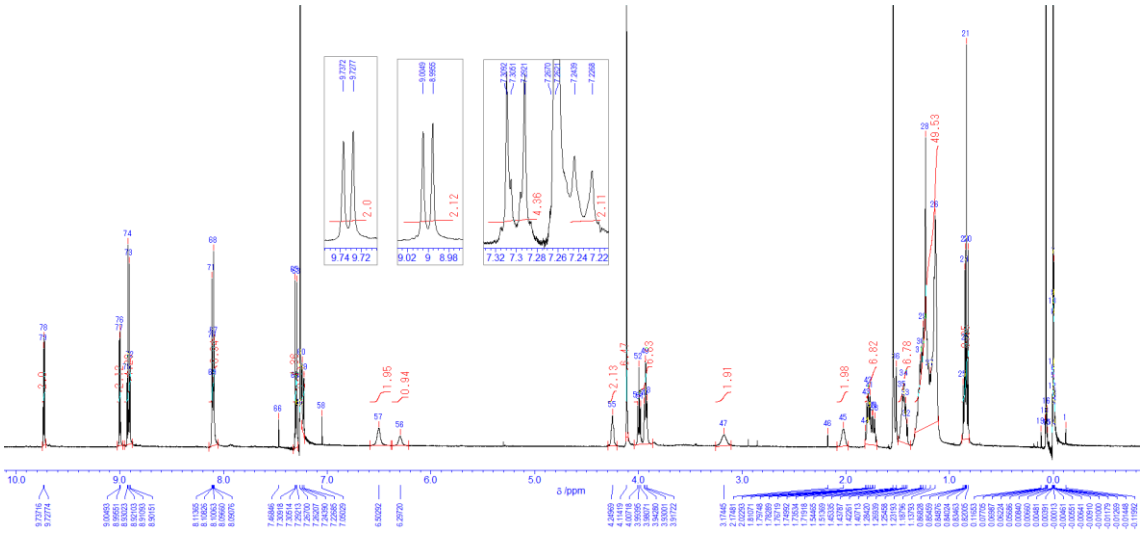


Chart S19 ^{1}H NMR spectrum of **14**.

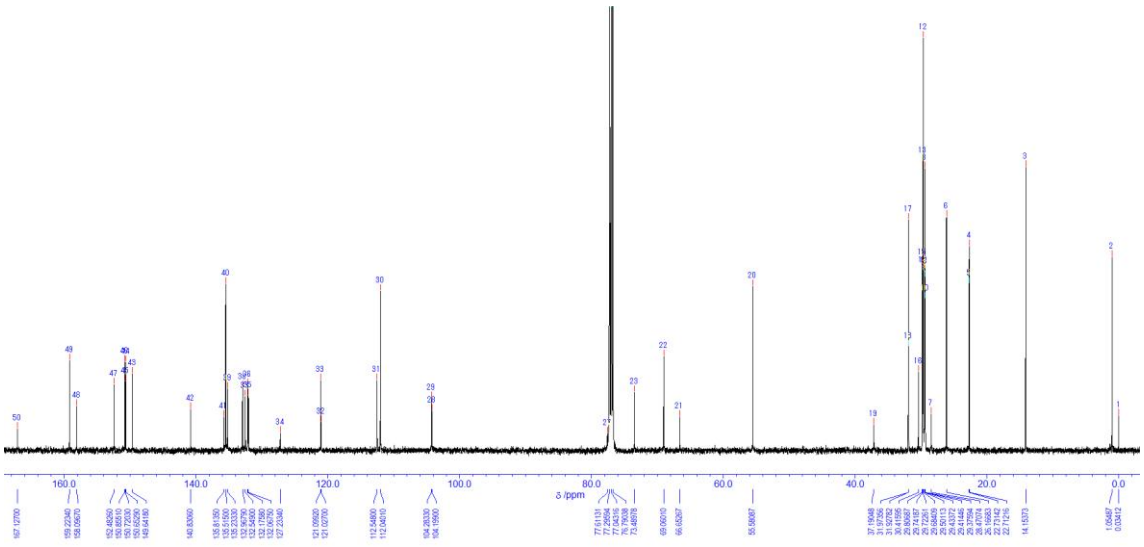


Chart S20 ^{13}C NMR spectrum of **14**.

