Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
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Supporting Information

Chiral Inversion and Enhanced Cooperative Self-assembly of Biosurfactant-Functionalized Porphyrin Chromophores

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S1. Materials and Methods

S1.1 Materials and routine analysis methods

The lactonic sophorolipid (LSL) acetylated at the 6'- and/or 6''- positions (LSL[6'Ac,6''Ac]) was separated from crude SLs by flash column chromatography eluting with chloroform and methanol (10:1), as previously reported by Peng *et al.*[1] All other chemicals and solvents were

analytical grade and used as received without further purification unless otherwise noted. Synthesized SLs and SL-porphyrin conjugated compounds were purified by flash chromatography on an automated Biotage SP system (Charlotte, NC, U.S.A.) using Biotage silica Snap Columns (25, 50 and 100 g per packing) by gradient elution with $CHCl_3$ and CH_3OH mixtures. Thin layer chromatography (TLC) was performed on aluminum-backed silica gel sheets purchased from Sigma–Aldrich (silica gel 60 matrix, 0.2 mm thickness) using methanol/chloroform as eluent. A cerium–ammonium–molybdate solution was used to visualize eluted compounds. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded in DMSO-d_6 on a Bruker spectrometer (Billerica, MA, U.S.A.) at 800 (201) or 600 (151) MHz respectively. Hydrogenation of sophorolipids were performed in a `Parr' shaking hydrogenation reactor (model: 3911EA 500 Ml) at ~3.0 barr of H_2 gas pressure. The LC/MS used for analysis of compound purity had an electrospray ionization mass spectrometer in positive mode. Melting point measurements were recorded on a Meltemp instrument.

S1.2 UV/vis and CD measurements

All spectroscopic measurements were at a molar concentration of 3.0×10^{-6} M in MeOH:water (1:1 v/v). Compounds **1C** and **2C** readily dissolved in MeOH at 6.0×10^{-6} M and room temperature. After sonication for 10 minutes neat deionized water (pH 7) was injected by syringe to attain the final target concentration 3.0×10^{-6} M in a 1:1 (v/v) mixture of MeOH:water. The UV/vis absorption and circular dichroism (CD) spectra were collected simultaneously in 1 cm path length cuvettes on a JASCO 815 CD spectrophotometer equipped with a Peltier (PFD-425s) temperature controller.

Variable-temperature spectral scans of prepared compounds were first heated to ~55 ˚C and held at this temperature for >15 minutes to allow the solution to thermally equilibrate. Each

sample solution was slow cooled at 1 ˚C min^{-1} and spectral scans were collected in increments of 5 ˚C per scan with a settling time of 30 seconds at each target temperature.

Temperature-dependent cooling curves, monitored at fixed wavelength, were collected by first heating samples to 50 ˚C such that they are in the monomeric state (high temperature) followed by slow cooling to 5 ˚C. A cooling rate of 1 ˚C min^{-1} was chosen to ensure that samples had sufficient time for thermal equilibration and to suppress kinetic effects while UV/vis absorption and CD ellipticity were recorded every 0.2 ˚C at 433 nm. A baseline measurement of 1:1 (v/v) MeOH:water was also recorded within the same temperature range at 433 nm which was used for baseline-correction of data.

S1.2 Electron microscopy images

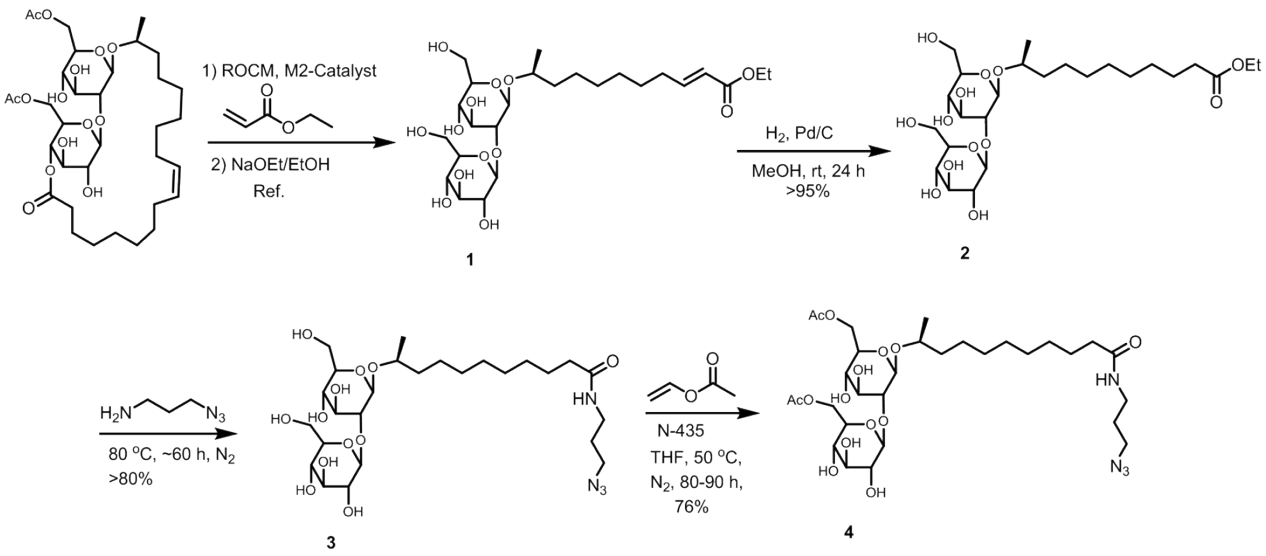
The recording of scanning electron microscopy (SEM) images was with a Tescan Vega-3 SEM in the Materials for Opto/Electronics Research and Education (MORE) center at Case Western Reserve University. Samples were prepared by drop-casting on a cooled aluminum SEM sample holder at 5 ˚C. Solutions were prepared by the aforementioned procedure to a target concentration of 1 mg mL^{-1} (450×10^{-6} M) in 1:1 (v/v) MeOH:water. Solutions were first heated to 60 ˚C and then slow cooled to 20 ˚C. To further promote the formation of assembled species, the solutions were cooled to 5 ˚C and then drop casted at this temperature (5 ˚C).

Transmission electron microscopy (TEM) images were recorded using a high-resolution analytical FEI Tecnai F30 instrument at the Swagelok Center for Surface Analysis of Materials (SCSAM) at Case Western Reserve University. Vials containing solutions of **2C** were prepared (0.5 mg mL^{-1}, 225×10^{-6} M) in MeOH:water. The vials were heated with an external bath to 60 ˚C and then slow cooled to about 10 ˚C. Samples were prepared on a clean 400 mesh Cu (UC-A on Lacey) TEM grid by floating the grid atop a drop of the solution for 60 seconds. The grid was

removed and excess solution was wicked with filter paper and allowed to dry. Subsequently, the sample was stained with uranyl acetate in water (2% by wt.)

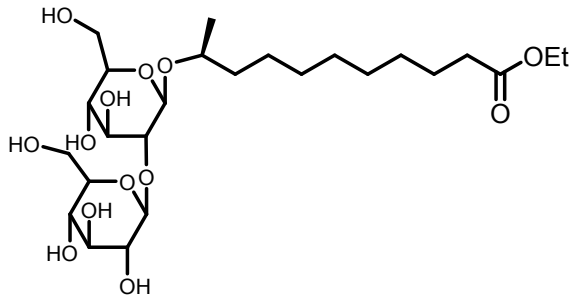
S2. Synthesis of short-chain sophorolipid derivatives:

Ring-opening of LSL was performed using Grubbs second generation ring-opening cross metathesis (ROCM) catalyst, then, alcoholysis with ethyl alcohol gave compound **1** (Scheme 1). Then, the double bond was hydrogenated with Pd/C to prepare the corresponding saturated ethyl ester compound **2** in >95% yield. Reaction of **2** with **3**-azido-**1**-propylamine gave the amide-functionalized azido-SL compound **3** in more than 80% yield. To increase the solubility of **3** in organic media, sophorose 6' and 6'' hydroxyl groups were regioselectively acetylated. This was accomplished using a commercially available immobilized form of *Candida antarctica* Lipase B (Novozyme 435, N435) to give column purified **4** in 76% yield. Di-conjugation of **4** to dialkynyl (Zn)porphyrin **5** followed our previously reported click reaction[2] yielding di-conjugated, di-acetylated, short-chain SL-(Zn)porphyrin (**2C-6',6''Ac**). Removal of acetyl groups to give **2C** was performed under alkaline conditions in >95% yield. Structures of both short-chain (**2C**) and long-chain (**1C**) analogues of di-conjugated SL-(Zn)porphyrin are displayed in Figure 1 of the main text.



Scheme 1. Synthetic route of sophorolipid derivatives **1**-**4.** Details of synthetic methods are given section S2.

