

Supporting Information

Photoactivated Supramolecular Assembly Using “Caged Chlorophylls” for the Generation of Nanotubular Self-Aggregates Having Controllable Lengths

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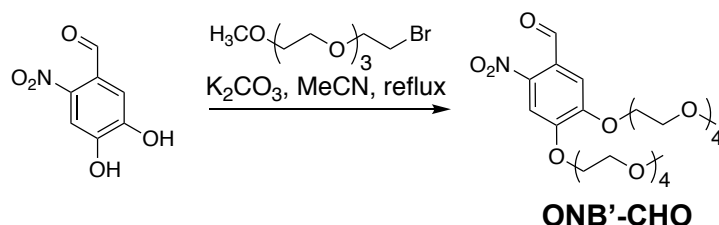
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1. Synthesis and Spectra Data

1-1. General Experimental Information

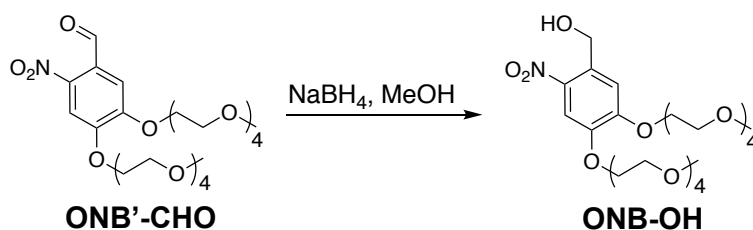
All the reactions were performed in the dark under nitrogen or argon atmosphere and monitored by thin layer chromatography (TLC) and vis absorption spectroscopy. Before the optical measurements, chlorophyll-*a* derivatives were purified by RP-HPLC; a Shimadzu LC-20AD_{VP} pump, SPD-M20A_{VP} diode-array detector, and SCL-20A_{VP} system controller with a packed ODS column (Cosmosil 5C₁₈AR-II, 10 ϕ \times 250 mm; Nacalai Tesque). UV-vis absorption and CD spectra were measured in solution with a 10 mm quartz cell at room temperature (r.t.) using a Hitachi U3500 spectrophotometer and a Jasco J-720W spectropolarimeter, respectively. ¹H and ¹³C NMR spectra were recorded in CDCl₃ using a JEOL ECA-600 (¹H: 600 MHz and ¹³C: 151 MHz) spectrometer. Tetramethylsilane (δ_{H} = 0.00 ppm) and ¹³CDCl₃ (δ_{C} = 77.0 ppm) were used as internal standards. For NMR measurements of zinc complexes, 5%(v/v) pyridine-*d*₅ was added for their monomerization. High-resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF II spectrometer; atmospheric pressure chemical ionization (APCI) 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 r.t. on a mica substrate, and a Bruker AXS silicon cantilever MPP-11100-10 was used.

1-2. Synthesis of **ONB'-CHO** ^{S1}



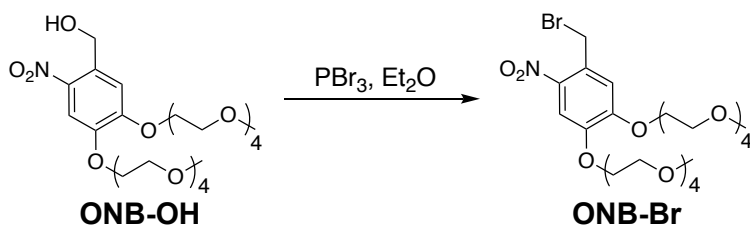
To an MeCN solution (20 mL) of 4,5-dihydroxy-2-nitrobenzaldehyde (1.83 g, 10.0 mmol) were added tri(ethylene glycol) 2-bromoethyl methyl ether (7.11 g, 26.2 mmol) and K₂CO₃ (2.76 g, 20.0 mmol), and the solution was refluxed for 4 h. After being cooled down to r.t., the reaction mixture was filtered from resulting potassium bromide and the salt was washed with MeCN. The solvent in the filtrate was evaporated *in vacuo*, and the residue was purified by gravity column chromatography (GCC, 1% MeOH–dichloromethane [DCM]) to give **ONB'-CHO** as yellow oil (3.62 g, 6.42 mmol, 64%): ¹H NMR (CDCl₃) δ = 10.41 (1H, s, 1-CHO), 7.70 (1H, s, 3-H), 7.44 (1H, s, 6-H), 4.33, 4.32 (each 2H, t, *J* = 5 Hz, 4-, 5-OCH₂), 3.934, 3.926 (each 2H, t, *J* = 5 Hz, 4-, 5-OCCH₂), 3.75–3.73, 3.68–3.63, 3.55–3.54 (24H, m, 4-, 5-OC₂(OCH₂CH₂)₃), 3.373, 3.372 (each 3H, s, 4-, 5-(OC₂)₄OCH₃); ¹³C NMR (CDCl₃) δ = 187.5, 152.8, 151.9, 143.5, 125.3, 111.2, 109.0, 71.7, 70.82, 70.78, 70.47, 70.46, 70.40, 70.39, 70.30, 69.3, 69.2, 69.1, 69.0, 58.8 [five ¹³C peaks in 4-, 5-tetra(ethylene glycol) moieties were overlapped with the others.]; HRMS (APCI) found: *m/z* = 564.2651, calcd for C₂₅H₄₂NO₁₃: MH⁺, 564.2651.

1-3. Synthesis of **ONB-OH**^{S1}



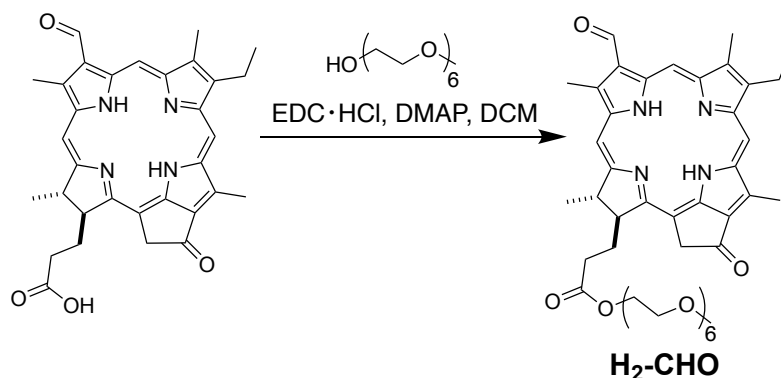
To a MeOH solution (20 mL) of **ONB'-CHO** (1.20 g, 2.13 mmol) was added NaBH₄ (121 mg, 3.19 mmol). After the solution were stirred for 6 h at r.t., the reaction was quenched by addition of water. The reaction mixture was extracted with AcOEt, washed with brine and water, and dried over Na₂SO₄. After all the solvents were evaporated *in vacuo*, the residue was purified by GCC (1% MeOH–DCM) to give **ONB-OH** as yellow oil (1.12 g, 1.98 mmol, 93%): ¹H NMR (CDCl₃) δ = 7.76 (1H, s, 3-H), 7.37 (1H, s, 6-H), 4.96 (2H, s, 1-CH₂), 4.33, 4.23 (each 2H, t, *J* = 5 Hz, 4-, 5-OCH₂), 3.897, 3.896 (each 2H, t, *J* = 5 Hz, 4-, 5-OCCH₂), 3.74–3.71, 3.68–3.62, 3.55–3.53 (24H, m, 4-, 5-OC₂(OCH₂CH₂)₃), 3.38, 3.37 (each 3H, s, 4-, 5-(OC₂)₄OCH₃) [the ¹H-OH peak was too broad to be observed.]; ¹³C NMR (CDCl₃) δ = 153.9, 147.2, 139.4, 133.2, 112.7, 110.6, 71.9, 71.8, 70.9, 70.8, 70.7, 70.6, 70.55, 70.54, 70.46, 70.45, 70.43, 69.7, 69.5, 69.1, 68.9, 62.4, 58.98, 58.97 [one ¹³C peak in 4-, 5-tetra(ethylene glycol) moieties was overlapped with the others.]; HRMS (APCI) found: *m/z* = 566.2808, calcd for C₂₅H₄₄NO₁₃: MH⁺, 566.2807.

1-4. Synthesis of **ONB-Br**^{S1}



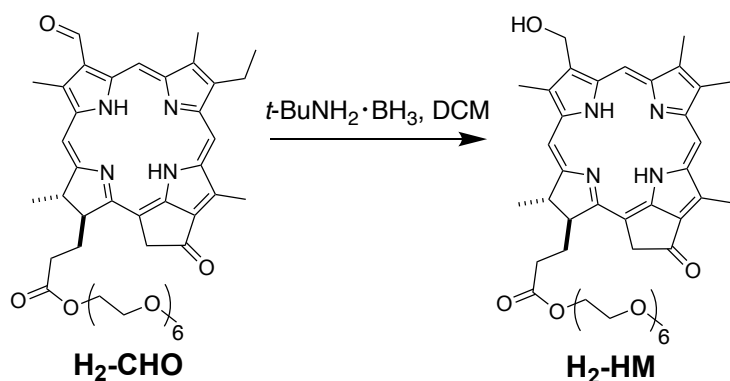
A Et₂O solution (5 mL) of **ONB-OH** (566.0 mg, 1.00 mmol) was added dropwise to a Et₂O solution (5 mL) of PBr₃ (800 mg, 2.96 mmol) at 0 °C, then the reaction mixture was warmed up to r.t. and stirred for 3 h. The resulting solution was diluted with Et₂O, washed with an aqueous sat. NaHCO₃ solution, brine, and water, and dried over Na₂SO₄. After all the solvent was evaporated *in vacuo*, the residue was purified by GCC (1% MeOH–DCM) to give **ONB-Br** as yellow oil (332 mg, 0.529 mmol, 53%): ¹H NMR (CDCl₃) δ = 7.73 (1H, s, 3-H), 7.03 (1H, s, 6-H), 4.84 (2H, s, 1-CH₂), 4.29, 4.24 (each 2H, t, *J* = 5 Hz, 4-, 5-OCH₂), 3.91, 3.90 (each 2H, t, *J* = 5 Hz, 4-, 5-OCCH₂), 3.74–3.72, 3.68–3.63, 3.56–3.54 (24H, m, 4-, 5-OC₂(OCH₂CH₂)₃), 3.38, 3.37 (each 3H, s, 4-, 5-(OC₂)₄OCH₃); ¹³C NMR (CDCl₃) δ = 152.9, 148.4, 140.0, 127.3, 115.7, 110.7, 71.67, 71.66, 71.65, 70.9, 70.7, 70.68, 70.40, 70.37, 70.35, 70.33, 70.26, 70.23, 69.21, 69.17, 69.0, 68.9, 58.8, 58.7, 30.1; HRMS (APCI) found: *m/z* = 628.1963, calcd for C₂₅H₄₃NO₁₂Br: MH⁺, 628.1963.