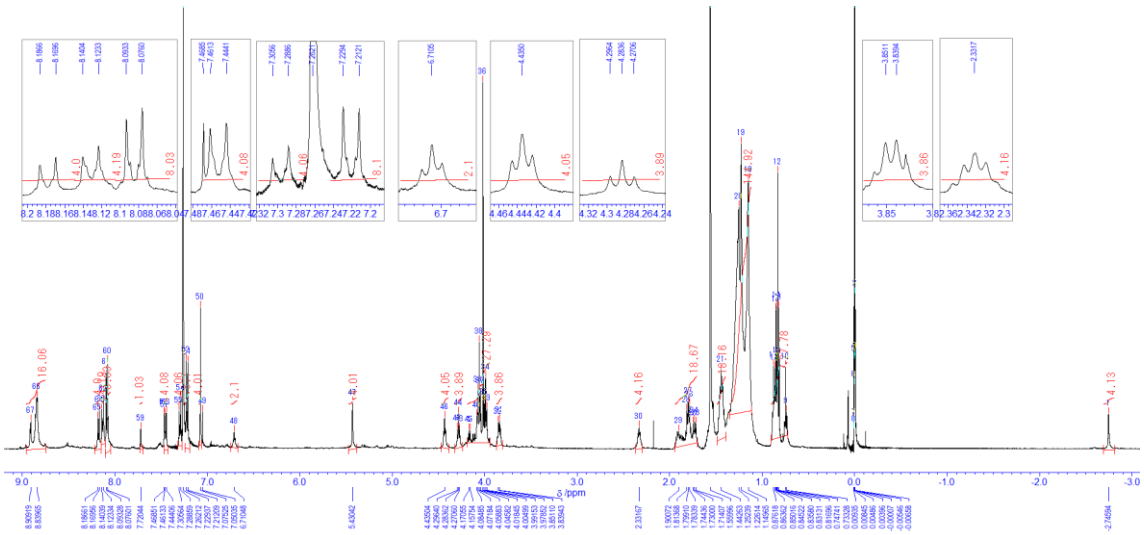


Chart S21 ^{1}H NMR spectrum of **Por$_{d}$**.

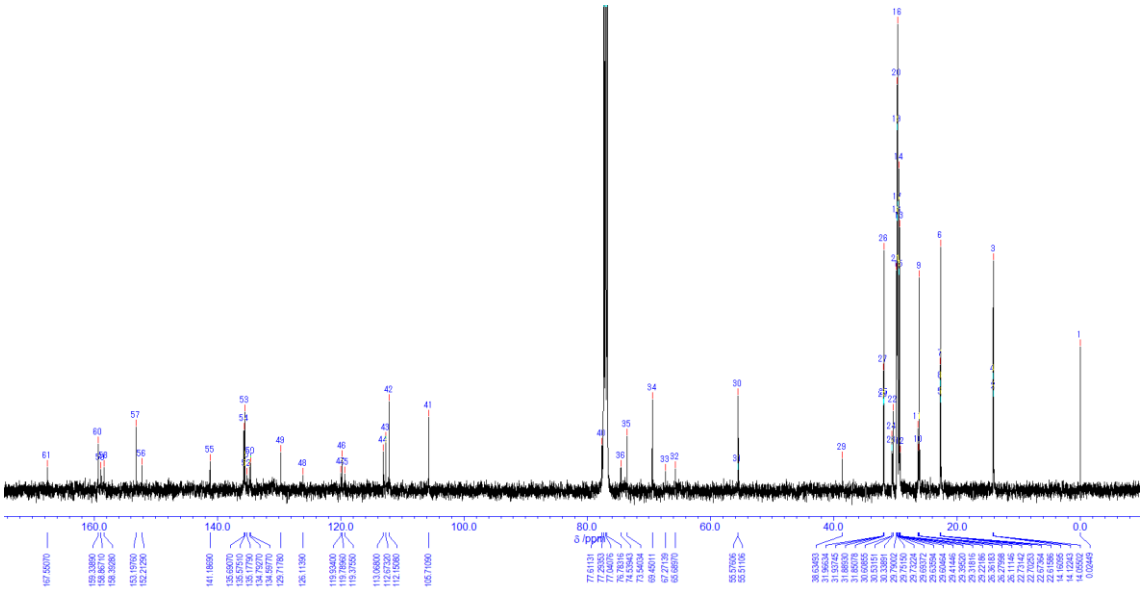


Chart S22 ^{13}C NMR spectrum of **Por$_{d}$**.

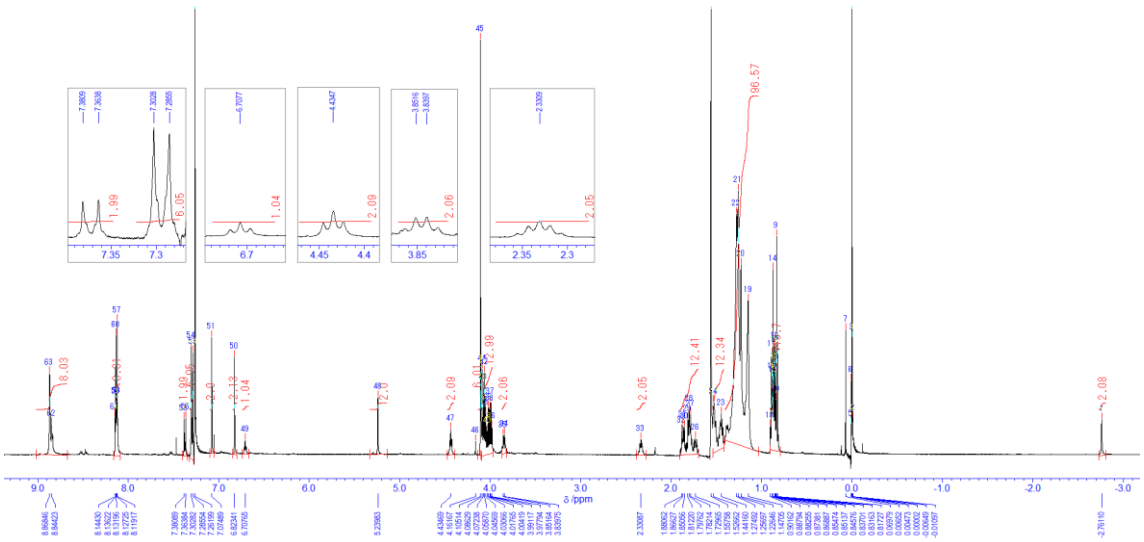


Chart S23 ^{1}H NMR spectrum of **Por$_{m}$**.