S2.1 Synthesis of compound 1:



2

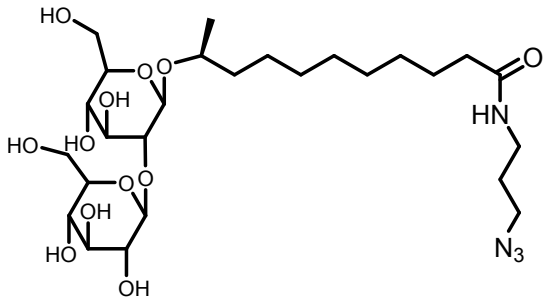
The ethyl ester of short chain sophorolipid compound **1** was synthesized exactly as was described in a previous report by our lab.[1]

S2.2 Synthesis of compound 2:

Hydrogenation of the double bond of Compound **1** was carried out by adapting a literature procedure [1] using a Parr shaker hydrogenation apparatus. MeOH was used as solvent since Compound **1** was not soluble in EtOH at room temperature. Compound **1** (0.5 g, 0.905 mmol) was dissolved in ~50 mL of MeOH and transferred to a 500 mL high pressure glass cylinder. Then, 50 mg (10% w/w) of Pd/C (10% Pd) was added slowly over the course of 10 mins under argon atmosphere while stirring to the glass cylinder. The reaction mixture was maintained under hydrogen atmosphere (~ 3 barr) at room temperature with shaking for 24 h. The reaction mixture was filtered through celite to remove Pd/C, the filtrate was collected, MeOH was removed using a rotovaporator to obtain Compound **2** as a white solid (MP: 138-143 °C, >95% yield) without further purification: ^{1}H NMR

(800 MHz, DMSO) δ 5.48 (d, *J* = 3.7 Hz, 1H), 5.20 (d, *J* = 3.4 Hz, 1H), 5.02 (d, *J* = 5.3 Hz, 1H), 4.94 (d, *J* = 4.8 Hz, 1H), 4.88 (d, *J* = 5.3 Hz, 1H), 4.43 (t, *J* = 5.8 Hz, 1H), 4.38 (d, *J* = 7.8 Hz, 1H), 4.30 (d, *J* = 7.7 Hz, 1H), 4.22 (t, *J* = 5.8 Hz, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.68 – 3.60 (m, 3H), 3.51 – 3.46 (m, 1H), 3.41 (dt, *J* = 11.6, 5.8 Hz, 1H), 3.39 – 3.34 (m, 1H), 3.20 (dd, *J* = 8.9, 7.9 Hz, 1H), 3.15 (td, *J* = 8.9, 4.8 Hz, 1H), 3.13 – 3.04 (m, 4H), 2.99 (ddd, *J* = 9.0, 8.0, 3.4 Hz, 1H), 2.26 (t, *J* = 7.4 Hz, 2H), 1.51 (dd, *J* = 12.9, 5.7 Hz, 3H), 1.36 – 1.20 (m, 11H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.13 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (201 MHz, DMSO) δ 173.85, 104.90, 101.99, 82.94, 77.91, 77.40, 77.15, 76.97, 76.82, 75.95, 70.88, 70.83, 61.94, 61.89, 60.56, 37.09, 34.45, 30.16, 29.87, 29.66, 29.39, 25.49, 25.42, 22.24, 15.08. HRMS (ESI-MS), calculated for $C_{25}H_{46}NaO_{13}$ $[M+Na]^+$, 577.2814, found, 577.2813.

S2.3 Synthesis of compound 3:

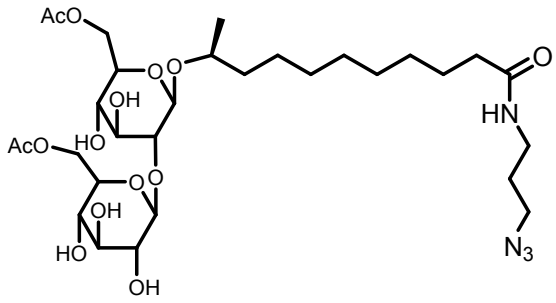


3

In a 10 mL round bottomed flask equipped with a magnetic stirrer was added 0.450 g (0.811 mmol) of **2** and 0.405 g (5.35 mmol, 6.6 equiv.) of 3-azido-1-propylamine. The reaction was maintained at 80 °C for about 60 h (2.5 days) under argon atmosphere with magnetic stirring. Monitoring of the reaction was by TLC (30% MeOH in $CHCl_3$). Then, the brown waxy crude was dissolved in a minimum amount of MeOH and the contents were transferred dropwise with magnetic stirring into a flask with ~ 50 mL of diethylether. Then resulting precipitated solid was collected by filtration and then purified by flash column chromatography (MeOH:$CHCl_3$, gradient elution). After solvent removal 0.404 g (82% yield) of Compound **3** was obtained that appeared as a light brown solid that melted at 135-138 °C: ^{1}H NMR (800 MHz, DMSO) δ 7.81 (t, *J* = 5.5 Hz, 1H), 4.39 (d, *J* = 7.8 Hz, 1H), 4.30 (d, *J* = 7.7 Hz, 1H), 3.69 – 3.59 (m, 3H), 3.48 (dd, *J* = 11.5, 4.9 Hz, 1H), 3.41 (dd, *J* = 11.7, 5.7 Hz, 1H), 3.39 (t, *J* = 6.8 Hz, 2H), 3.37 – 3.32 (m, 8H), 3.20 (dd, *J* = 8.9, 7.9 Hz, 1H), 3.15 (t, *J* = 8.9 Hz, 1H), 3.13 – 3.03 (m, 6H), 2.99 (dd, *J* = 8.8, 8.1 Hz, 1H), 2.62 (t, *J* = 6.8 Hz, 2H), 2.04 (t, *J* = 7.5 Hz, 2H), 1.66 – 1.59 (m, 4H), 1.56 – 1.44 (m, 3H), 1.36 – 1.19 (m, 10H), 1.13 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (201 MHz, DMSO) δ 173.14, 104.88, 102.00, 82.91, 77.90, 77.40, 77.15, 76.97, 76.83, 75.95, 70.88, 70.84, 61.95, 61.89, 49.36, 49.28, 39.29, 37.10, 36.66, 36.35, 32.13,

30.22, 29.96, 29.77, 29.62, 29.39, 26.23, 25.52, 22.24. HRMS (ESI-MS), Calculated for $C_{26}H_{49}N4O_{12}$ $[M+H]^+$, 609.3341, found, 609.3332.

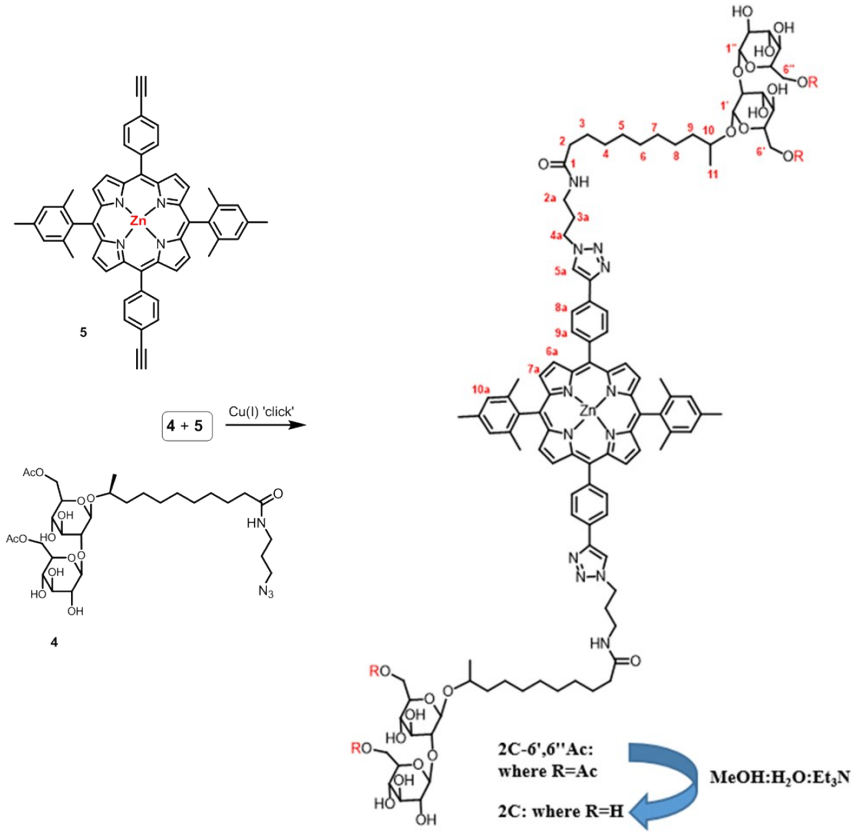
S2.4 Synthesis of compound 4:



4

In an oven dried 25 mL round bottomed flask equipped with a magnetic stirrer was added 0.3 g (0.492 mmol) of **3**, dissolved in 6 mL of dry THF, followed by the addition of 0.421g (4.9 mmol, 10.0 equiv.) of vinylacetate and 100 mg of Novozyme 435 (N435). The reaction contents were maintained at 50 ˚C under argon atmosphere for 4-5 days with magnetic stirring. TLC (20% MeOH:$CHCl_3$) was used to monitor reaction progress. The suspension was filtered to remove N435 beads and the and the solvent was removed by rotoevaporation. The crude product was purified by the flash column chromatography (MeOH:$CHCl_3$, gradient elution). The resulting product Compound **4** (260 mg, 76% yield) appeared as a light yellow solid with a melting point range from 92-96 ^oC: ^1H NMR (800 MHz, DMSO) δ 7.80 (t, *J* = 5.5 Hz, 1H), 5.59 (s, 1H), 5.43 (s, 1H), 5.29 (d, *J* = 5.6 Hz, 1H), 5.17 (d, *J* = 5.6 Hz, 1H), 5.09 (d, *J* = 4.9 Hz, 1H), 4.40 (d, *J* = 7.8 Hz, 1H), 4.36 (d, *J* = 7.8 Hz, 1H), 4.22 (ddd, *J* = 19.4, 11.7, 1.8 Hz, 2H), 4.04 (dd, *J* = 11.8, 6.8 Hz, 1H), 4.00 (dd, *J* = 11.7, 5.8 Hz, 1H), 3.61 (dt, *J* = 12.0, 6.0 Hz, 1H), 3.41 – 3.35 (m, 2H), 3.18 (ddd, *J* = 13.9, 8.9, 6.5 Hz, 2H), 3.13 – 3.06 (m, 4H), 3.01 (t, *J* = 8.5 Hz, 1H), 2.03 (t, *J* = 7.5 Hz, 2H), 2.00 (d, *J* = 0.6 Hz, 6H), 1.63 (p, *J* = 6.8 Hz, 2H), 1.47 (dd, *J* = 14.1, 7.3 Hz, 3H), 1.34 – 1.16 (m, 12H), 1.10 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (201 MHz, DMSO) δ 173.11, 171.18, 171.15, 105.32, 101.77, 83.76, 77.09, 76.99, 76.76, 75.84, 74.71, 74.04, 70.74, 70.66, 64.74, 64.43, 49.35, 37.19, 36.65, 36.35, 30.14, 29.98, 29.78, 29.63, 29.39, 26.24, 25.46, 22.19, 21.59. HRMS (ESI-MS), calculated for $C_{30}H_{52}N_4NaO_{14}$ $[M+Na]^+$, 715.3343, found, 715.3356.