1-5. Synthesis of **H₂-CHO**^{S2}



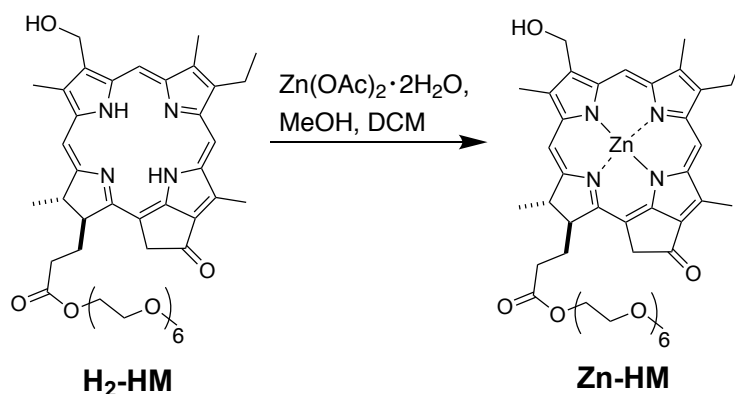
To a DCM solution (5 mL) of pyropheophorbide-*d* (25.9 mg, 48.3 μmol) were added hexa(ethylene glycol) monomethyl ether (22.6 mg, 76.3 μmol), EDC·HCl (44.9 mg, 234 μmol), and DMAP (10.8 mg, 88.4 μmol). After the solution was stirred overnight at r.t., the reaction mixture was directly purified by GCC (1% MeOH–DCM) to give **H₂-CHO** as brown solid (27.9 mg, 34.2 μmol , 71%): Vis (CHCl_3) λ_{max} = 698 (relative intensity, 0.83), 636 (0.09), 557 (0.17), 524 (0.15), 431 (1.00), 390 nm (0.89); ^1H NMR (CDCl_3) δ = 11.45 (1H, s, 3-CHO), 10.11 (1H, s, 5-H), 9.43 (1H, s, 10-H), 8.80 (1H, s, 20-H), 5.32, 5.18 (each 1H, d, J = 19 Hz, 13¹-CH₂), 4.56 (1H, dq, J = 2, 7 Hz, 18-H), 4.39 (1H, dt, J = 8, 2 Hz, 17-H), 4.21–4.14 (2H, m, 17²-CO₂CH₂), 3.73 (3H, s, 2-CH₃), 3.64 (3H, s, 12-CH₃), 3.60–3.49 (24H, m, 8-CH₂, 17²-CO₂CCH₂(OCH₂CH₂)₅), 3.34 (3H, s, 17²-C(OC₂)₆OCH₃), 3.19 (3H, s, 7-CH₃), 2.77–2.71, 2.66–2.61, 2.36–2.26 (2H+1H+1H, m, 17-CH₂CH₂), 1.85 (3H, d, J = 7 Hz, 18-CH₃), 1.64 (3H, t, J = 7 Hz, 8¹-CH₃), –0.33, –2.24 (each 1H, s, NH \times 2); ^{13}C NMR (CDCl_3) δ = 195.8, 188.0, 172.9, 169.6, 161.7, 154.6, 151.9, 148.3, 144.4, 140.3, 139.4, 138.0, 137.2, 133.6, 131.5, 129.7, 128.9, 106.9, 102.8, 99.4, 94.7, 71.8, 70.39, 70.37, 70.36, 70.34, 70.33, 70.32, 70.31, 68.9, 63.6, 58.9, 52.1, 49.3, 48.1, 30.9, 29.6, 23.3, 19.1, 17.2, 11.9, 11.1, 10.9 [two ^{13}C peaks in hexa(ethylene glycol) ester were overlapped with the others.]; HRMS (APCI) found: m/z = 815.4224, calcd for C₄₅H₅₉N₄O₁₀: MH⁺, 815.4226.

1-6. Synthesis of **H₂-HM**^{S2}



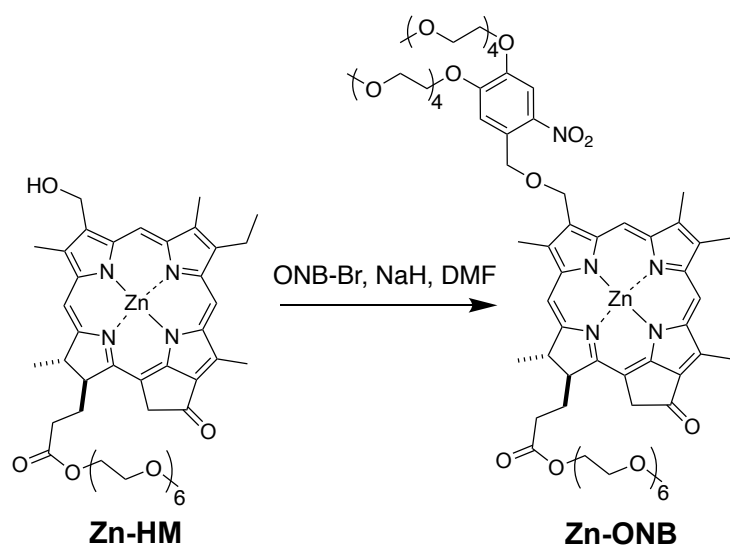
To a DCM solution (15 mL) of **H₂-CHO** (124 mg, 152 μmol) was added $t\text{-BuNH}_2 \cdot \text{BH}_3$ (33.4 mg, 384 μmol). After the solution was stirred for 2 h at r.t., the reaction mixture was directly purified by GCC (2% MeOH–DCM) to give **H₂-HM** as black solid (101 mg, 124 μmol , 81%): Vis (CHCl_3) $\lambda_{\text{max}} = 663$ (relative intensity, 0.49), 608 (0.08), 538 (0.10), 507 (0.10), 412 nm (1.00); ^1H NMR (CDCl_3) $\delta = 9.26$ (1H, s, 5-H), 9.16 (1H, s, 10-H), 8.45 (1H, s, 20-H), 5.72, 5.68 (each 1H, d, $J = 13$ Hz, 3- CH_2), 5.03, 4.93 (each 1H, d, $J = 19$ Hz, 13¹- CH_2), 4.35 (1H, dq, $J = 2, 7$ Hz, 18-H), 4.16–4.06 (2H, m, 17²- CO_2CH_2), 4.11 (1H, dt, $J = 8, 2$ Hz, 17-H), 3.56–3.40 (22H, m, 17²- $\text{CO}_2\text{CCH}_2(\text{OCH}_2\text{CH}_2)_5$), 3.51 (2H, q, $J = 7$ Hz, 8- CH_2), 3.43 (3H, s, 12- CH_3), 3.33 (3H, s, 2- CH_3), 3.32 (3H, s, 17²- $\text{C}(\text{OC}_2)_6\text{OCH}_3$), 3.14 (3H, s, 7- CH_3), 2.76 (1H, br, 3¹-OH), 2.53–2.48, 2.24–2.20, 2.11–2.04 (1H+1H+2H, m, 17- CH_2CH_2), 1.71 (3H, d, $J = 7$ Hz, 18- CH_3), 1.60 (3H, t, $J = 7$ Hz, 8¹- CH_3), –0.08, –2.05 (each 1H, s, $\text{NH} \times 2$); ^{13}C NMR (CDCl_3) $\delta = 196.2, 173.0, 171.1, 159.9, 154.9, 150.5, 148.5, 144.8, 141.0, 137.5, 136.6, 136.0, 135.9, 133.4, 130.1, 128.1, 105.8, 103.7, 96.7, 92.9, 71.8, 70.4, 70.35, 70.34, 70.31, 70.28, 70.27, 68.8, 63.6, 58.9, 56.0, 51.4, 49.8, 47.8, 30.9, 29.5, 22.9, 19.3, 17.3, 11.8, 11.1, 11.0$ [three ^{13}C peaks in hexa(ethylene glycol) moieties were overlapped with the others.]; HRMS (APCI) found: $m/z = 817.4377$, calcd for $\text{C}_{45}\text{H}_{61}\text{N}_4\text{O}_{10}$: MH^+ , 817.4382.