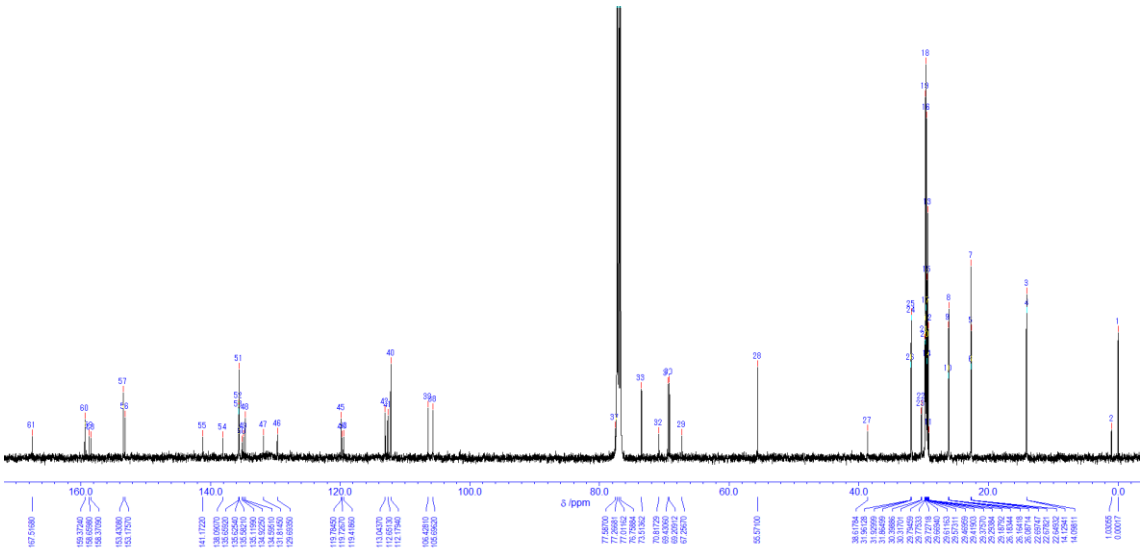


Chart S24 ^{13}C NMR spectrum of **Por$_{m}$**.

3. Supporting Figures

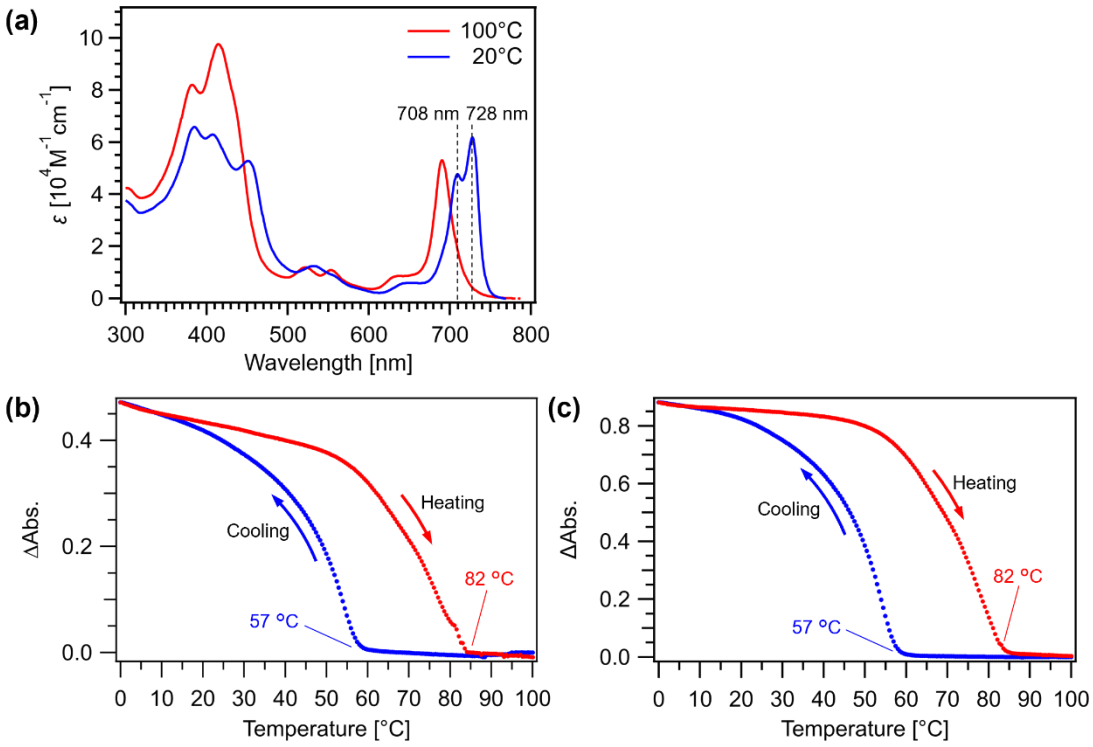


Figure S1. (a) UV/Vis absorption spectra of **Chl$_d$** at 100 °C (red) and 20 °C (blue) during cooling a solution (c = 100 µM) in MCH from 100 °C (red) to 20 °C (blue) at a rate of 1 °C min^{-1}. (b,c) Cooling (blue) and heating (red) curves of **Chl$_d$** obtained by plotting change in the absorption at 708 (b) and 728 nm (c) as a function of temperature.