2.5 'Click' reaction conditions for the synthesis of compound 2C-6',6''Ac:



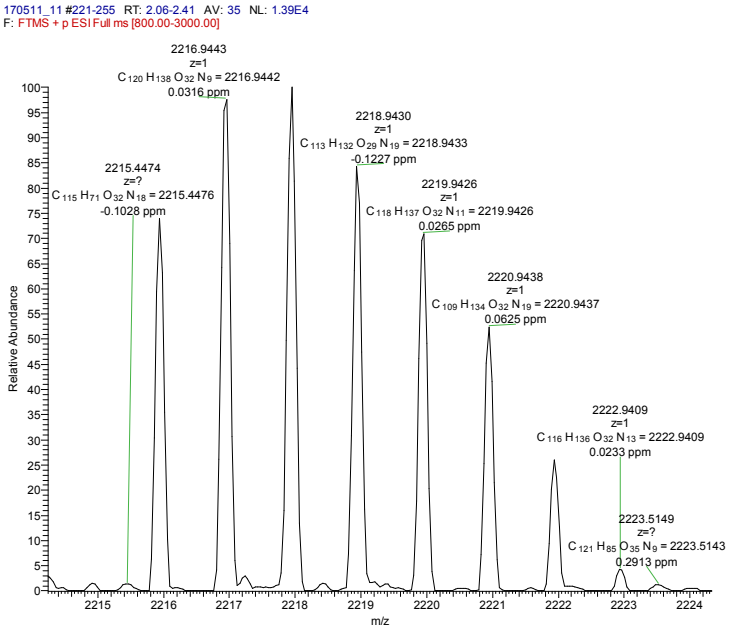
In the following order, the following compounds were added to a 25 mL round bottomed flask equipped with a magnetic stirring: Compound **4** (80 mg, 2.2 equiv., 0.1155 mmol) dissolved in THF (5 mL); Compound **5** (dialkynyl functionalized Zn-porphyrin, 42.5 mg, 1.0 equiv., 0.0525 mmol), whose synthesis was reported in Ref. 2; water (5 mL); $CuSO_4{\cdot}5H_2O$ (26.2 mg, 2.0 equiv., 0.105 mmol) and sodium ascorbate (31.2 mg, 3.0 equiv., 0.157 mmol). The flask was attached to a water condenser with an argon inlet and the reaction was performed under argon at 60 °C for 12 h with stirring. Reaction progress was monitored by TLC (20% MeOH:$CHCl_3$, R_f of the starting material **4** and product **2C-6',6''Ac** are 0.4 and 0.33 respectively). After cooling to room temperature, THF and water were removed by rotoevaporation at 55 °C and 150 torr. The crude product was lyophilized overnight and then purified by flash silica-gel column chromatography using gradient elution (MeOH:$CHCl_3$). The product **2C-6',6''Ac** (98 mg, 85% yield) appears as a red/purple solid: ^{1}H NMR (800 MHz, DMSO) δ 8.86 (s, 2H), 8.80 (d, J = 4.4 Hz, 4H), 8.59 (d, J = 4.4 Hz, 4H), 8.25 (dd, J = 26.1, 7.9 Hz, 8H), 7.96 (t, J = 5.6 Hz, 2H), 7.32 (s, 4H), 5.58 (d, J =

3.4 Hz, 2H), 5.43 (d, *J* = 3.2 Hz, 2H), 5.28 (d, *J* = 5.5 Hz, 2H), 5.18 (d, *J* = 5.5 Hz, 2H), 5.10 (d, *J* = 4.7 Hz, 2H), 4.53 (t, *J* = 6.7 Hz, 4H), 4.41 (d, *J* = 7.8 Hz, 2H), 4.36 (d, *J* = 7.7 Hz, 2H), 4.26 – 4.19 (m, 4H), 4.03 (ddd, *J* = 17.6, 11.8, 6.3 Hz, 4H), 3.64 – 3.58 (m, 2H), 3.41 – 3.35 (m, 5H), 3.22 – 3.15 (m, 8H), 3.10 (dtd, *J* = 14.6, 9.4, 5.4 Hz, 4H), 3.02 (td, *J* = 9.0, 3.0 Hz, 2H), 2.58 (s, 6H), 2.11 (td, *J* = 7.1, 3.4 Hz, 8H), 1.99 (d, *J* = 15.5 Hz, 12H), 1.79 (s, 12H), 1.49 (ddd, *J* = 13.4, 12.0, 6.6 Hz, 6H), 1.38 – 1.16 (m, 24H), 1.09 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (201 MHz, DMSO) δ 173.33, 171.19, 171.13, 150.06, 149.94, 147.22, 143.07, 140.07, 139.30, 137.79, 135.65, 132.87, 131.10, 130.84, 128.49, 124.27, 122.84, 120.13, 119.03, 105.31, 101.79, 83.73, 77.11, 77.00, 76.77, 75.84, 74.71, 74.04, 70.74, 70.67, 64.75, 64.43, 48.53, 37.20, 36.71, 36.44, 30.89, 30.17, 30.01, 29.83, 29.73, 26.28, 25.46, 22.35, 22.20, 21.97, 21.60, 21.57. HRMS (ESI-MS), Calculated for $C_{114}H_{144}N_{12}NaO_{28}Zn$ $[M+Na]^+$, 2215.4476, found, 2215.4474.

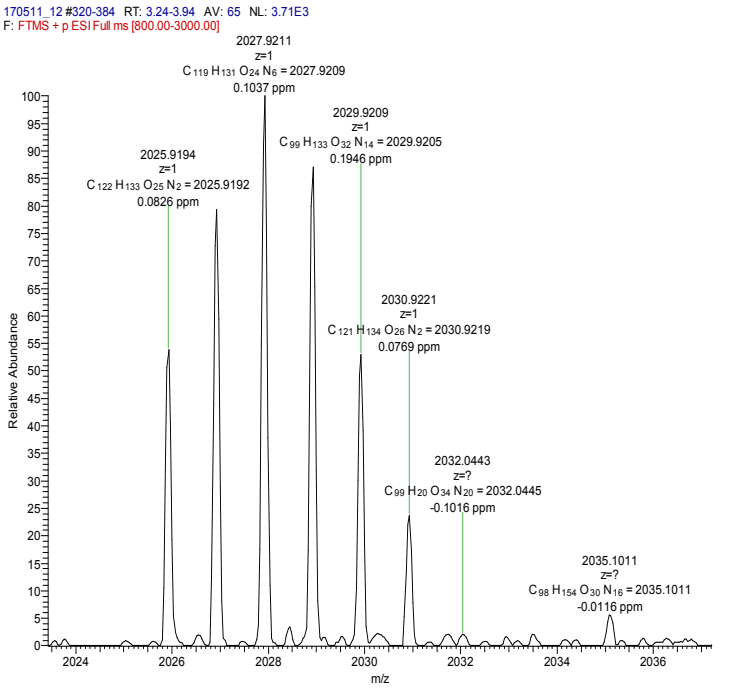
S2.6 Synthesis of compound 2C (deacetylation of 2C-6',6''Ac):

Compound **2C-6',6''Ac** (66.0 mg, 0.030 mmol) was dissolved in 9 mL of the solvent mixture MeOH:H_2O:Et_3N (5:1:1 v/v/v). The deacetylation reaction was conducted at room temperature, under argon for about 2 days while monitoring by TLC (MeOH:$CHCl_3$ 1:3 v/v). After complete deacetylation, partial removal of solvents were stripped by rotoevaporation followed by co-evaporation of Et_3N with toluene (3x10 mL) and then MeOH (1x10 mL) which gave a waxy substance. Further drying under vacuum for 24 h gave product **2C** that appears as a red/purple solid in nearly quantitative yield (>95%): ^{1}H NMR (800 MHz, DMSO) δ 8.86 (s, 2H), 8.80 (d, *J* = 4.4 Hz, 4H), 8.59 (d, *J* = 4.4 Hz, 4H), 8.25 (dd, *J* = 25.2, 8.0 Hz, 8H), 7.97 (t, *J* = 5.6 Hz, 2H), 7.32 (s, 4H), 5.51 (s, 2H), 5.22 (s, 2H), 4.98 (d, *J* = 93.8 Hz, 6H), 4.53 (t, *J* = 6.7 Hz, 4H), 4.44 (s, 2H), 4.40 (d, *J* = 7.8 Hz, 2H), 4.31 (d, *J* = 7.7 Hz, 2H), 4.24 (s, 2H), 3.71 – 3.61 (m, 6H), 3.50 (dd, *J* = 10.8, 4.1 Hz, 2H), 3.41 (dd, *J* = 11.6, 5.6 Hz, 2H), 3.23 – 3.19 (m, 2H), 3.14 – 3.05 (m, 8H), 3.05 – 2.98 (m, 2H), 2.58 (s, 6H), 2.15 – 2.07 (m, 8H), 1.79 (s, 12H), 1.54 (d, *J* = 6.5 Hz, 4H), 1.38 – 1.21 (m, 14H), 1.13 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (201 MHz, DMSO) δ 173.35, 150.07, 149.95, 147.23, 143.08, 140.08, 139.31, 137.80, 135.66, 132.86, 131.10, 130.84, 128.50, 124.28, 122.85, 120.13, 119.03, 104.90, 102.02, 82.91, 77.91, 77.40, 77.16, 76.98, 76.85, 75.97, 70.88, 70.85, 61.96, 61.89, 46.61, 37.12, 36.71, 36.44, 30.90, 30.25, 29.99, 29.82, 29.72, 26.28, 25.53, 22.36, 22.25, 21.98. HRMS (ESI-MS), Calculated for $C_{106}H_{137}N_{12}O_{24}Zn$ $[M+H]^+$, 2025.9192, found, 2025.9194.