1-7. Synthesis of **Zn-HM**^{S2}



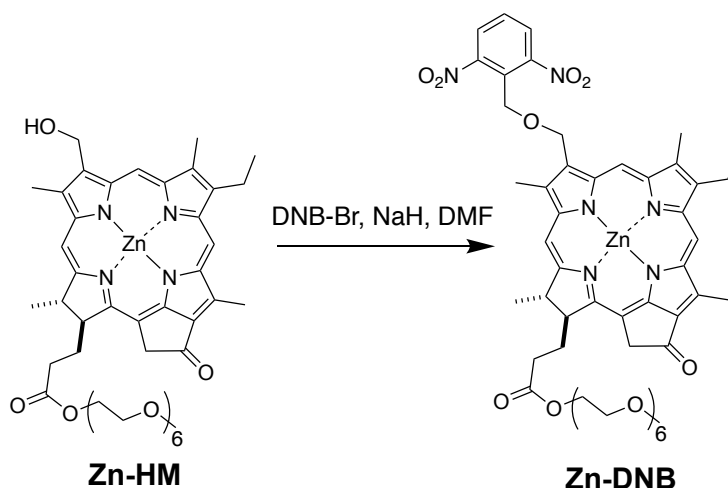
To a DCM solution (10 mL) of **H₂-HM** (100.9 mg, 124 μmol) was added a MeOH solution saturated with $\text{Zn(OAc)}_2 \cdot 2\text{H}_2\text{O}$ (1 mL). After the mixed solution was stirred for 3 h at r.t., the reaction was quenched by addition of water. The reaction mixture was extracted with DCM, washed with an aqueous saturated NaHCO_3 solution and water, and dried over Na_2SO_4 . After all the solvents were evaporated *in vacuo*, the residue was purified by reprecipitation from hexane and DCM to give **Zn-HM** as green solid (103.0 mg, 117 μmol , 95%): Vis (THF) $\lambda_{\text{max}} = 648$ ($\epsilon = 8.66 \times 10^4$), 602 (1.19×10^4), 567 (6.32×10^3), 522 (3.74×10^3), 425 nm (1.16×10^5); ^1H NMR (5% pyridine-*d*₅- CDCl_3) $\delta = 9.55$ (1H, s, 10-H), 9.34 (1H, s, 5-H), 8.33 (1H, s, 20-H), 5.82 (2H, s, 3- CH_2), 5.17, 5.04 (each 1H, d, $J = 19$ Hz, 13¹- CH_2), 4.38 (1H, dq, $J = 2, 7$ Hz, 18-H), 4.19 (1H, dt, $J = 8, 2$ Hz, 17-H), 4.12–4.02 (2H, m, 17²- CO_2CH_2), 3.78 (1H, br, 3¹-OH), 4.74 (2H, q, $J = 7$ Hz, 8- CH_2), 3.68 (3H, s, 12- CH_3), 3.57–3.44 (22H, m, 17²- $\text{CO}_2\text{CCH}_2(\text{OCH}_2\text{CH}_2)_5$), 3.33 (3H, s, 17²- $\text{CO}_2\text{C}_2(\text{OC}_2)_5\text{OCH}_3$), 3.32 (3H, s, 2- CH_3), 3.22 (3H, s, 7- CH_3), 2.58–2.51, 2.39–2.33, 2.30–2.23, 1.93–1.88 (each 1H, m, 17- CH_2CH_2), 1.70 (3H, d, $J = 7$ Hz, 18- CH_3), 1.69 (3H, t, $J = 7$ Hz, 8¹- CH_3); ^{13}C NMR (5% pyridine-*d*₅- CDCl_3) $\delta = 196.9, 173.0, 167.8, 161.0, 155.3, 153.5, 151.2, 147.6, 147.3, 145.4, 143.5, 139.9, 136.7, 133.8, 133.3, 131.8, 105.9, 105.1, 98.2, 91.8, 71.8, 70.4, 70.32, 70.30, 70.28, 70.26, 70.2, 68.8, 63.4, 58.9, 56.2, 50.4, 48.6, 48.3, 30.2, 29.5, 23.3, 19.4, 17.4, 12.7, 11.3, 10.9$ [three ^{13}C peaks in hexa(ethylene glycol) ester were overlapped with the others.]; HRMS (APCI) found: $m/z = 879.3517$, calcd for $\text{C}_{45}\text{H}_{59}\text{N}_4\text{O}_{10}\text{Zn}$: MH^+ , 879.3517.

1-8. Synthesis of **Zn-ONB**



To an *N,N*-dimethylformamide (DMF) solution (2 mL) of **Zn-HM** (44.5 mg, 50.5 μmol) was added **ONB-Br** (133.0, 212 μmol) and 60% NaH dispersed in mineral oil (4.4 mg, 110 μmol) at 0 °C, then the reaction mixture was warmed up to r.t. and stirred for 3 h. The reaction was quenched by addition of water. The reaction mixture was extracted with DCM, washed with water twice, and dried over Na_2SO_4 . After all the solvents were evaporated *in vacuo*, the residue was purified by RP-HPLC (Cosmosil 5C₁₈AR-II, 10 $\phi \times 250$ mm, MeCN : H₂O : pyridine = 80 : 20 : 0.5, 3.0 mL/min) to give **Zn-ONB** as green solid (61.0 mg, 42.7 μmol , 85%): Vis (THF) $\lambda_{\text{max}} = 650$ ($\epsilon = 8.73 \times 10^4$), 606 (1.11×10^4), 569 (5.90×10^3), 524 (3.47×10^3), 426 nm (1.18×10^5); ¹H NMR (5% pyridine-*d*₅-CDCl₃) δ = 9.57 (1H, s, 10-H), 9.35 (1H, s, 5-H), 8.37 (1H, s, 20-H), 7.73 (1H, s, 3-H of 3³-Ar), 7.40 (1H, s, 6-H of 3³-Ar), 5.88, 5.83 (each 1H, d, $J = 12$ Hz, 3-CH₂), 5.29, 5.26 (each 1H, d, $J = 15$ Hz, 3¹-OCH₂), 5.19, 5.07 (each 1H, d, $J = 19$ Hz, 13¹-CH₂), 4.40 (1H, dq, $J = 2, 7$ Hz, 18-H), 4.22 (1H, dt, $J = 8, 2$ Hz, 17-H), 4.15 (2H, t, $J = 5$ Hz, 17²-CO₂CH₂), 4.14 (2H, q, $J = 7$ Hz, 8-CH₂), 3.82 (2H, t, $J = 5$ Hz, 17²-CO₂CCH₂), 3.77–3.30 (61H, m, 4-, 5-(OCH₂CH₂)₄OCH₃ of 3³-Ar, 17²-CO₂C₂(OCH₂CH₂)₅OCH₃), 3.70 (3H, s, 12-CH₃), 3.34 (3H, s, 2-CH₃), 3.21 (3H, s, 7-CH₃), 2.59–2.56, 2.45–2.39, 2.28–2.22, 2.01–1.96 (each 1H, m, 17-CH₂CH₂), 1.72 (3H, d, $J = 7$ Hz, 18-CH₃), 1.71 (3H, t, $J = 7$ Hz, 8¹-CH₃); ¹³C NMR (5% pyridine-*d*₅-CDCl₃) δ = 196.8, 172.9, 167.7, 161.0, 155.6, 153.6, 153.1, 151.0, 147.8, 147.4, 146.9, 145.4, 143.5, 139.2, 137.9, 136.3, 133.9, 133.2, 131.9, 131.3, 111.4, 110.5, 105.8, 105.2, 98.3, 92.0, 71.8, 71.7, 70.7, 70.50, 70.46, 70.44, 70.43, 70.40, 70.38, 70.37, 70.36, 70.34, 70.31, 70.27, 70.26, 70.22, 70.19, 69.4, 69.1, 68.9, 68.7, 68.4, 64.5, 64.4, 58.88, 58.87, 58.82, 50.5, 48.6, 48.3, 30.3, 29.6, 23.3, 19.4, 17.4, 12.7, 11.5, 11.0 [six ¹³C peaks in oligo(ethylene glycol) moieties were overlapped with the others.]; HRMS (APCI) found: $m/z = 1426.6147$, calcd for C₇₀H₁₀₀N₅O₂₂Zn: MH⁺, 1426.6146.

1-9. Synthesis of Zn-DNB



To a DMF solution (2 mL) of **Zn-HM** (45.2 mg, 51.3 μmol) was added 2,6-dinitrobenzyl bromide (**DNB-Br**)^{S3} (72.5, 278 μmol) and 60% NaH dispersed in mineral oil (5.0 mg, 125 μmol) at 0 °C, then the reaction mixture was warmed up to r.t. and stirred for 3 h. The reaction was quenched by addition of water. The reaction mixture was extracted with DCM, washed with water twice, and dried over Na₂SO₄. After all the solvents were evaporated *in vacuo*, the residue was purified by RP-HPLC (Cosmosil 5C₁₈AR-II, 10 ϕ \times 250 mm, MeCN : H₂O : pyridine = 90 : 10 : 0.5, 3.0 mL/min) to give **Zn-DNB** as green solid (13.6 mg, 12.8 μmol , 25%): Vis (THF) λ_{max} = 651 (ϵ = 8.99 $\times 10^4$), 607 (1.16 $\times 10^4$), 569 (6.23 $\times 10^3$), 525 (3.74 $\times 10^3$), 426 nm (1.17 $\times 10^5$); ¹H NMR (5% pyridine-*d*₅-CDCl₃) δ = 9.56 (1H, s, 10-H), 9.22 (1H, s, 5-H), 8.34 (1H, s, 20-H), 7.73/7.72 (2H, d, *J* = 8 Hz, 3-, 5-H of 3³-Ar), 7.26/7.25 (1H, t, *J* = 8 Hz, 4-H of 3³-Ar), 5.66, 5.64 (each 1H, d, *J* = 12 Hz, 3-CH₂), 5.22 (2H, s, 3¹-OCH₂), 5.19, 5.07 (each 1H, d, *J* = 19 Hz, 13¹-CH₂), 4.38 (1H, dq, *J* = 2, 7 Hz, 18-H), 4.21 (1H, dt, *J* = 8, 2 Hz, 17-H), 4.15–4.07 (2H, m, 17²-CO₂CH₂), 3.45 (2H, q, *J* = 7 Hz, 8-CH₂), 3.69 (3H, s, 12-CH₃), 3.59–3.49 (22H, m, 17²-CO₂CCH₂(OCH₂CH₂)₅), 3.34 (3H, s, 17²-CO₂(C₂O)₆CH₃), 3.29 (3H, s, 7-CH₃), 3.28 (3H, s, 2-CH₃), 2.57–2.53, 2.42–2.37, 2.29–2.23, 1.98–1.92 (each 1H, m, 17-CH₂CH₂), 1.711 (3H, d, *J* = 7 Hz, 18-CH₃), 1.705 (3H, t, *J* = 7 Hz, 8¹-CH₃); ¹³C NMR (5% pyridine-*d*₅-CDCl₃) δ = 196.9, 173.0, 167.6, 161.0, 155.5, 152.9, 151.3, 150.8, 149.4, 147.6, 147.4, 145.6, 143.5, 138.6, 135.8, 135.1, 133.8, 131.8, 129.0, 128.2, 127.2, 123.6, 105.8, 105.1, 98.3, 92.1, 71.8, 70.42, 70.37, 70.35, 70.34, 70.32, 70.29, 68.9, 64.8, 64.0, 63.4, 58.9, 50.5, 48.5, 48.3, 30.2, 29.6, 23.3, 19.4, 17.4, 12.7, 11.3, 10.9 [three ¹³C peaks in hexa(ethylene glycol) ester were overlapped with the others.]; HRMS (APCI) found: *m/z* = 1059.3688, calcd for C₅₂H₆₃N₆O₁₄Zn: MH⁺, 1059.3688.