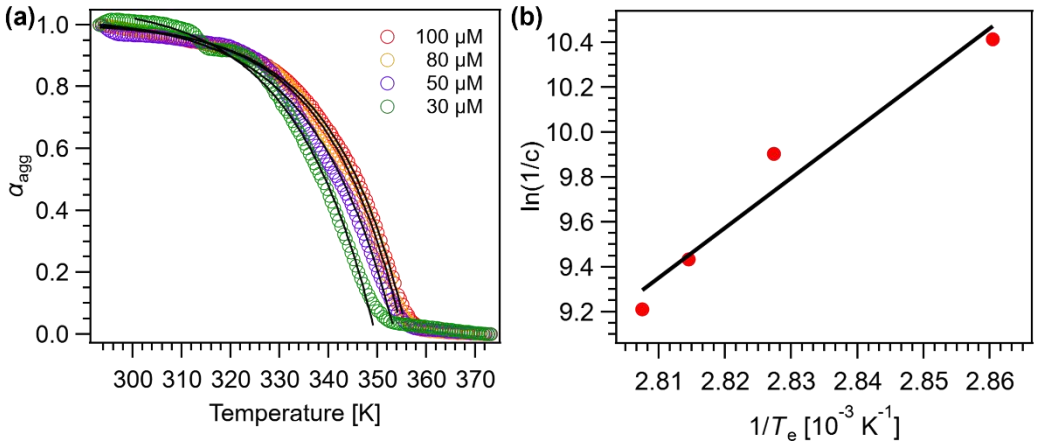


Figure S2. (a) Heating curves of **Chl$_d$** at various concentrations obtained by plotting change in the absorption at λ = 728 nm in MCH. Degree of aggregation (α) at a given temperature (T) was calculated from equation: $\alpha_{agg} = (\varepsilon(T) - \varepsilon_{mon}) / (\varepsilon_{agg} - \varepsilon_{mon})$. The black solid curves are obtained by fitting experimental data to the cooperative model proposed by Meijer and co-workers.[S7] (b) van't Hoff analysis of **Chl$_d$** by plotting the natural logarithm of monomer concentration as a function of T_e^{-1}. The black line shows the corresponding linear fit.

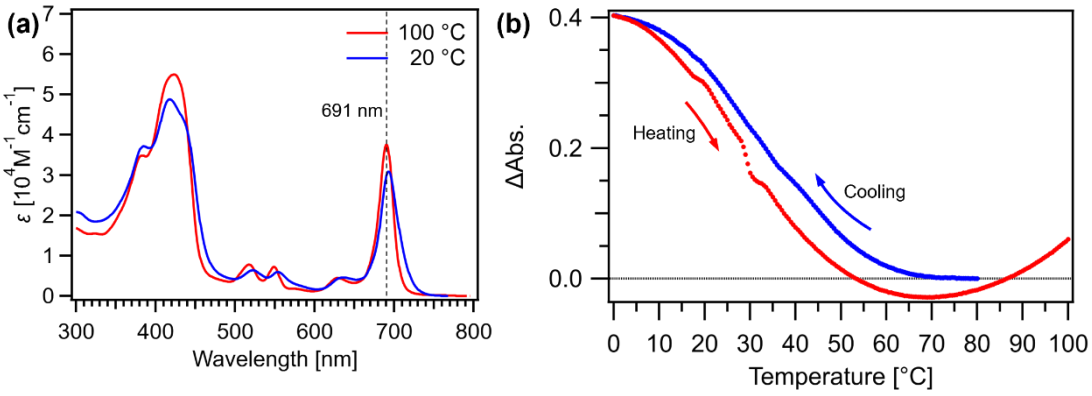


Figure S3. (a) UV/Vis absorption spectra of **Chl$_m$** at 100 and 20 °C during cooling a solution (c = 300 μM) in MCH from 100 to 20 °C at a rate of 1 °C min^{-1}. (b) Cooling (blue) and heating (red) curves of **Chl$_m$** obtained by plotting change in the absorption at 691 nm as a function of temperature.