S3. ESI-MS of compound 2C-6',6''Ac and 2C:

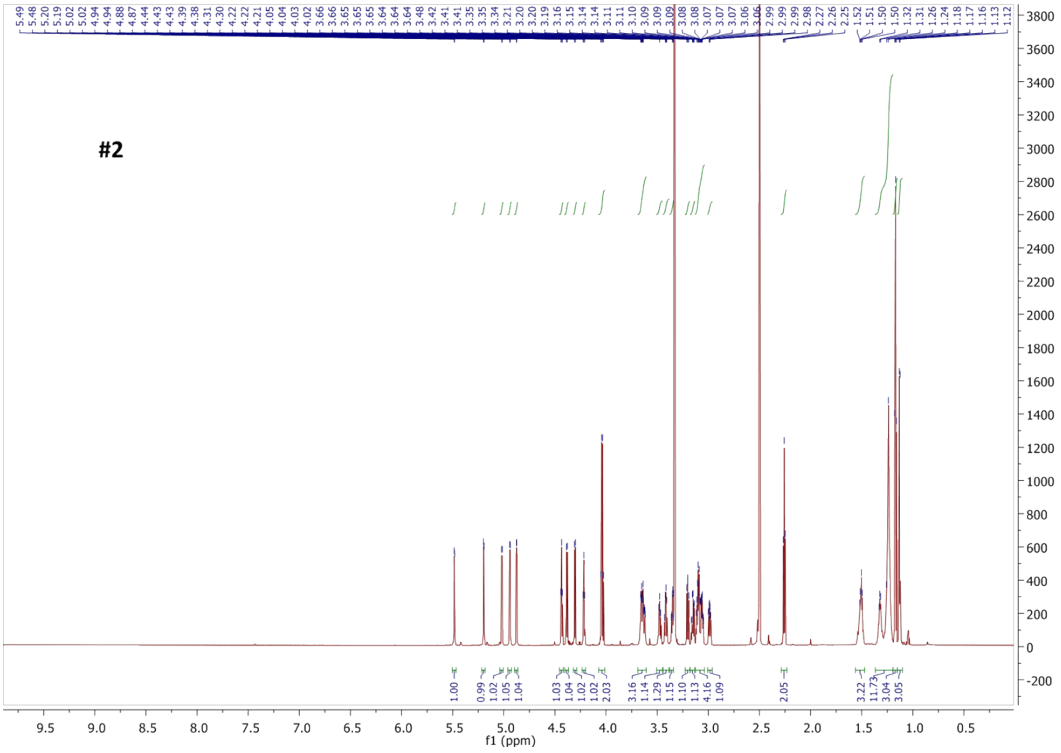


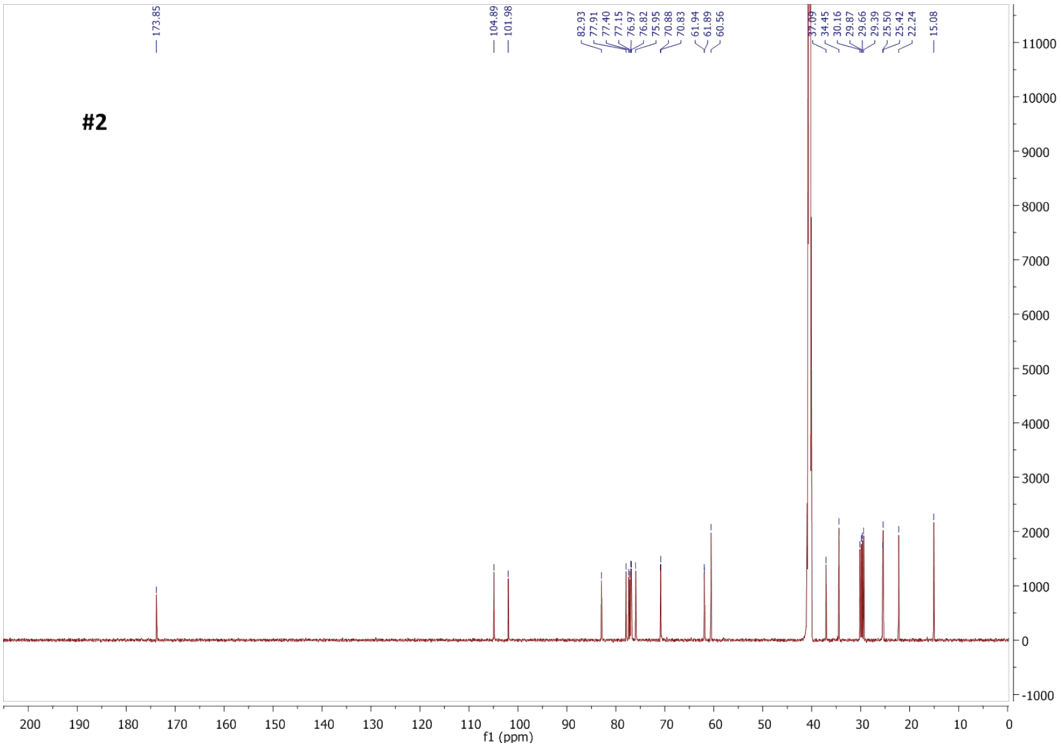
ESI-MS of compound **2C-6',6''Ac**: HRMS, Calculated for $C_{114}H_{144}N_{12}NaO_{28}Zn$ $[M+Na]^+$, 2215.4476, found, 2215.4474.

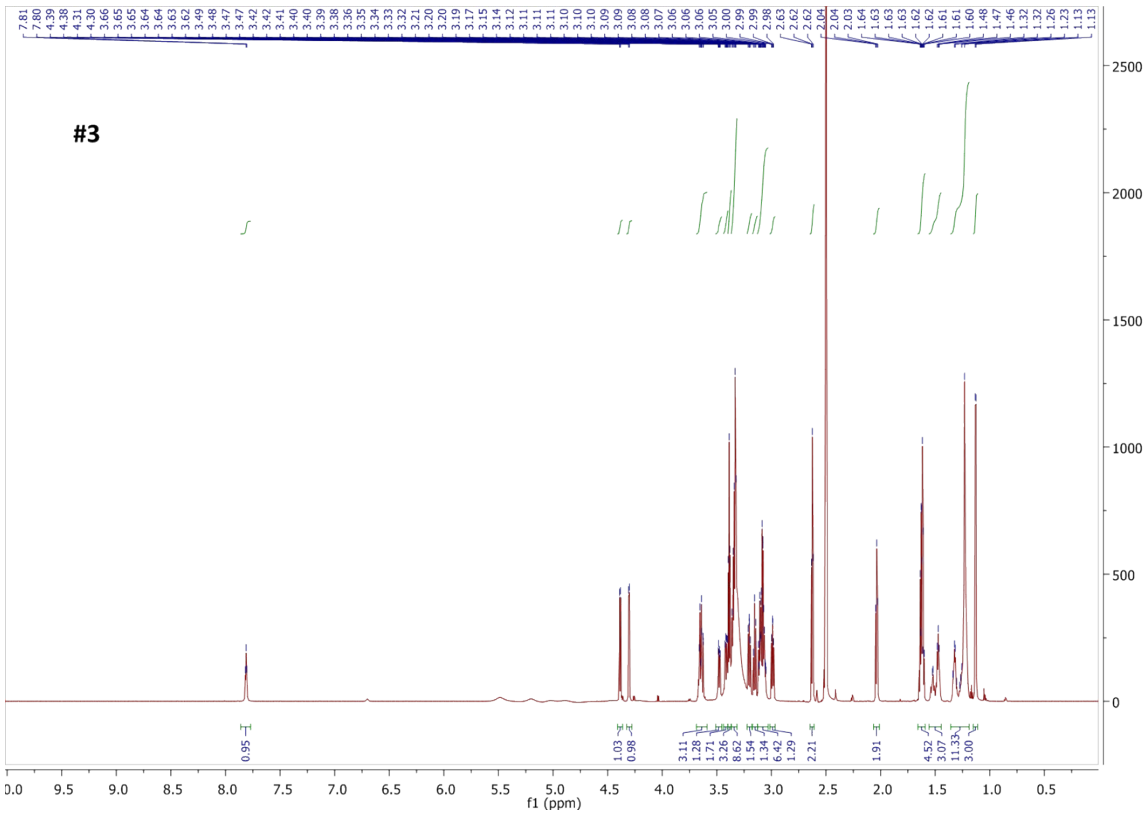


ESI-MS of compound **2C**: HRMS, Calculated for $C_{106}H_{137}N_{12}O_{24}Zn$ $[M+H]^+$, 2025.9192, found, 2025.9194.

S4. ^{1}H and ^{13}C NMR spectra of compounds 2, 3, 4, 2C-6',6''Ac and 2C:



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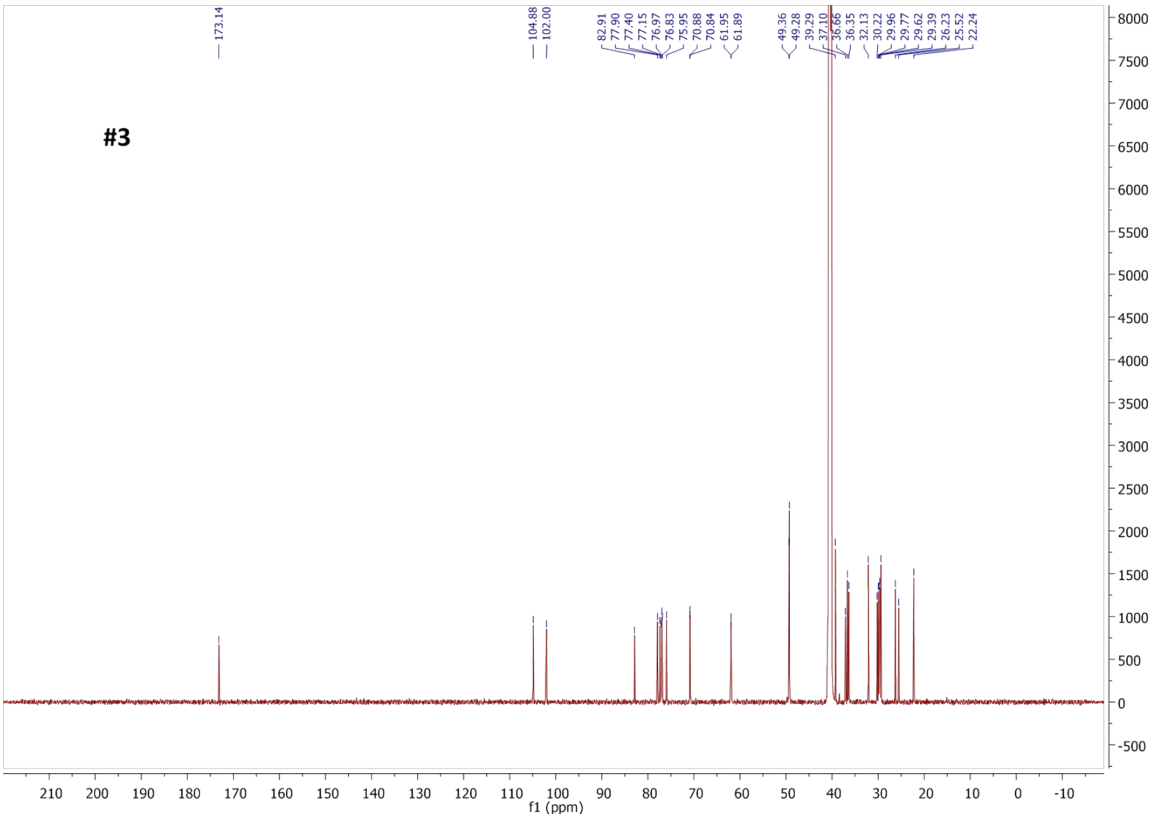
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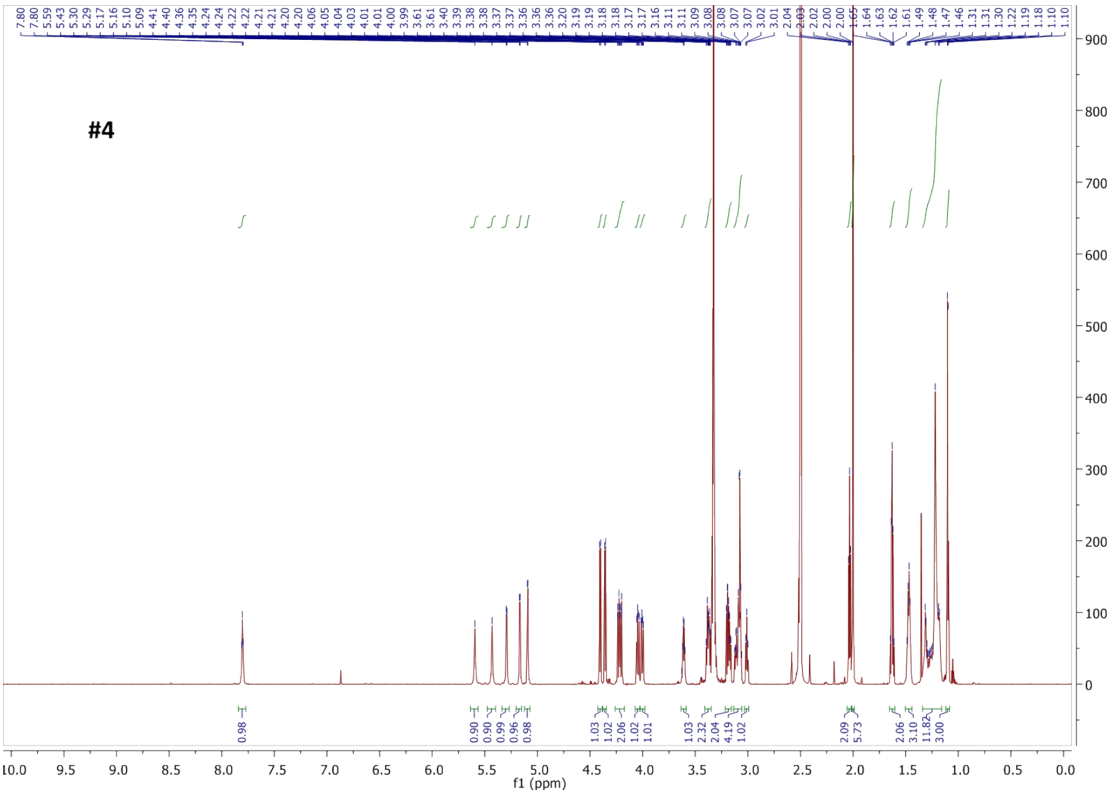
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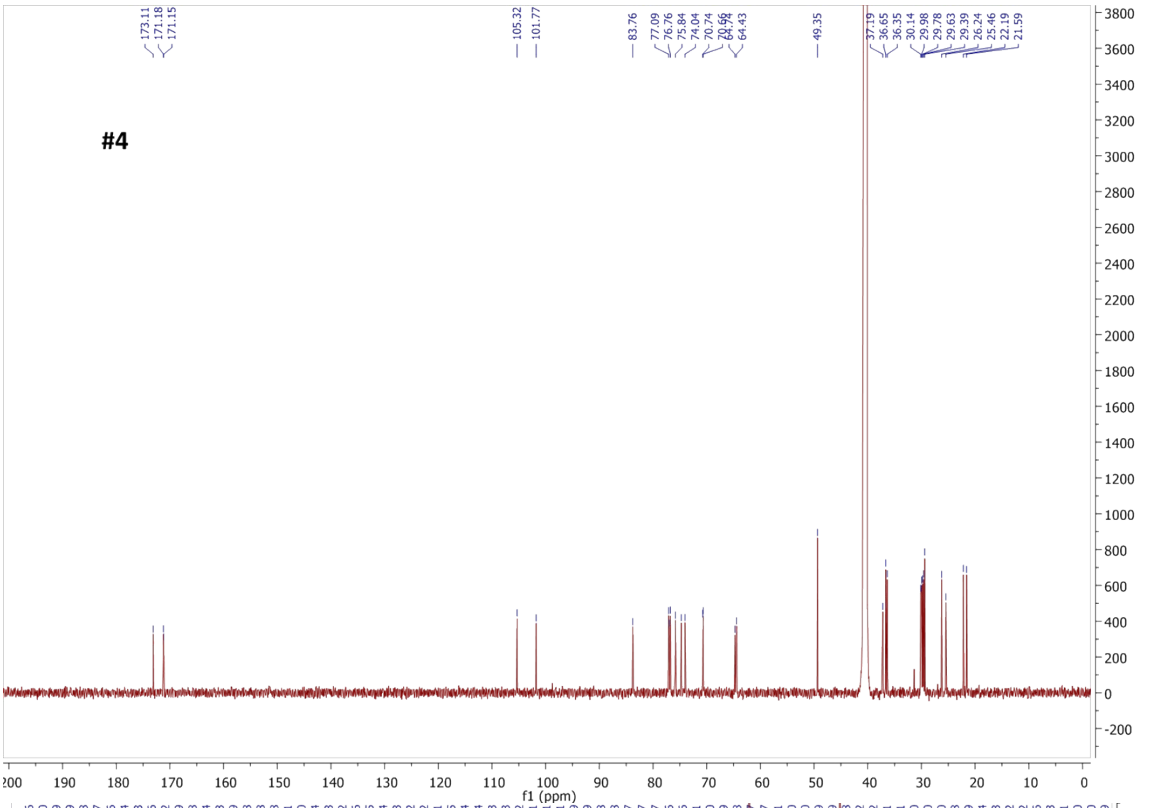