2. ^1H and ^{13}C NMR Spectra

2-1. ^1H and ^{13}C NMR spectra of **ONB'-CHO**

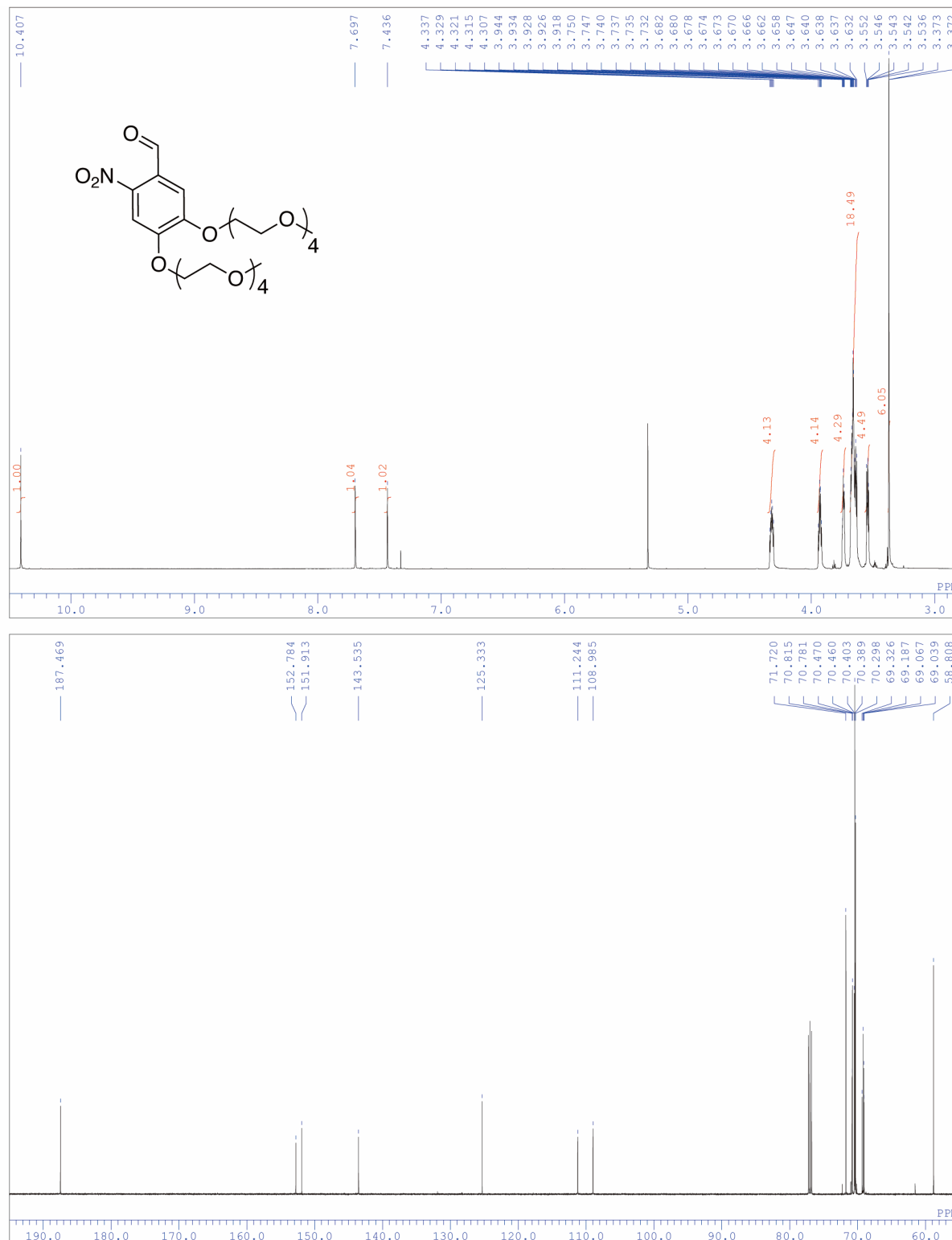


Figure S1. ^1H (upper) and ^{13}C NMR spectra (lower) of **ONB'-CHO** in CDCl_3 .

2-2. ^1H and ^{13}C NMR spectra of **ONB-OH**

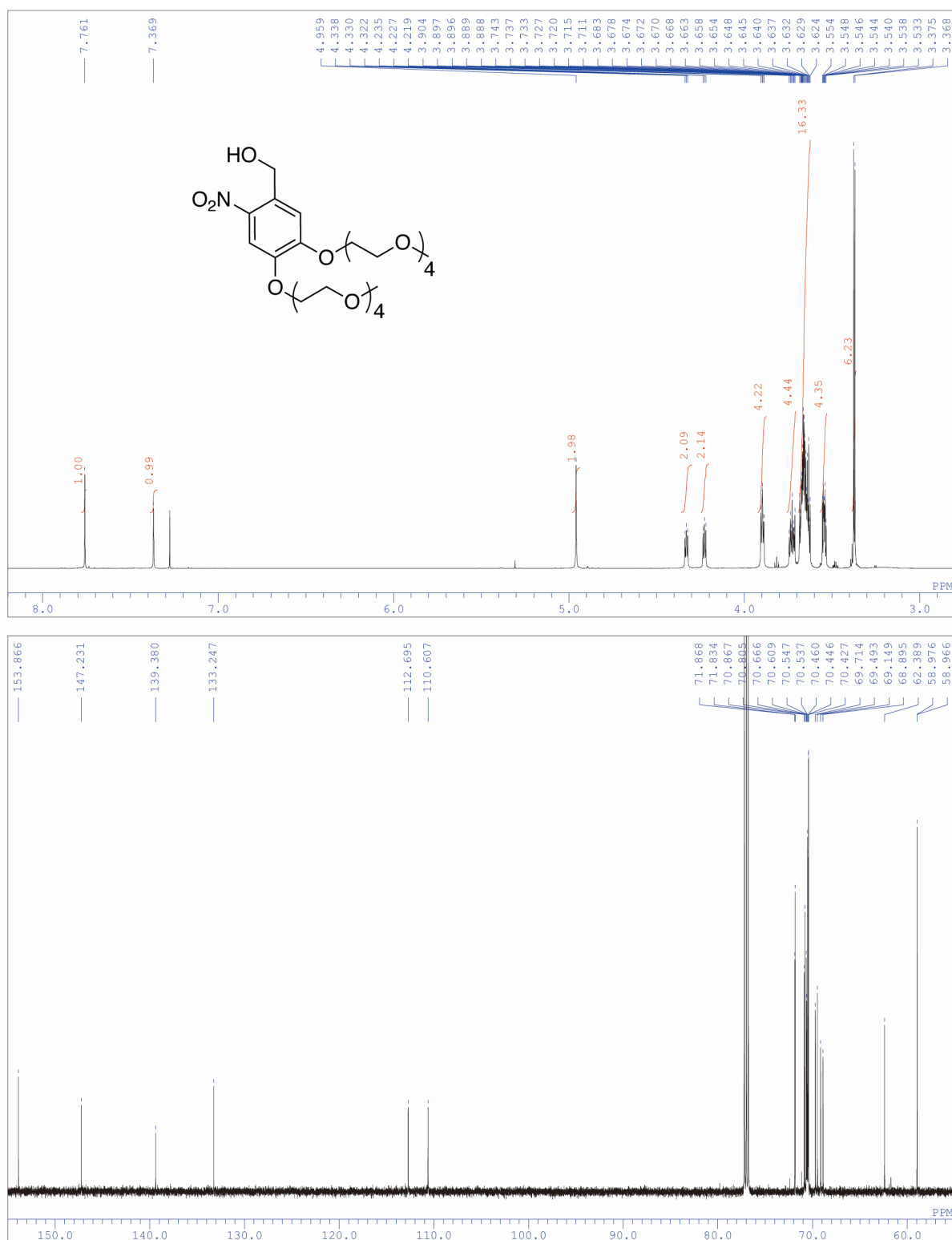


Figure S2. ^1H (upper) and ^{13}C NMR spectra (lower) of **ONB-OH** in CDCl_3 .

2-3. ^1H and ^{13}C NMR spectra of **ONB-Br**

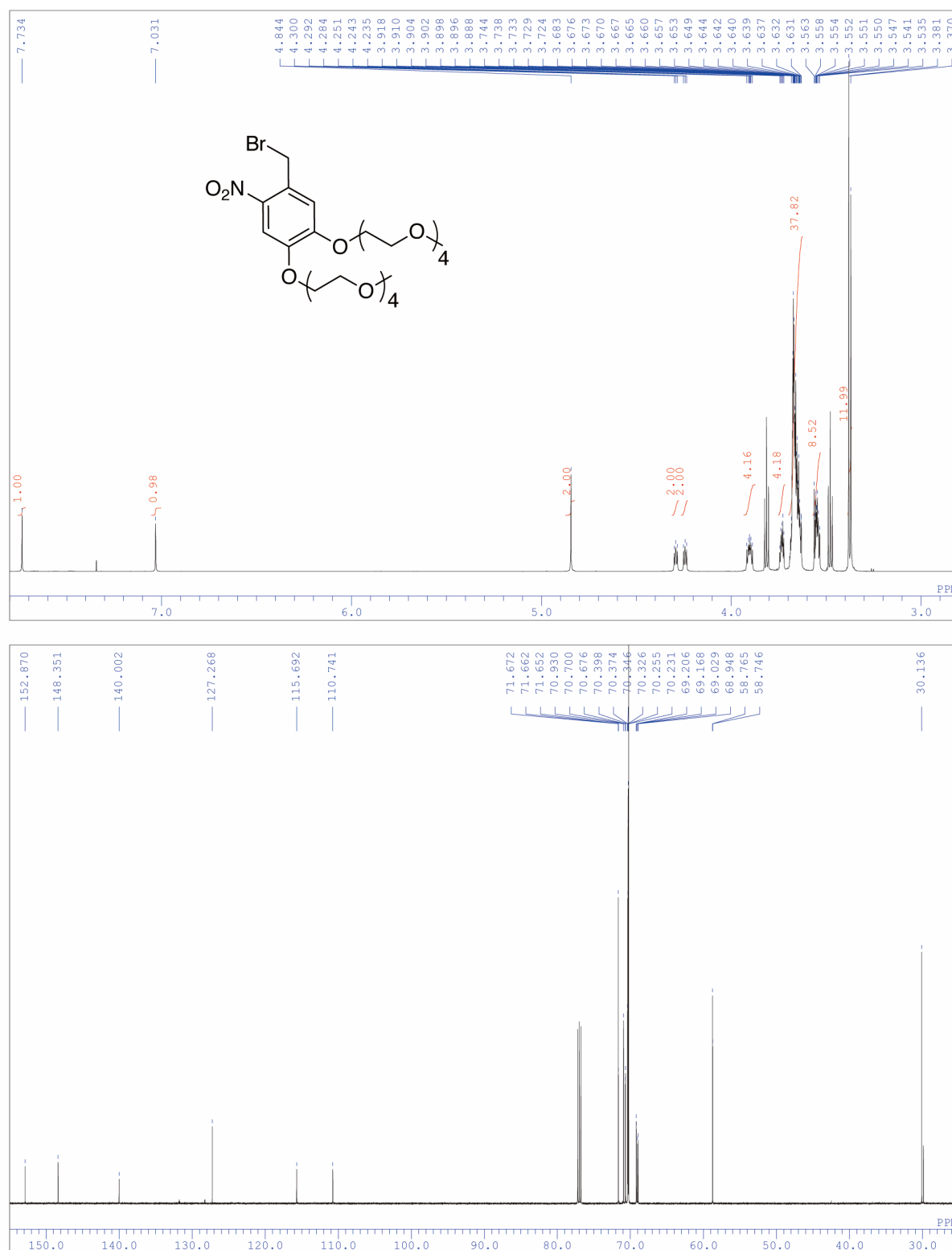


Figure S3. ^1H (upper) and ^{13}C NMR spectra (lower) of **ONB-Br** in CDCl_3 .