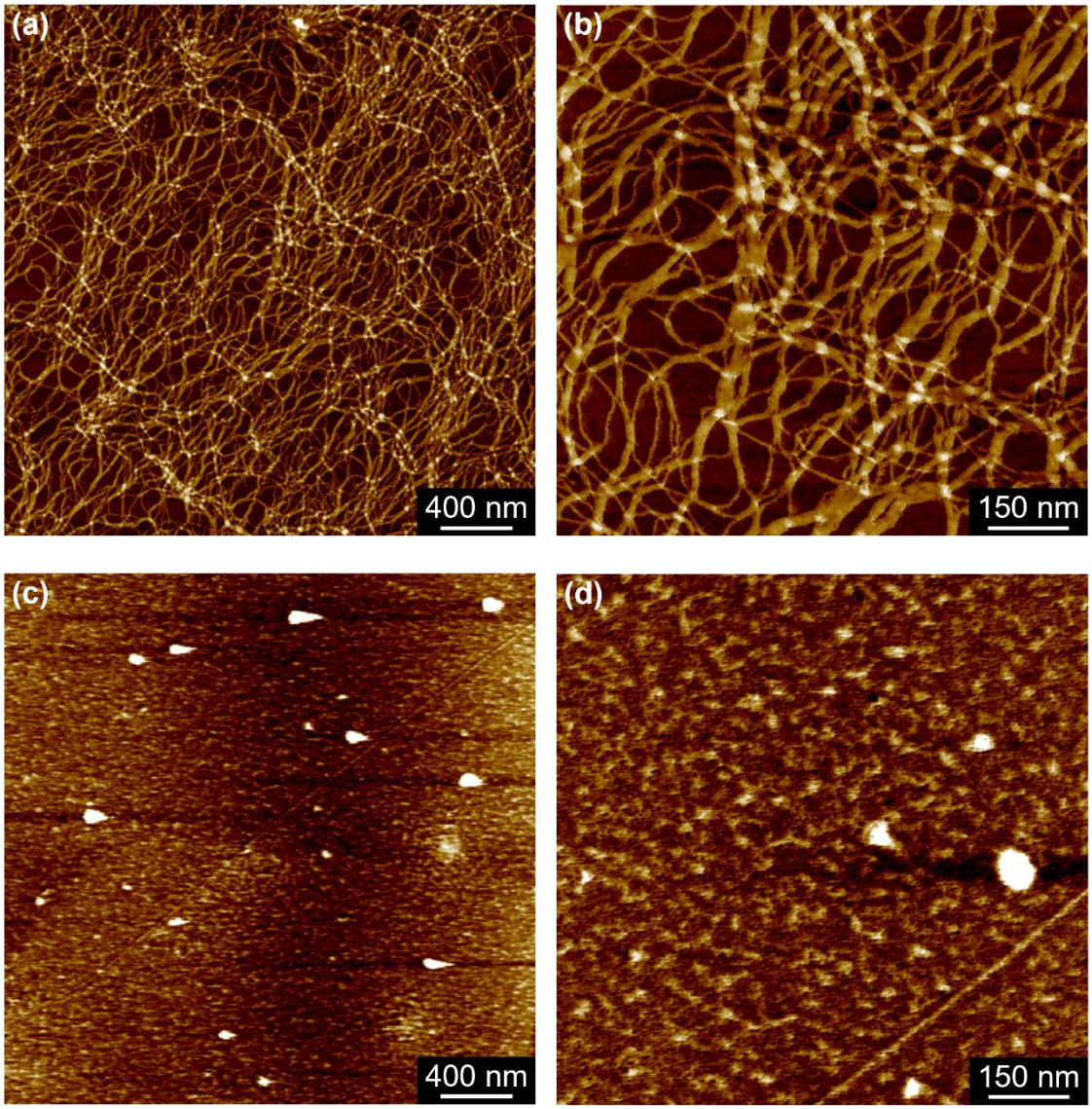


Figure S4. (a,b) AFM images of helical nanofibers of **Chl$_d$** (c = 100 μM) formed in MCH. (c,d) AFM images of ill-defined agglomerates of **Chl$_m$** (c = 300 μM) formed in MCH.