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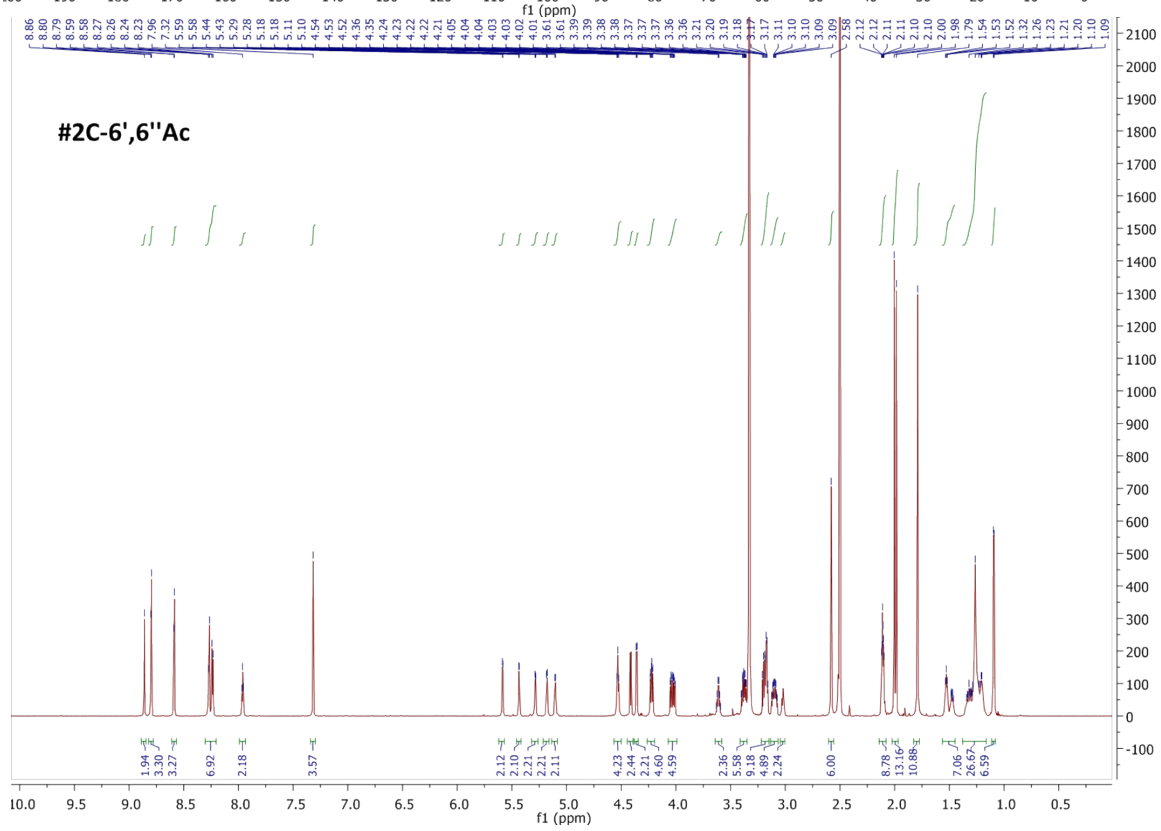
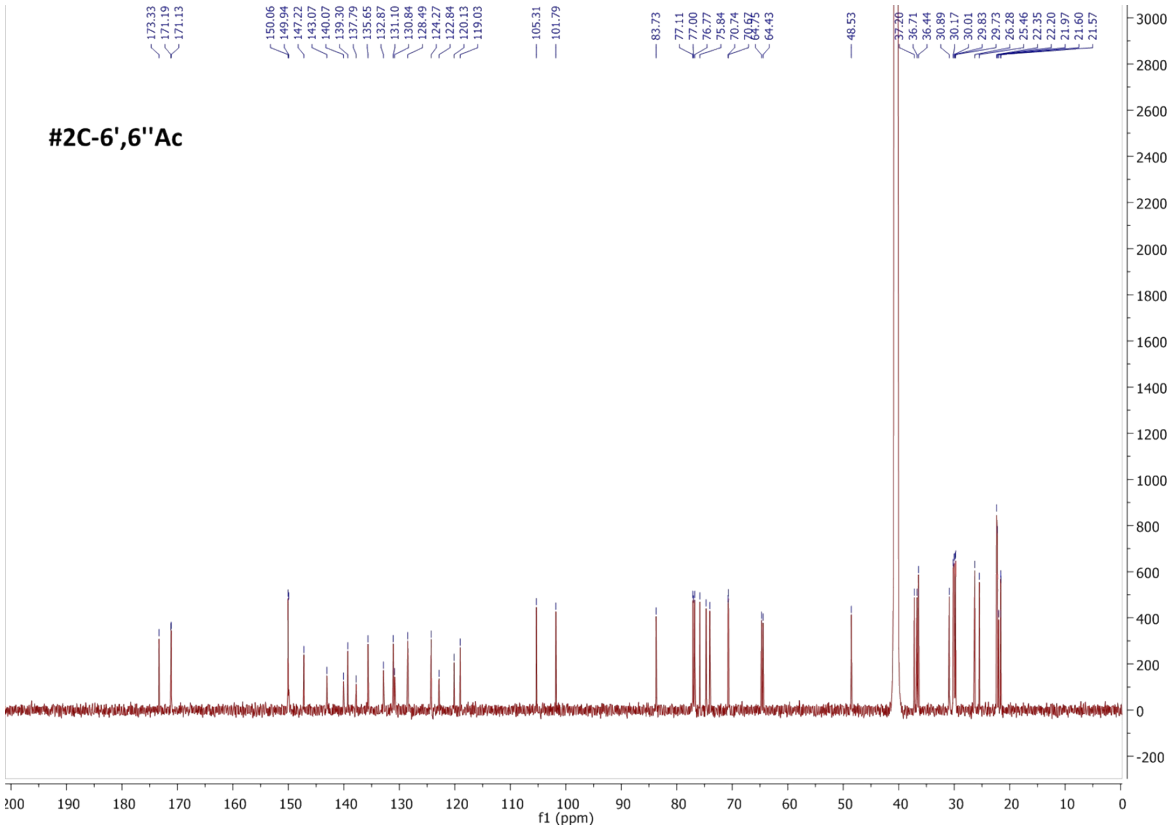
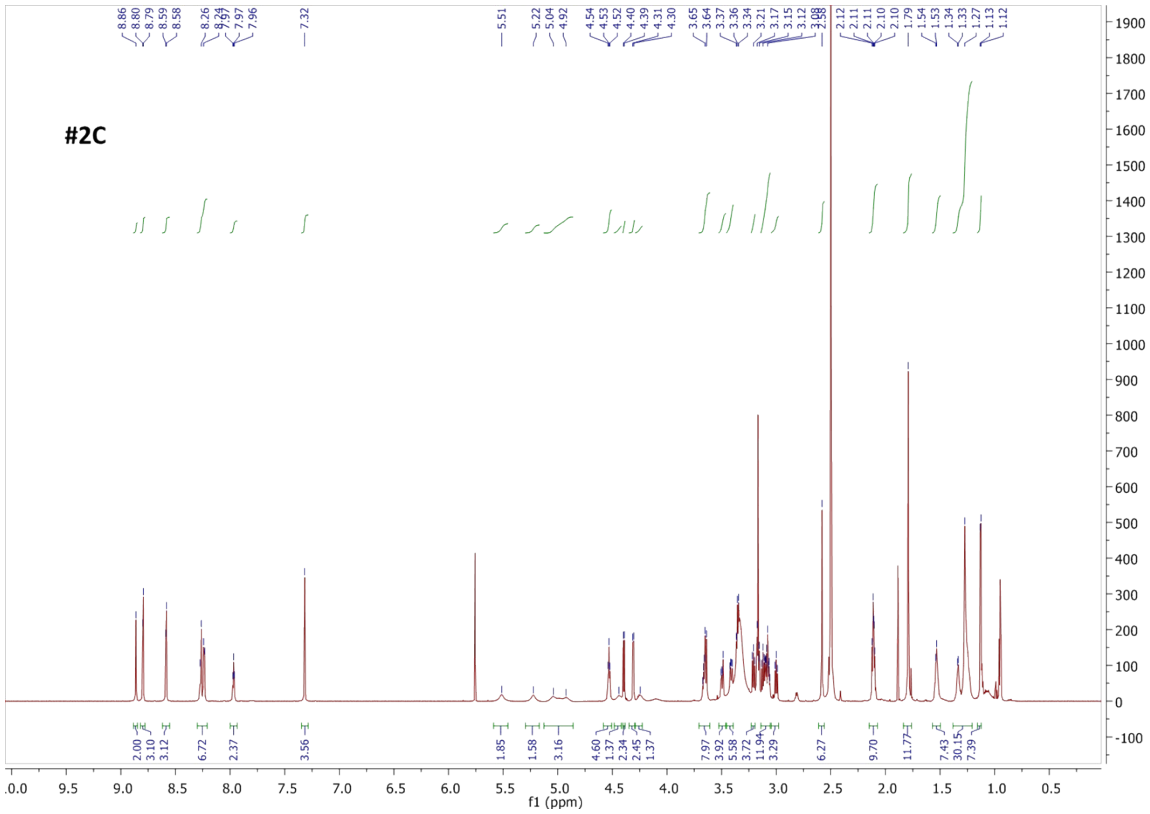
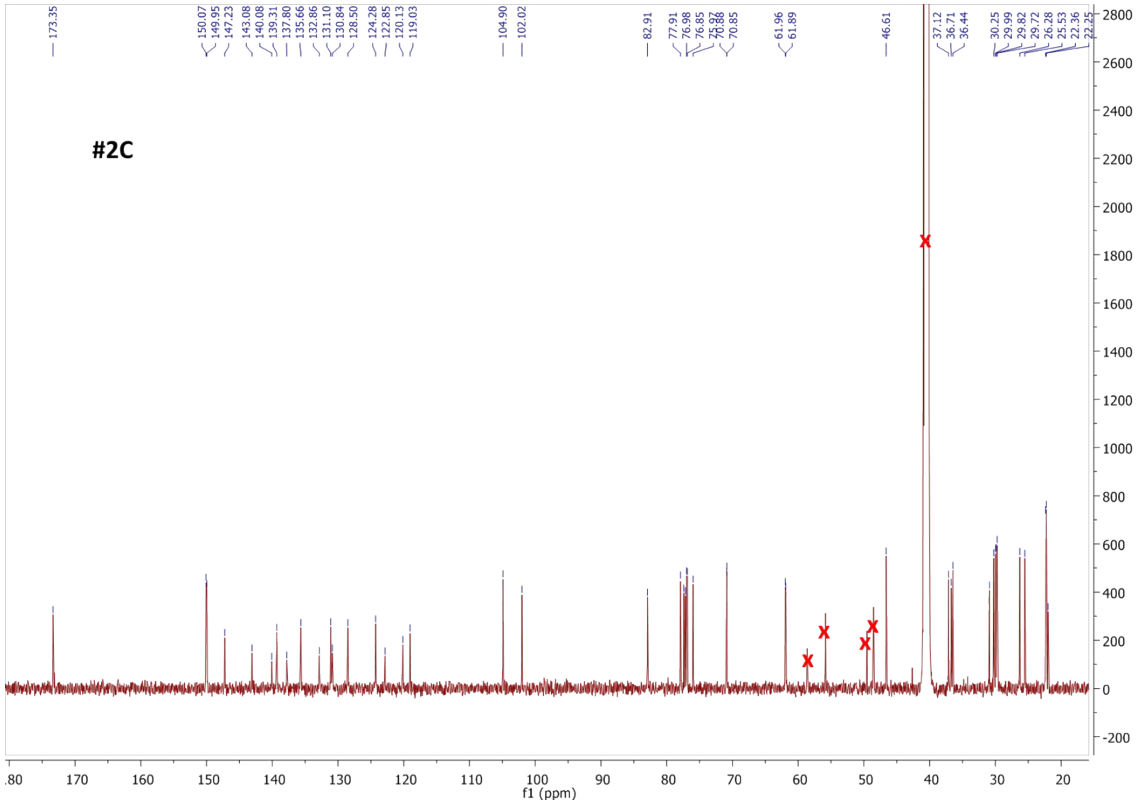
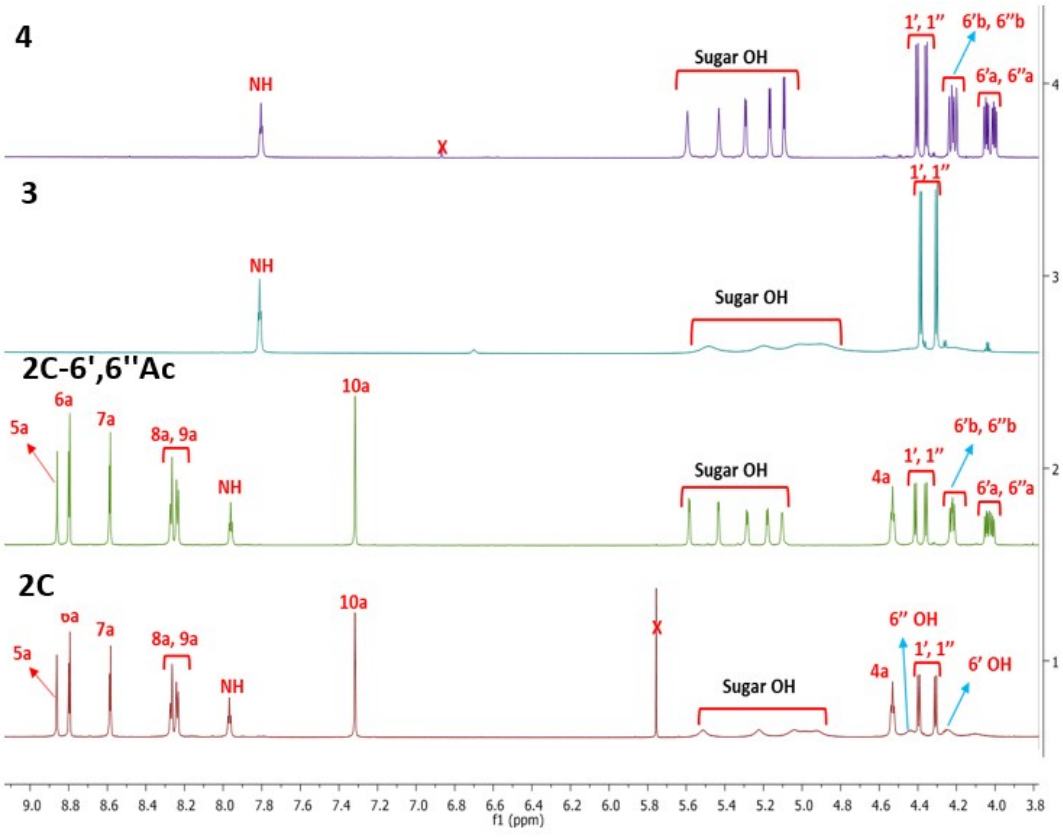