2-4. ^1H and ^{13}C NMR spectra of $\text{H}_2\text{-CHO}$

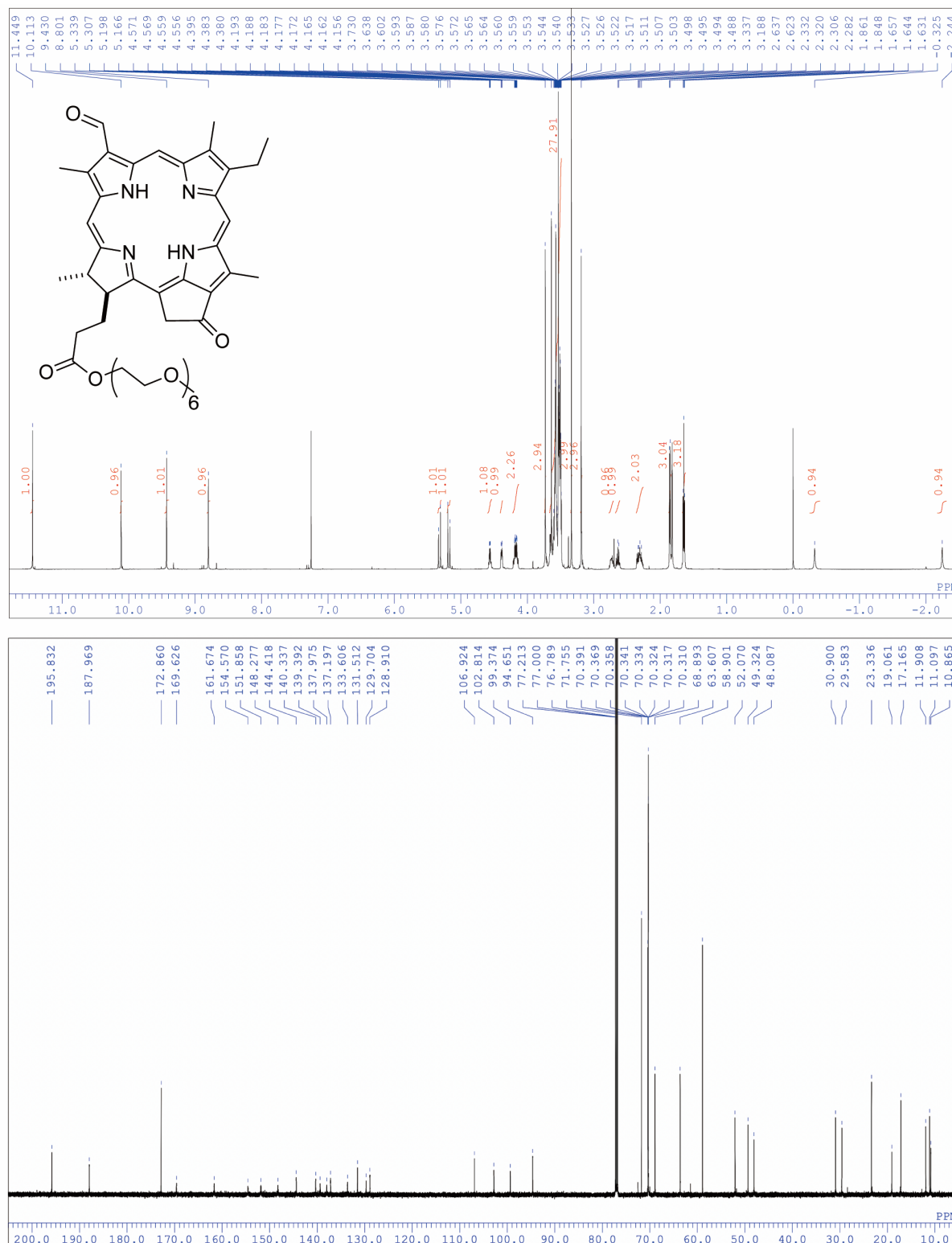


Figure S4. ^1H (upper) and ^{13}C NMR spectra (lower) of $\text{H}_2\text{-CHO}$ in CDCl_3 .

2-5. ^1H and ^{13}C NMR spectra of **H₂-HM**

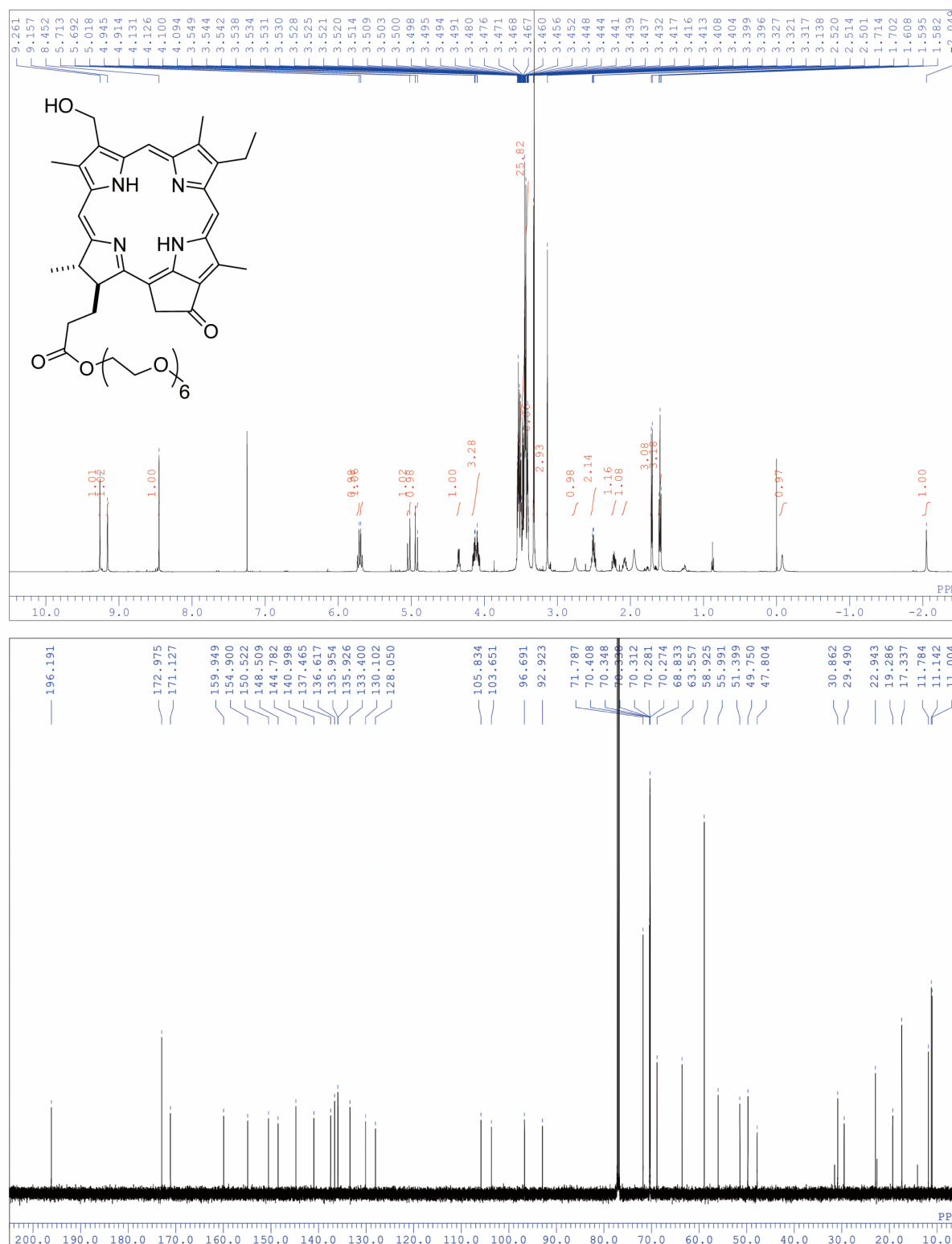


Figure S5. ^1H (upper) and ^{13}C NMR spectra (lower) of **H₂-HM** in CDCl_3 .