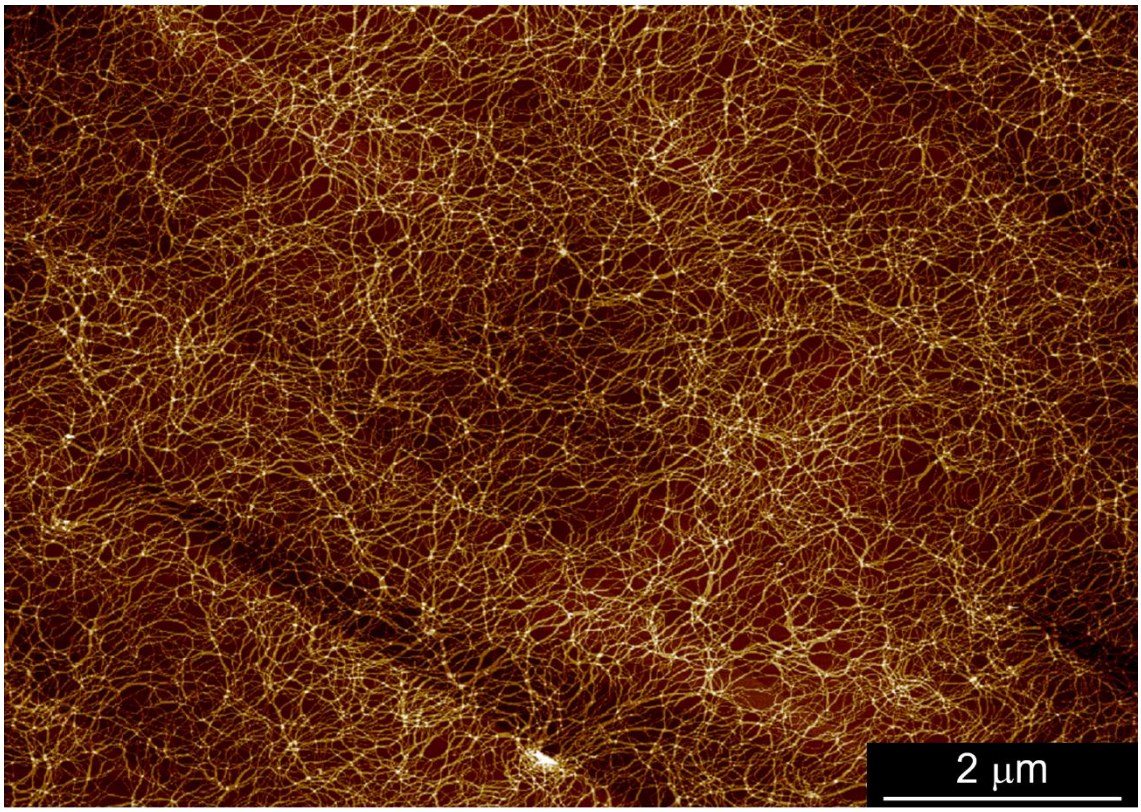


Figure S5. Wide-range AFM image of nanofibers of **Chl$_d$** formed in MCH (c = 100 μM) at 20 °C.