#2C-6',6''Ac
f1 (ppm)


#2C-6',6''Ac
173.33
171.19
171.13
150.06
149.94
147.22
143.07
140.07
139.30
137.79
135.65
132.87
131.10
130.84
128.49
124.27
122.84
120.13
119.03
105.31
101.79
83.73
77.11
77.00
76.77
75.84
70.74
70.62
64.75
64.43
48.53
37.20
36.71
36.44
30.89
30.17
30.01
29.83
29.73
26.28
25.46
22.35
22.20
21.97
21.60
21.57
f1 (ppm)

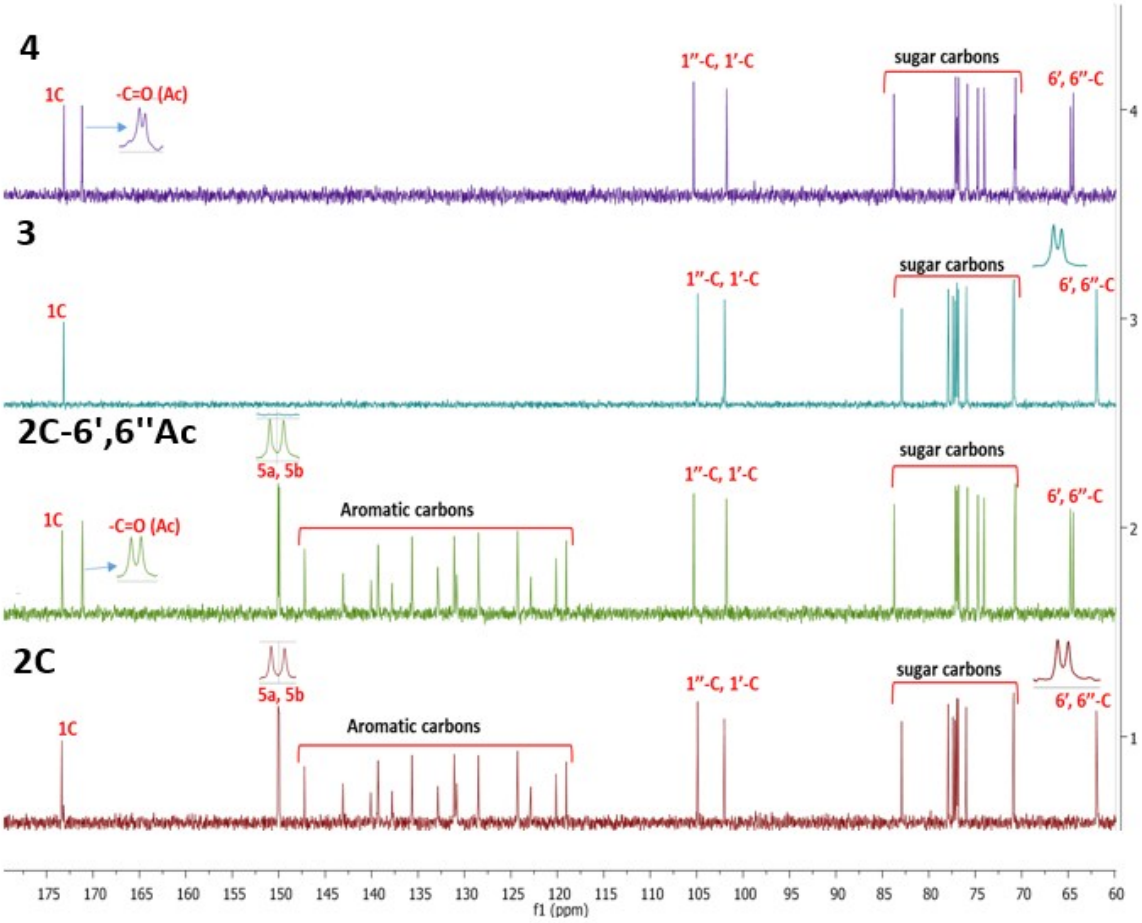

#2C
f1 (ppm)


#2C
f1 (ppm)

S5. Stacked ^{1}H-NMR (partial) of compounds 3, 4, 2C-6',6''Ac and 2C.



S6. Stacked ^{13}C-NMR (partial) of compounds 3, 4, 2C-6',6''Ac and 2C.



S7. Additional spectroscopic measurements

S7.1 Room temperature photoluminescence

Photoluminescence measurements were recorder for compound **2C** (short-chain) and **1C** (long-chain) in MeOH and MeOH:water (1:1 v/v) at 3.0×10^{-6} M (Figure S1). The corresponding Soret emission band is narrowed and red-shifted compared to the molecularly dissolved state in MeOH for both 7 and 8 by 14.2 nm and 11.8 nm, respectively. These spectral bands shift further indicating the presence of J-type chromophore aggregation.[3]

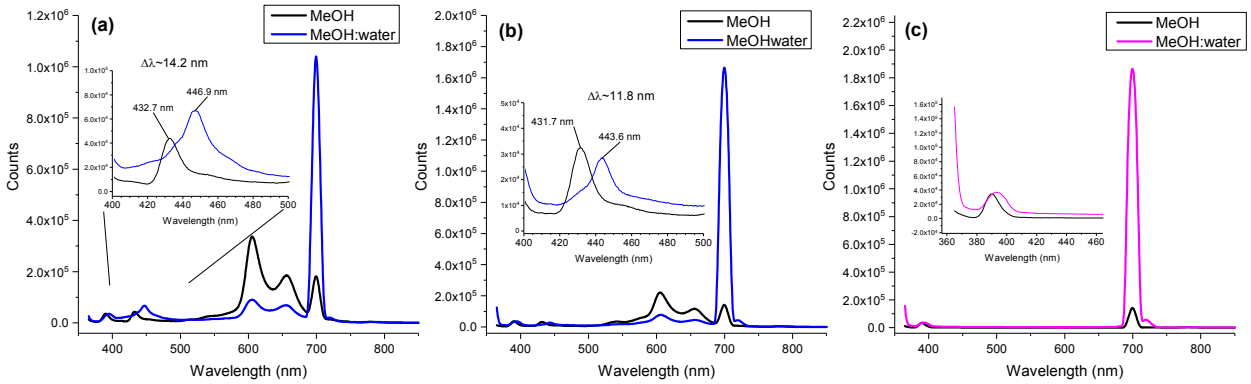


Figure S1. Room temperature emission of **2C** (a) and **1C** (b) in MeOH (black line) and MeOH:water (1:1 v/v, blue line) at 3.0×10^{-6} M and (c) the solvent for comparison. Inset are a zoom corresponding to the Soret emission region as indicated.

S7.2 Room temperature UV/vis and CD

UV/vis absorption and CD for compound 2C was recorded in different MeOH:water-content mixtures (25%, 50%, 75% water content) displayed in Figure S2. Results show no evidence of exciton coupling for 25% water content, optimal exciton coupling for 50% and a decrease of exciton coupling for 75% realized by a diminished UV/vis and CD response.

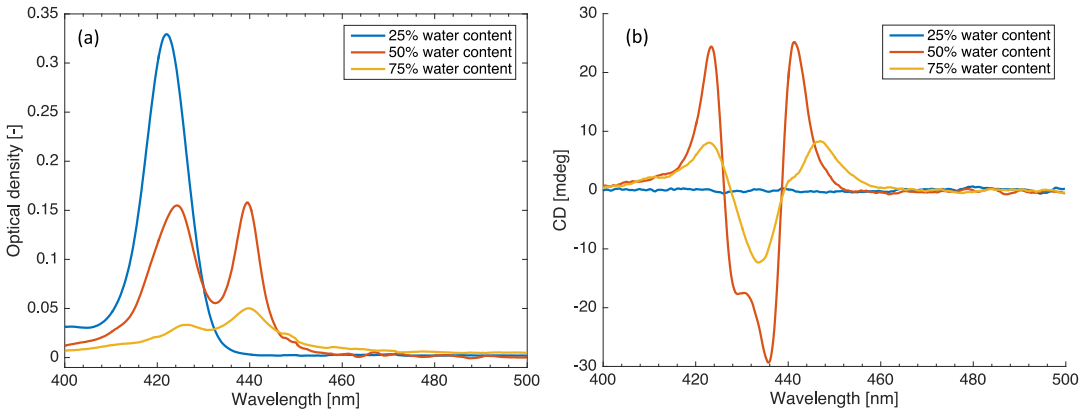


Figure S2. UV/vis absorption (a) and CD (b) measurements recorded in different water-content MeOH:water mixtures at fixed concentration (1.0×10^{-6} M).