2-6. ^1H and ^{13}C NMR spectra of **Zn-HM**

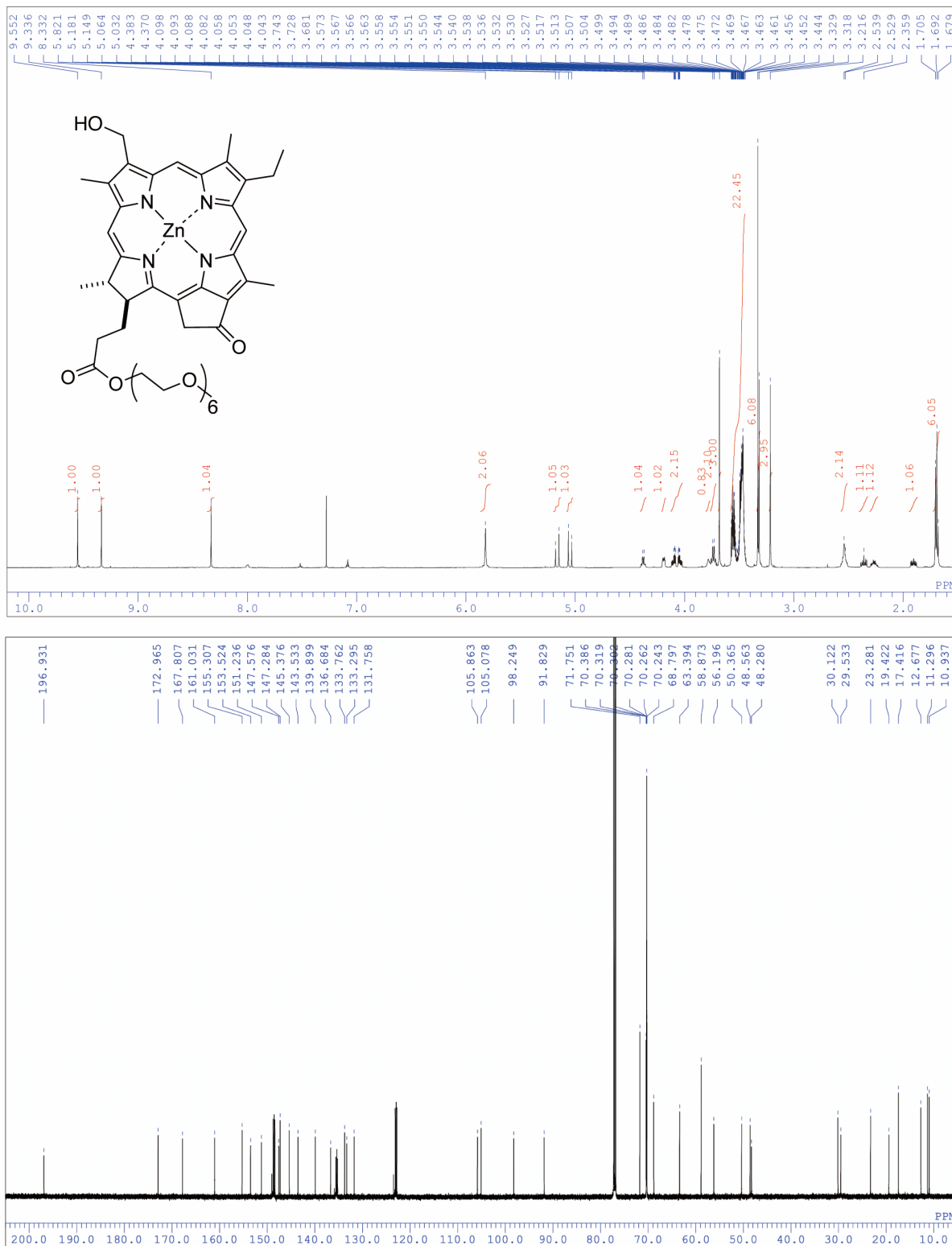


Figure S6. ^1H (upper) and ^{13}C NMR spectra (lower) of **Zn-HM** in CDCl_3 containing 5%(v/v) pyridine- d_5 .

2-7. ^1H and ^{13}C NMR spectra of **Zn-ONB**

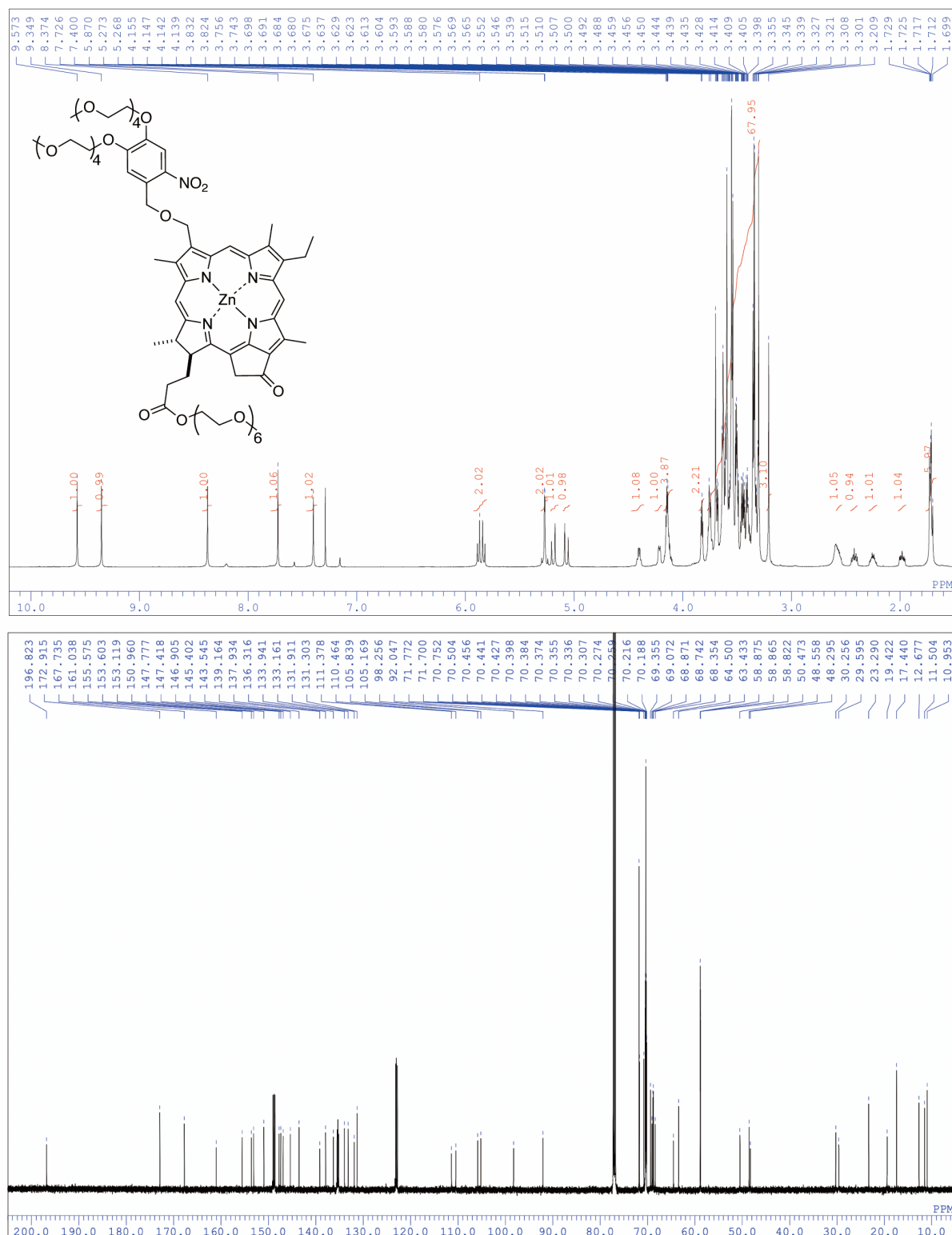


Figure S7. ^1H (upper) and ^{13}C NMR spectra (lower) of **Zn-ONB** in CDCl_3 containing 5% (v/v) pyridine- d_5 .

2-8. ^1H and ^{13}C NMR spectra of **Zn-DNB**

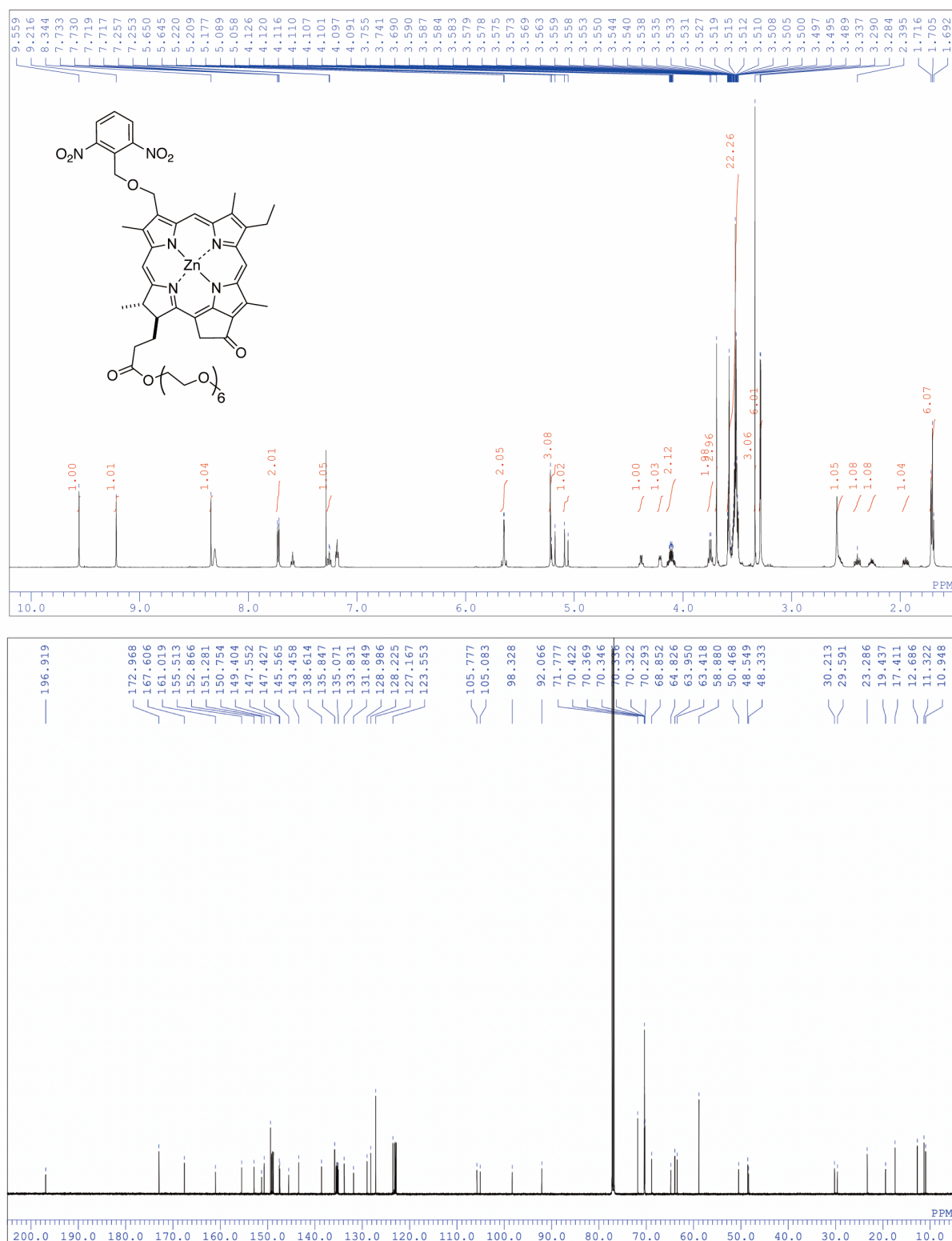


Figure S8. ^1H (upper) and ^{13}C NMR spectra (lower) of **Zn-DNB** in CDCl_3 containing 5%(v/v) pyridine- d_5 .