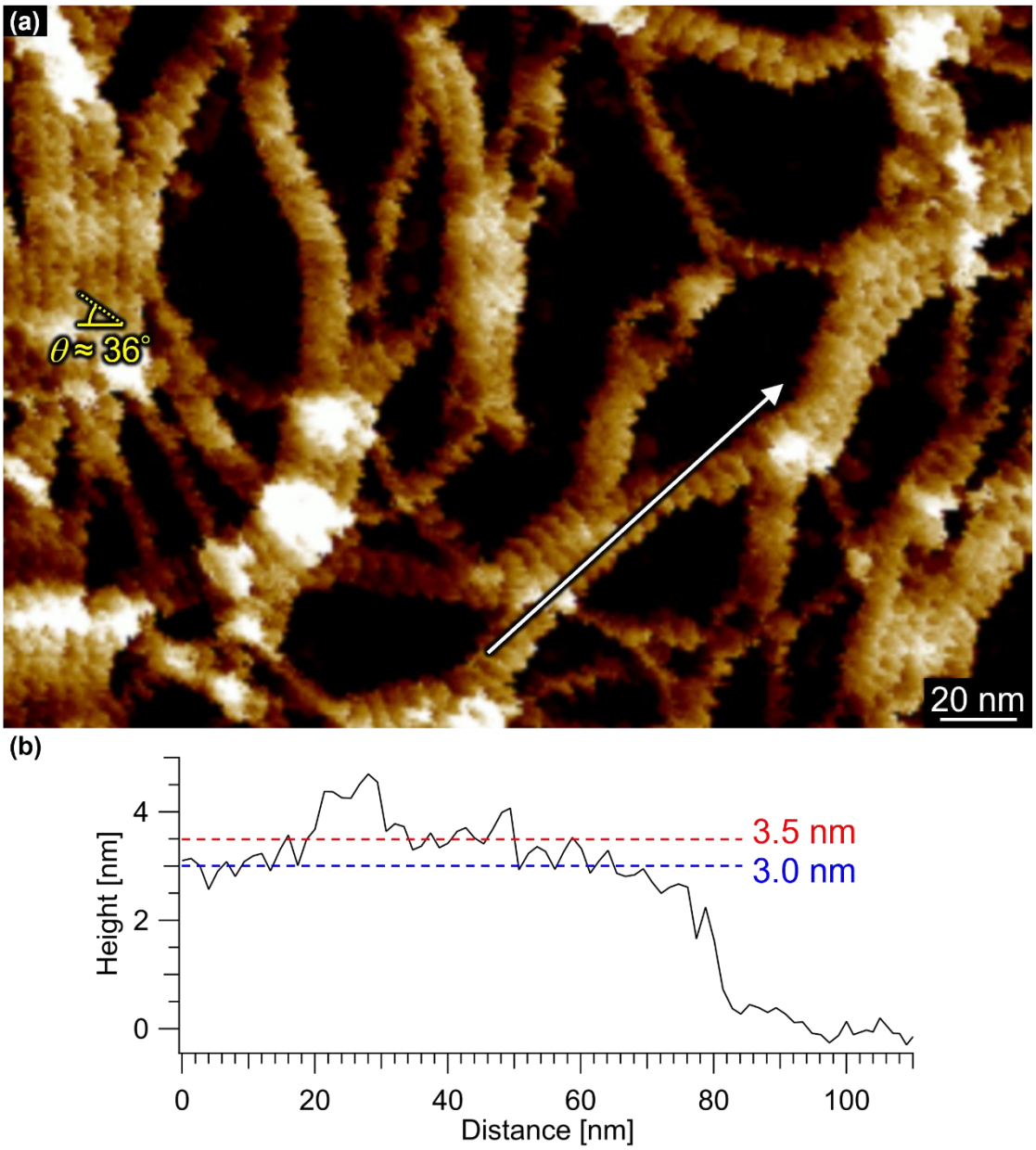


Figure S6. (a) AFM images of helical nanofibers of **Chl$_d$** (c = 100 μM) formed in MCH. Periodic grooves inclined at an angle of 36° relative to the short axis of the fibers are shown by yellow dotted lines along the long axis of the fibers. (b) AFM height analysis of **Chl$_d$** nanofibers along the white arrows in (a). The height measured at the groove positions was approximately 3.0 nm, while that at the inter-groove regions was measured to be around 3.5 nm.

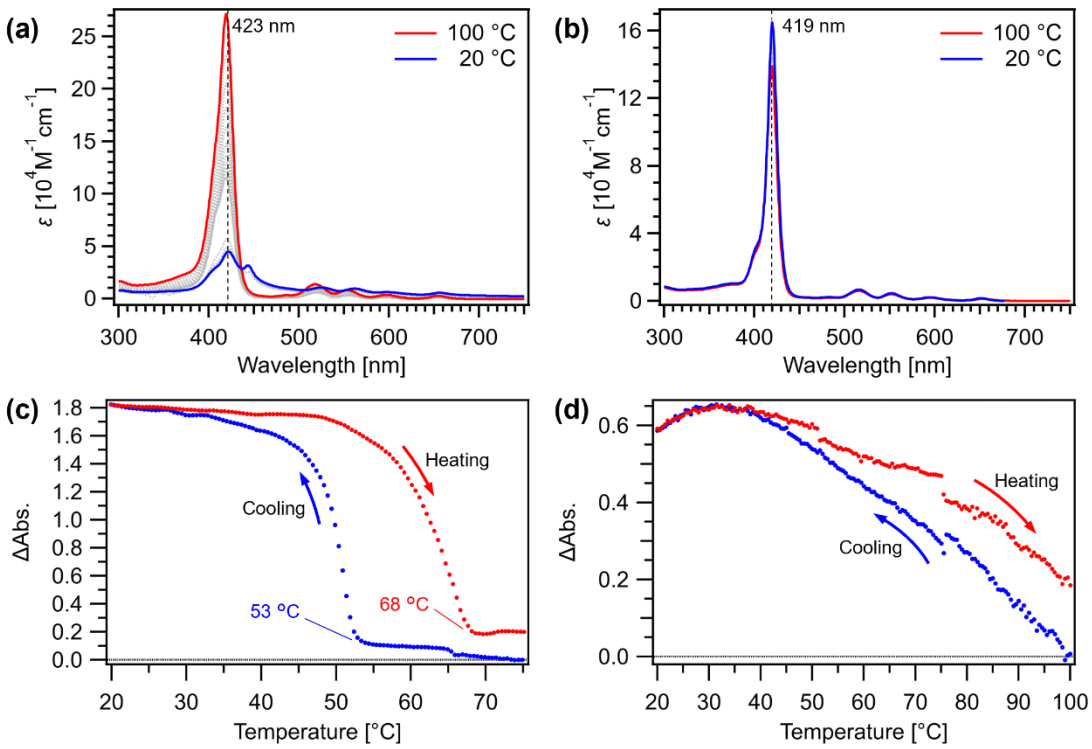


Figure S7. (a,b) UV/Vis absorption spectra of **Por$_d$** (a) and **Por$_m$** (b) during cooling their corresponding solutions in MCH from 100 (red) to 20 °C (blue) at a rate of 1 °C min^{-1} at c = 100 and 200 μM, respectively. (c,d) Cooling (blue) and heating (red) curves of **Por$_d$** (c) and **Por$_m$** (d) obtained by plotting change in the absorption at 423 nm as a function of temperature.