UV/vis absorption of both **1C** and **2C** in methanol (Fig. S3) displayed Soret band transitions between 450-400 nm with maximal extinction at 421 nm and two lower energy Q-bands near 550 and 600 nm, indicating that, in methanol, the zinc porphyrin chromophores are non-interacting (Figure S3).[4,5] The chiroptic activity, recorded simultaneously, displayed a CD-silent response signifying the absence of excitonic interactions. Hence, the chiroptic and UV/vis results suggest that a chiral inversion from left-handed (**1C**) to a right-handed (**2C**) system of excitonically-coupled J-aggregates is formed as a result of shortening the hydrocarbon chain linker-length.

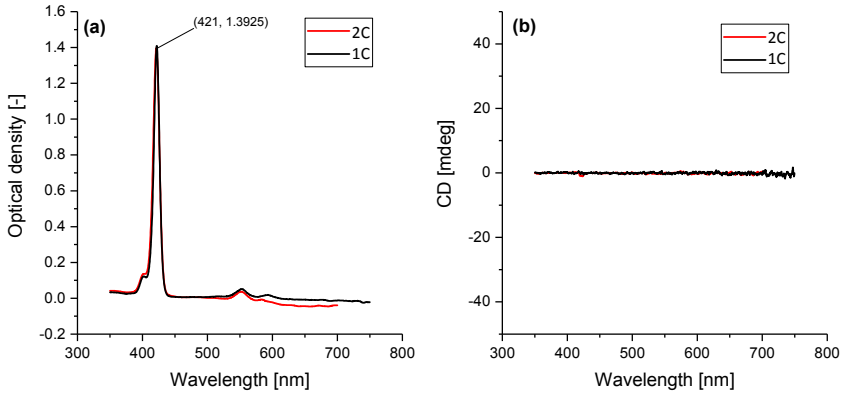


Figure S3. Room temperature UV/vis absorption (a) and CD (b) measurements recorded in MeOH (a good solvent) at 3.0×10^{-6} M.

S8. Cooling curve fitting

Collected CD and UV/vis data were normalized between 0 and 1 by the following equation;

$$\phi_n(T) = \frac{DATA(T)}{DATA_{max}}, \quad \text{(S1)}$$

where DATA(T) is the circular dichroism and/or UV/vis response monitored at fixed wavelength 442 nm and $DATA_{max}$ is the response at low temperature corresponding to the fully aggregated state. To model the normalized cooling curves, methods developed by Meijer and coworkers were employed.[6,7] In their simplified model, the normalized fraction of aggregated molecules below the elongation temperature (T_e) as a function of temperature in the cooperative elongation regime ($T < T_e$) is described by;

$$\phi_n(T) = \phi_{sat}\left(1 - exp\left[-\frac{h_e}{RT_e^2}(T - T_e)\right]\right) + \phi_o, \quad \text{(S2)}$$

and in the nucleation regime ($T > T_e$);

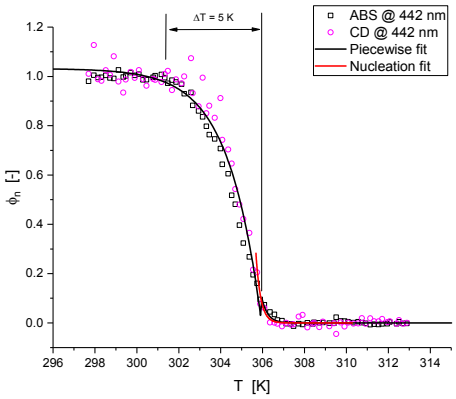
$$\phi_n(T) = \phi_{sat} K_a^{1/3} exp\left[\left(\frac{2}{3K_a^{1/3}} - 1\right)\frac{h_e}{RT_e^2}(T - T_e)\right], \quad \text{(S3)}$$

where T_e is the elongation temperature, h_e is the elongation enthalpy release due to noncovalent interactions, K_a is the dimensionless equilibrium constant governing the activation step in the nucleating regime, ϕ_{sat} is a normalization constant imposed to ensure that ϕ_n/ϕ_{sat} does not exceed unity and ϕ_o is the baseline offset. Together, Eq. S2 and S3 represent the fraction of aggregated molecules (degree of aggregation), which in terms of circular dichroism represents the systems net

helicity. This model allows an estimate of the average length of the nucleated aggregate averaged over all nucleating species $\langle N_n(T_e)\rangle$,

$$\langle N_n(T_e)\rangle = \frac{1}{K_a^{1/3}}, \qquad \text{(S4)}$$

which can be envisioned as the starting building blocks of the elongation, and thus the polymerization process. The value of K_a is associated with the system's degree of cooperativity. An increasing degree of cooperativity is reflected by a small K_a value, and thus a larger nucleated building block size (Eq. S4). Nonlinear curve fitting of Eq. S2 and S3 to the normalized data was performed by a custom Origin (OriginLab, Northampton, MA) piecewise function. From the piecewise fit, T_e, ϕ_{sat} and h_e were determined then used as a fixed parameter for a second fitting to Eq. S3 to extract an accurate value for K_a. Extracted fitting parameters are in Table S1, and all fitting parameters are in the table inset of Figure S4.



Model	CooperativePiecewise (User)	
Plot	Norm CD @ 442nm	Norm ABS @ 442nm
phi_sat*	1.03182 ± 0.00854	1.03182 ± 0.00854
he*	-494.8102 ± 19.80721	-494.8102 ± 19.80721
Te*	305.95087 ± 0.04626	305.95087 ± 0.04626
Ka*	0.00106 ± 0.00101	0.00106 ± 0.00101
Reduced Chi-Sqr*	0.00182	
R-Square(COD)	0.98891	0.99357
R-Square(COD)*	0.99116	
Adj. R-Square*	0.99095	

Model	NucleationFit (User)	
Plot	Norm CD @ 442nm	Norm ABS @ 442nm
phi_sat*	1.031 ± 0	1.031 ± 0
Ka*	6.07189E-4 ± 1.61436E-4	6.07189E-4 ± 1.61436E-4
he*	-494.8 ± 0	-494.8 ± 0
Te*	305.95 ± 0	305.95 ± 0
Reduced Chi-Sqr*	2.46841E-4	
R-Square(COD)	0.52646	0.75188
R-Square(COD)*	0.65418	
Adj. R-Square*	0.65418	

Figure S4. Normalized CD and UV/vis cooling curve of compound **2C** monitored at 442 nm when slow cooled from elevated temperatures (3.0×10^{-6} M).

Table S1: Thermodynamic parameters for global fit at λ_{probe} = 433 nm.

Compound	Method	ϕ_{sat} [-]	T_e [K]	h_e [kJ mol^{-1}]	K_a [-]	$N_n(T_e)$ [-]
2C	CD, UV/vis	1.03	305.9	-494 ± 19	6.07 ± 1.61 x 10^{-4}	7.2 ± 0.6

S9. Additional electron microscopy image

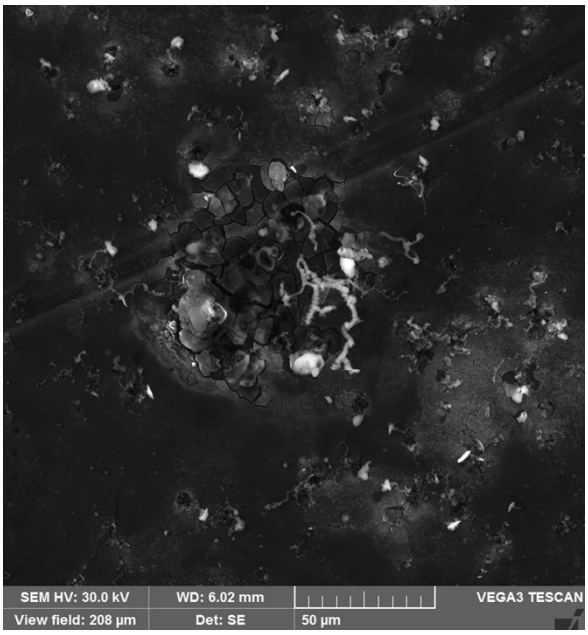


Figure S5. SEM images of compound **2C** in the solid state taken at 1.0kx.

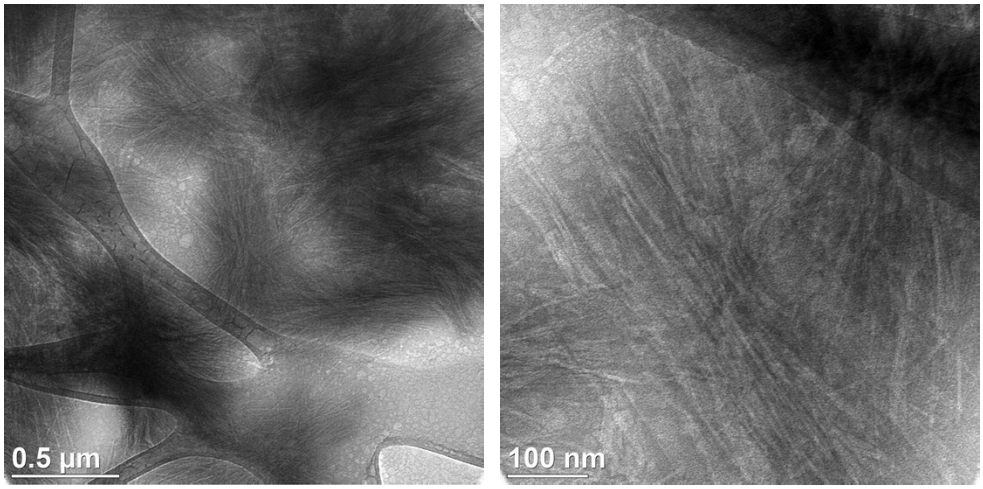


Figure S6. TEM images of compound **2C** in the solid state taken at 11.5kx (left) and 42kx (right).

S10. References

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(5) Gouterman, M.; Wagnière, G. H.; Snyder, L. C. Spectra of Porphyrins: Part II. Four Orbital Model. *J. Mol. Spectrosc.* **1963**, *11* (1–6), 108–127.
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