3. Preparations of Chlorophyll Aggregates

3-1. Diluted Assembly

Assembling Chl **Zn-HM** dissolved in CHCl_3 was injected into a sample tube, and the solvent was evaporated *in vacuo*. Dried **Zn-HM** in the sample tube was dissolved in EtOH (20 μL), and then 99-fold water (1980 μL) was added into the monomeric EtOH solution to give 1%(v/v) EtOH– H_2O (2 mL). Just after preparation of the aqueous solution, the solution was drop-casted on a mica substrate. The solvents were evaporated to provide a sample for AFM.

3-2. Photoactivated Assembly

Caged Chl **Zn-DNB** dissolved in CHCl_3 was injected into a sample tube, and the solvent was evaporated *in vacuo*. Dried **Zn-DNB** in the sample tube was dissolved in EtOH, and then 99-fold water (1980 μL) was added into the monomeric EtOH solution to give 1%(v/v) EtOH– H_2O . The aqueous solution of **Zn-DNB** in a 10 mm quartz cell was UV-irradiated at r.t. (Figure S9) to give self-aggregates of deprotected **Zn-HM**. Just after preparation of the aqueous of **Zn-HM** aggregates, the solution was drop-casted on a mica substrate. The solvents were evaporated to provide a sample for AFM.

The illuminated wavelength of UV-light was set at 290 nm with the full width at half maxima (FWHM) of 10 nm. The UV-light source was Asahi Spectra MAX-303 with a 300 W xenon lamp using a UV-type mirror module (250–385 nm) and a bandpass filter LX0290 ($T\% \geq 60$): a light power at 290 nm was ca. 100 mW/cm² with LX0290.

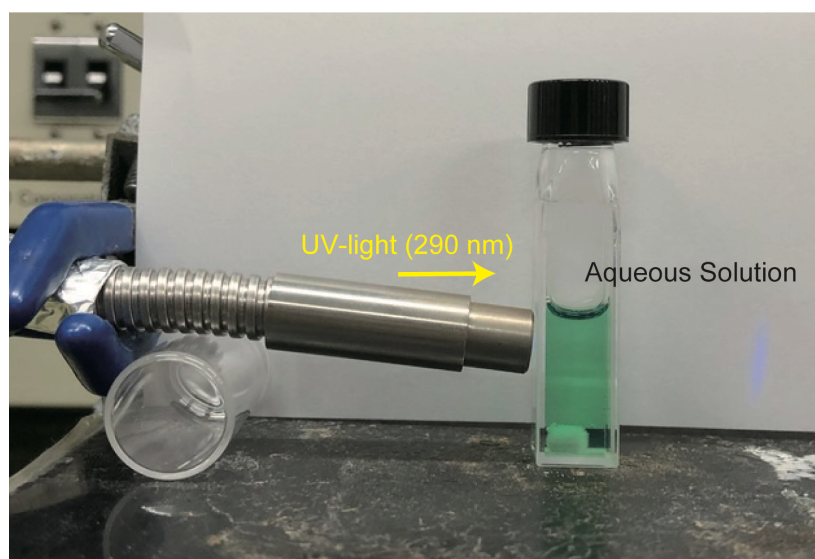


Figure S9. Photograph of UV-irradiation experiment.

4. UV-Vis Absorption and CD Spectra of Zn-ONB

The EtOH solution of **Zn-ONB** gave sharp UV-visible (vis) absorption peaks, indicating that **Zn-ONB** was monomeric in EtOH (Figure S10a, black dotted line). However, 1%(v/v) EtOH-H₂O solution of **Zn-ONB** showed a slightly red-shifted (656 nm to 668 nm) and broadened Qy absorption band where an S-shaped circular dichroism (CD) signal was observed (Figure S10a, red solid line). The observation was different from the spectral changes driven from chlorosomal self-assembly of **Zn-HM** (Figure 2c), implying the formation of closed dimer of **Zn-ONB** (Figure S10b).^[S4-S6] The strongly interacted **Zn-ONB** dimer was photostable, thus the deprotection in the species did not proceed by UV-irradiation in the aqueous solution (Figure S10a, gray and blue lines).

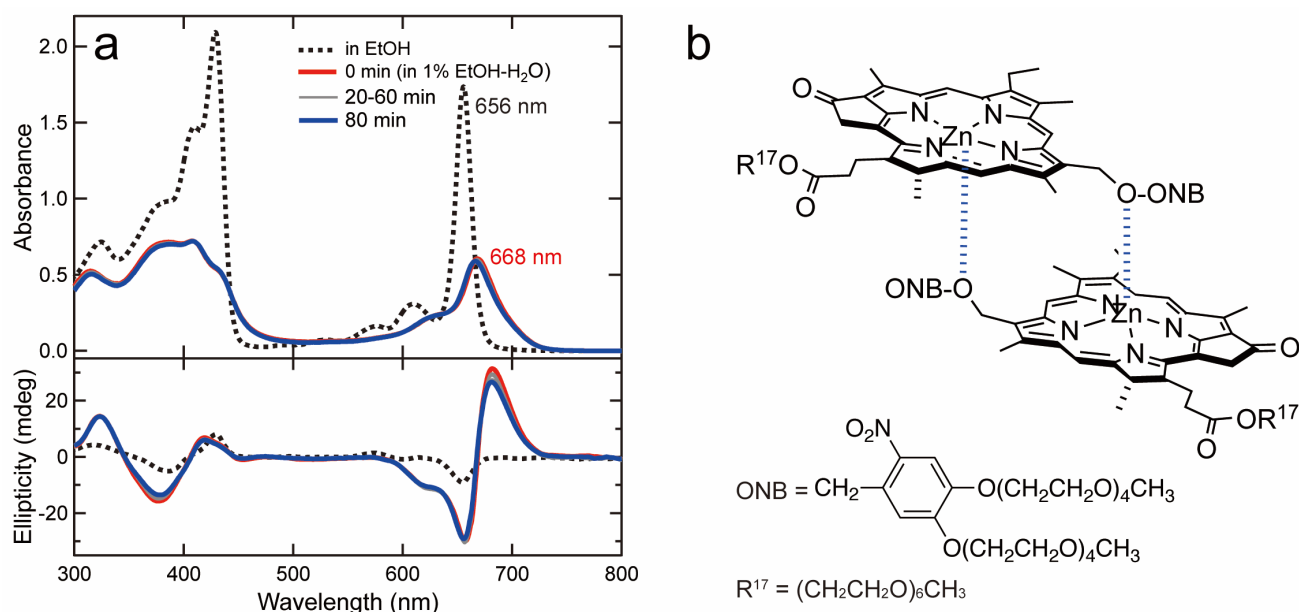


Figure S10. (a) UV-vis absorption and CD spectra of **Zn-ONB** in EtOH (black dotted line) as well as 1%(v/v) EtOH-H₂O before UV-irradiation (red solid line) and after UV-irradiation for 20, 40, 60 (gray solid lines), and 80 min (blue solid line). (b) Chemical structure of closed **Zn-ONB** dimer.

5. Photo-Deprotection of Zn-DNB

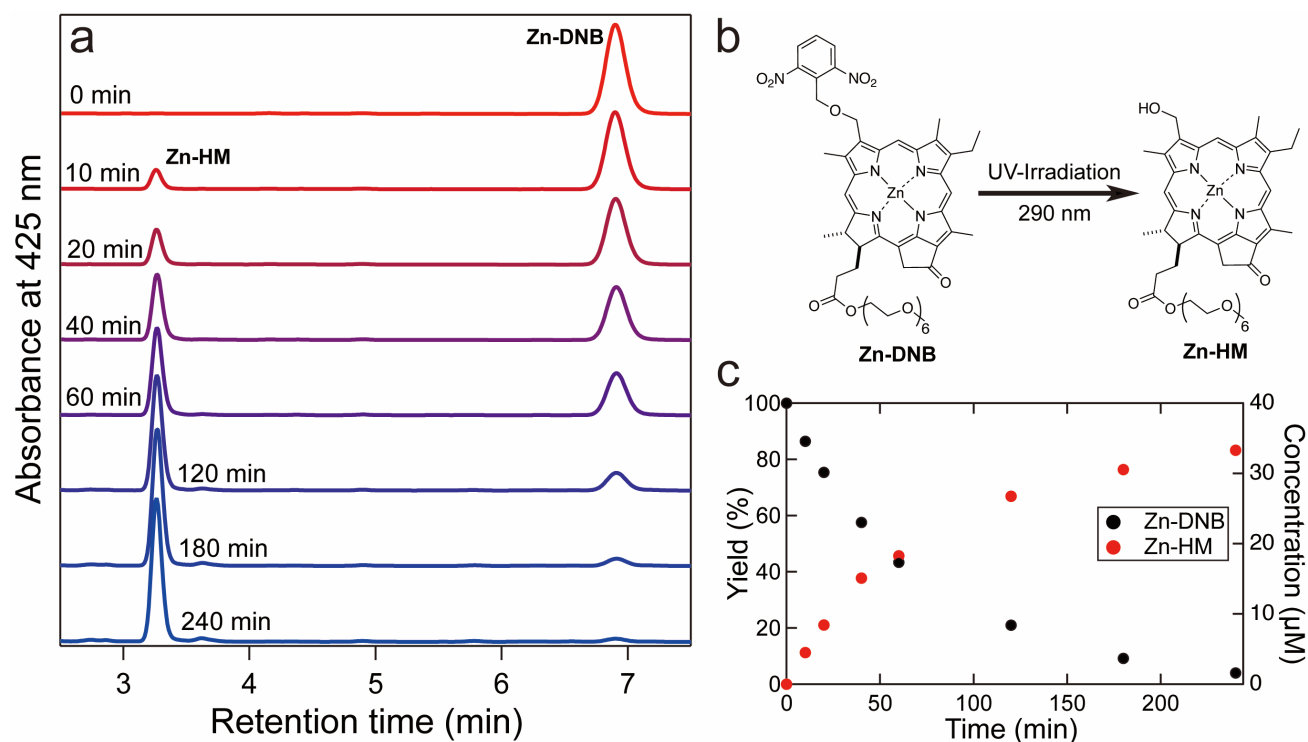


Figure S11. (a) Time-dependent HPL chromatographic changes of **Zn-DNB** (40 μM) with UV-irradiation (red to blue). HPLC conditions: ODS column (Cosmosil 5C₁₈AR-II) 4.6 φ × 150 mm, acetonitrile : H₂O : pyridine = 80 : 20 : 0.5, 1.0 mL/min. Peaks at 3.2 and 6.9 min were assigned to **Zn-HM** and **Zn-DNB**, respectively. (b) Chemical structures of **Zn-DNB** and photo-deprotected **Zn-HM**. (c) Photo-deprotection yield of **Zn-DNB** (black) to **Zn-HM** (red) and their corresponding concentration in 1%(v/v) EtOH–H₂O.