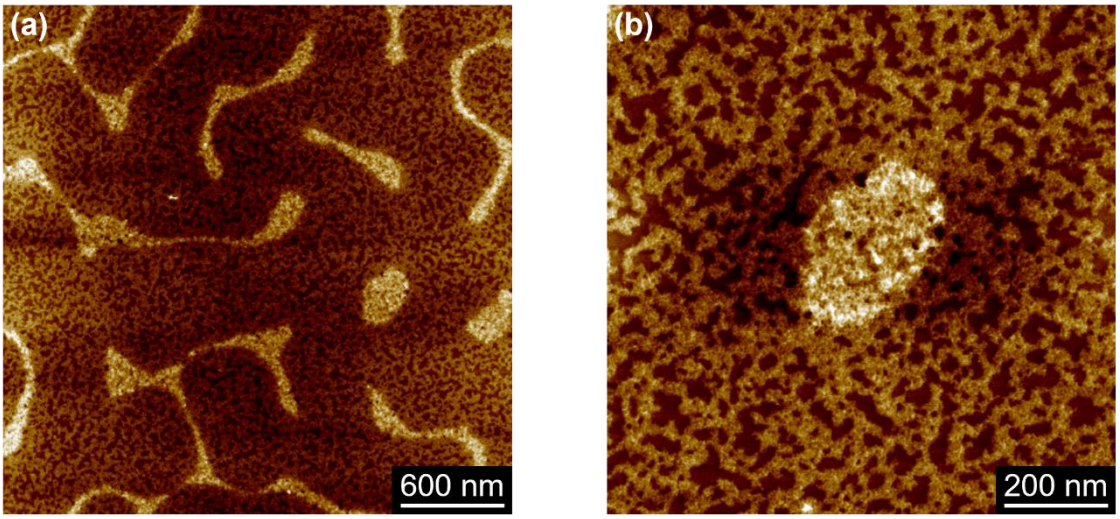


Figure S8. (a,b) AFM images of ill-defined agglomerates of **Por$_m$** formed in MCH (*c* = 200 μM).

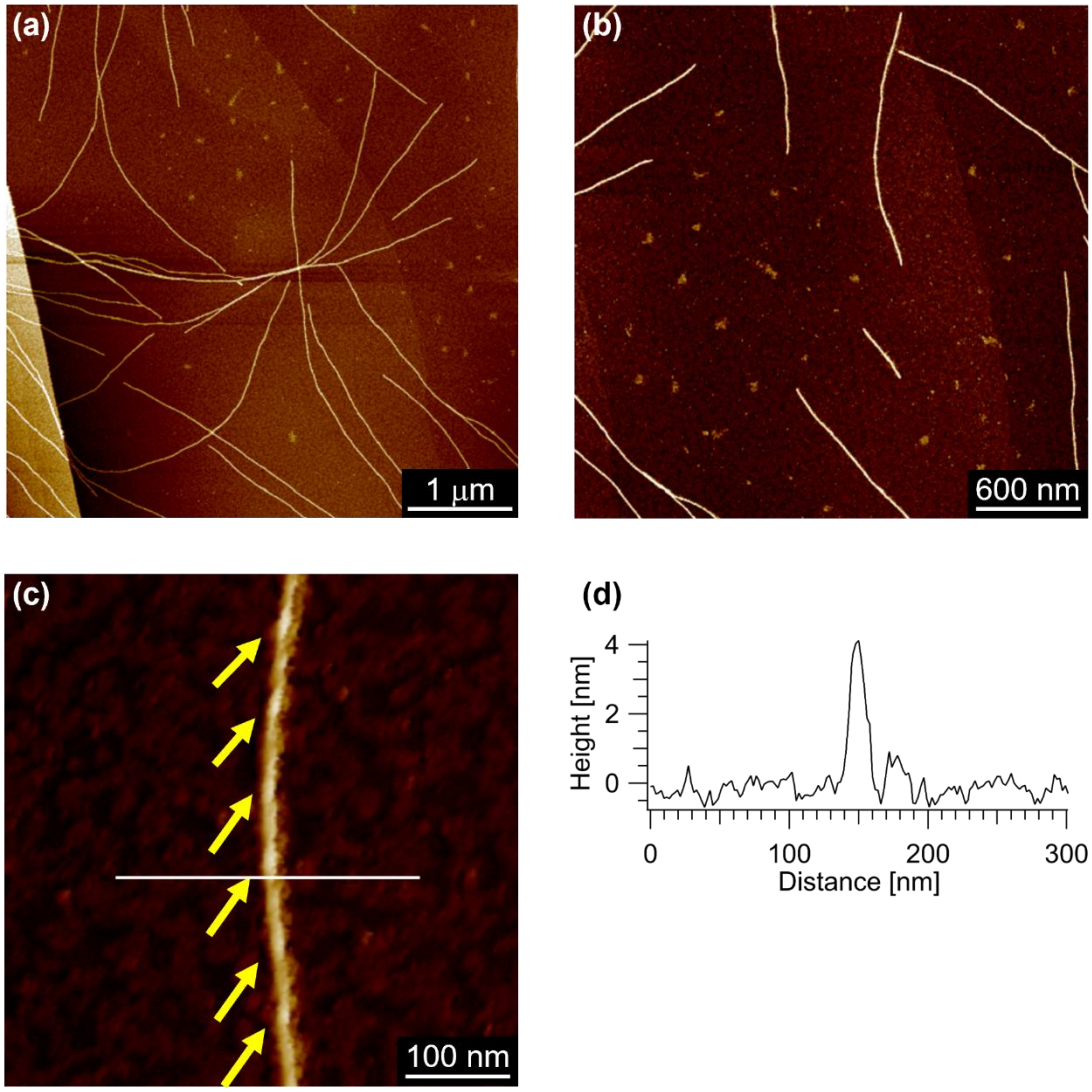


Figure S9. (a–c) AFM images of nanofibers of $\mathbf{Por_d}$ formed in MCH (c = 100 μM). The yellow arrows in (c) show the helicity of a nanofiber. (d) Cross-sectional analysis of a nanofiber of $\mathbf{Por_d}$ along the white line in (c).

4. Supporting References

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