6. AFM Images of Chlorophyll Aggregates

6-1. AFM Images of **Zn-DNB** Aggregates before UV-Irradiation

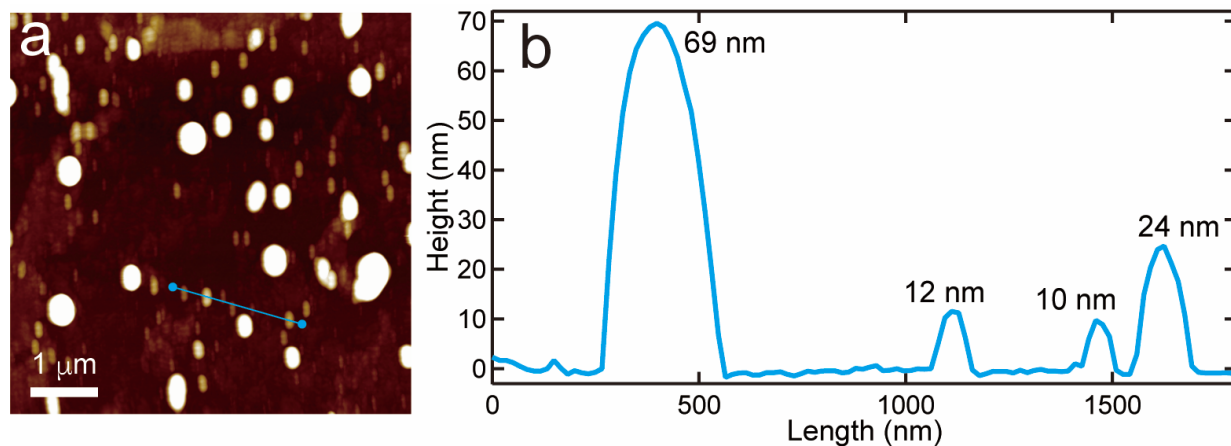


Figure S12. (a) AFM image of **Zn-DNB** aggregates before UV-irradiation. The scale bar is 1 μm. (b) Height profile of particle-like **Zn-DNB** aggregates.

6-2. AFM Images of Nanoparticles of **Zn-HM** and **Zn-DNB**

AFM images of the sample after UV-irradiation with half-intensity for 15 min showed small and large particles, and nanotubes were not observed (Figure S13a). We guess that small particles with a 3–5 nm height (Figure S13b) were **Zn-HM** aggregates before construction of nanotubes, while large particles were amorphous **Zn-DNB** aggregates. The small particles decreased and tubular aggregates increased after further UV-irradiation (30–120 min), supporting that the small particle was nucleus of nanotubes.

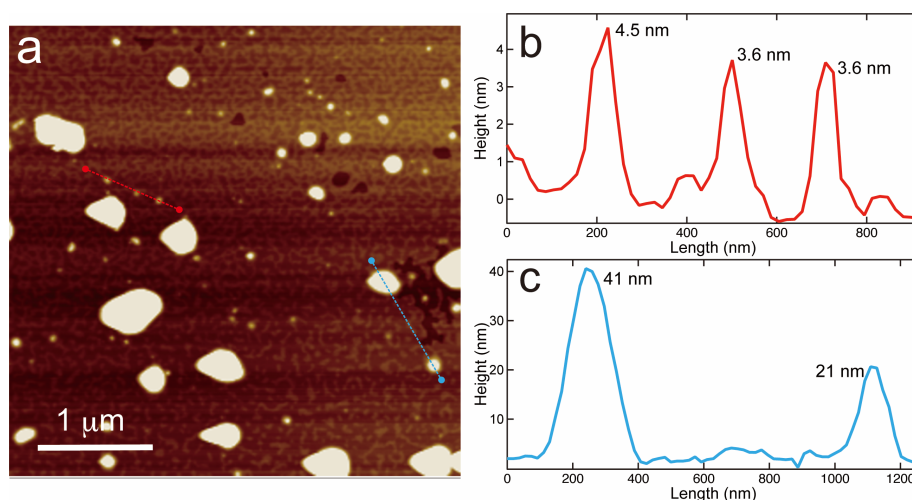


Figure S13. (a) AFM image of particle-like aggregates prepared by UV-irradiation with half-intensity for 15 min. The scale bar is 1 μm. (b,c) Height profiles of small (b) and large nanoparticles (c).

6-3. Length Distribution of Nanotubes from AFM Images

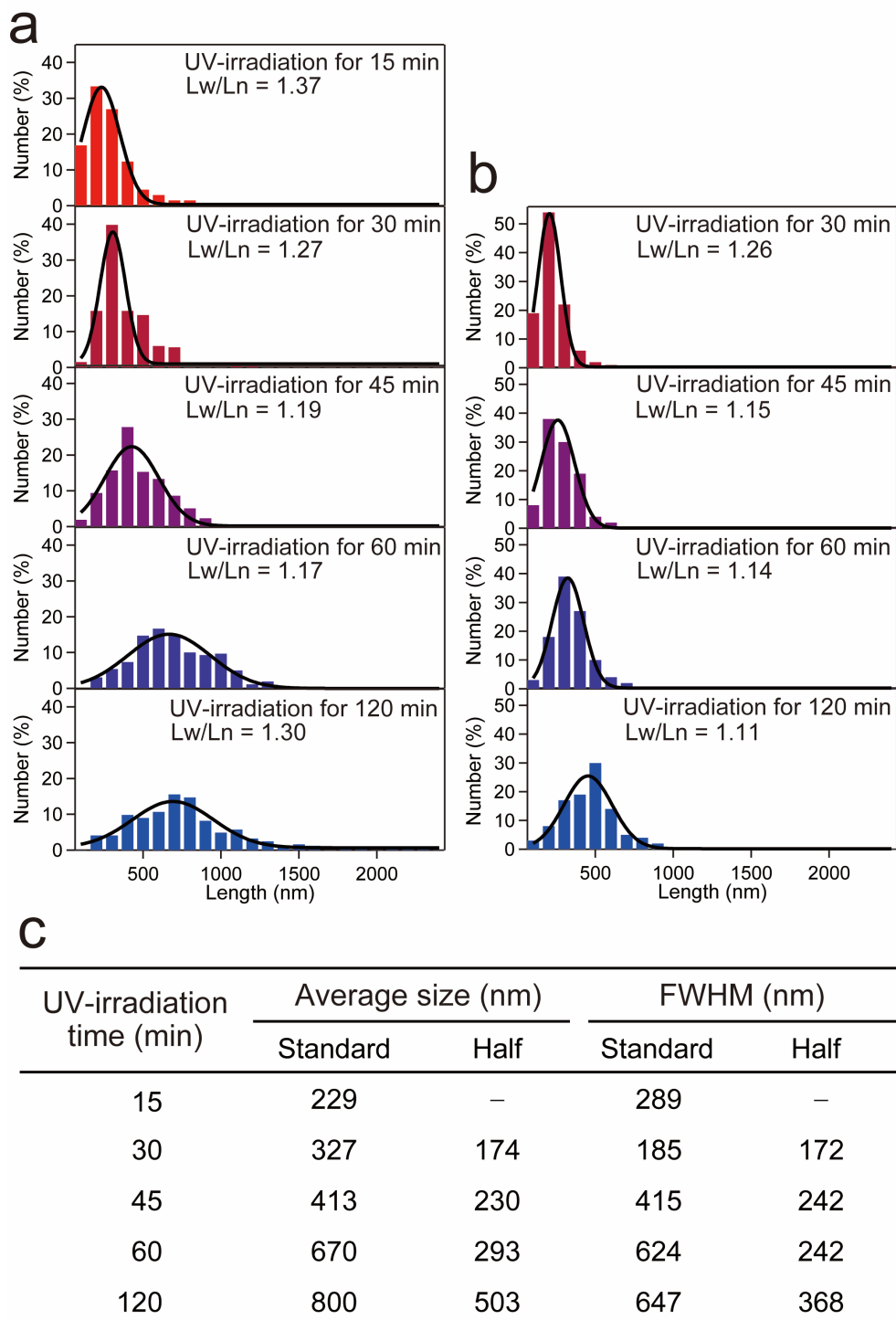


Figure S14. (a,b) Length distribution of tube-like aggregates of **Zn-HM** prepared by UV-irradiation with standard- (a) and half-intensity (b) for 15, 30, 45, 60, 120 min and their Gaussian curve fittings. (c) Average lengths of tube-like aggregates of **Zn-HM** prepared by photoinduced assembly and FWHM of length distributions.

The length distributions of nanotubes prepared by photoactivated assembly were determined by counting the number of produced nanotubes (the number of analyzed nanotubes was ca. 200 in each experiments) from AFM images. The length of the nanotubes was measured from the end-to-end distance of the nanotubes. In case of the largely bent nanotubes, the length was a sum of end-to-bend and bend-to-bend distances.

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