

Electronic Supporting Information for

## **Covalently stabilized self-assembled chlorophyll nanorods by olefin metathesis**

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## Experimental Section

**Reagents and solvents:** All commercially available reagents and chemicals were obtained from common suppliers and used as such without further purification, unless otherwise stated. Some of the solvents such as tetrahydrofuran (THF) were dried according to literature known methods.<sup>1</sup>

**Column chromatography:** Column chromatography under normal pressure and flash was carried out were done using silica gel Si60 (mesh size 0.032-0.063 mm) from Merck KGaA (Hohenbrunn, Germany) as a stationary phase. The eluents are mentioned in the respective synthesis procedures. Column chromatography of chlorin derivatives were carried out in a darkened hood.

**High performance liquid chromatography (HPLC):** Analytical HPLC was performed on a system (PU 2080 PLUS) with a photodiode array detector (MD 2015) from JASCO equipped with a ternary gradient unit (LG 2080-02) and line degasser (DG-2080-533). Semipreparative HPLC was performed on a system (PU 2080 PLUS) with a photodiode array detector (UV 2077 PLUS) from JASCO. Reverse phase columns (analytical: EC 250/4.6 NUCLEODUR 100-5 C18 ec, pre-column: CC 8/4 NUCLEODUR 100-5 C18 ec; semipreparative: SP 250/21 NUCLEODUR 100-7 C18 ec, pre-column semipreparative: SP 50/21 NUCLEODUR 100-7 C18 ec) obtained from Macherey-Nagel (Germany) were used. HPLC grade solvents supplied by VWR (Darmstadt, Germany) were used.

**<sup>1</sup>H NMR spectroscopy:** <sup>1</sup>H NMR spectra were recorded at 25 °C with a 400 MHz spectrometer from Bruker GmbH, Ettlingen (Bruker Avance 400). The chemical shifts ( $\delta$ ) are given in reference to TMS or the residual solvent signals in ppm values. The coupling constants  $J$  are expressed in Hertz (Hz) and values up to two decimal are given.

**Mass spectrometry (MS):** The high resolution electron spray ionization (ESI) mass spectra were measured with a Bruker Daltonics Micro TOF Focus instrument.

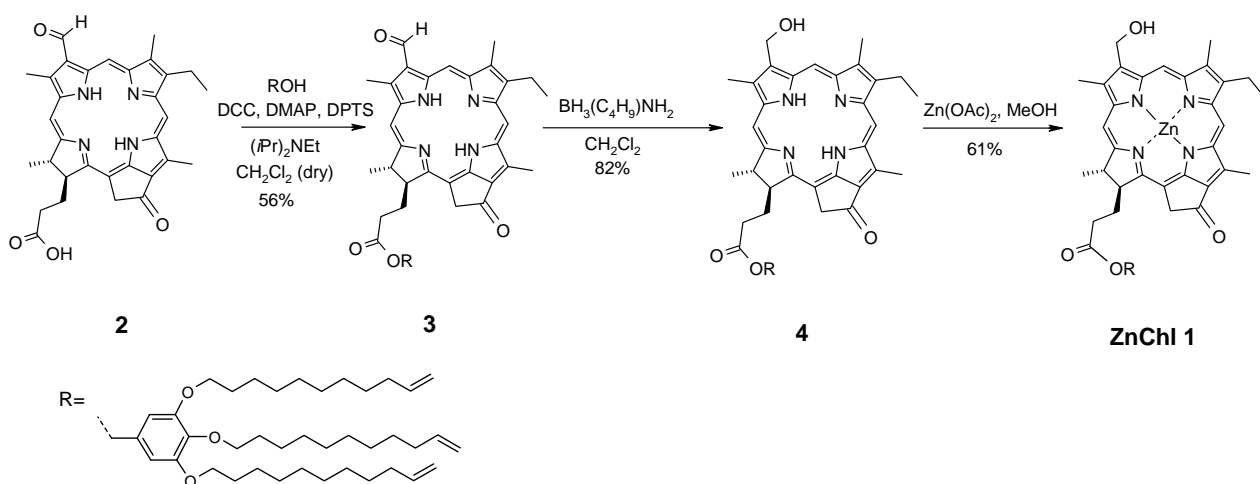
**UV/Vis spectroscopy:** All spectroscopic measurements were performed in pure spectroscopic grade solvents (Merck UVASOL) in 0.5 cm or 1 cm quartz glass cuvettes. Studies for the monomers and aggregates of zinc chlorins were performed in water-free solvents *n*-hexane and tetrahydrofuran (THF). The UV/Vis spectra were measured with a PE Lambda 40 P instrument from Perkin Elmer GmbH (Rodgau, Germany) under ambient conditions. Molar extinction coefficient  $\epsilon$  was calculated according to Lambert-Beer's law and is referred to respective monomers.

**Atomic force microscopy (AFM):** The AFM measurements were performed with a Multimode Nanoscope IV system (Veeco Instruments Inc., Santa Barbara) in Tapping Mode in air. Silicon cantilever (Olympus, OMCL-AC160TS) with a resonance frequency of  $\sim 300$  kHz was used. The aggregate samples of ZnChl **1** in *n*-hexane/THF (100:1, v/v) were spin-coated (4000 rpm) onto highly oriented pyrolytic graphite (HOPG) and measured under ambient conditions.

**Dynamic light scattering (DLS):** DLS measurements were performed at 25 °C on a N5 Submicron Particle Size Analyzer, Beckman Coulter, using a 25 mW helium-neon laser (632.8 nm). Sample solutions were filtered in to a dust-free vial through a 0.45  $\mu\text{m}$  hydrophobic polytetrafluoroethylene (PTFE) filter. Data were collected at scattering angles of 10.6°, 15.1°, 22°, 28.8°, 63.8°, 90° and analyzed with a PCS control software.

**Fourier transform infrared (FTIR) spectroscopy:** FTIR spectra were measured on a Jasco FTIR-410 spectrometer with solid samples of ZnChl **1** prepared as KBr pellets.

### Synthetic procedures and product characterizations:



#### Synthesis of 3,4,5-triundec-1-ene-oxybenzylester:

3,4,5-Trihydroxyethylbenzoate (300 mg, 1.51 mmol) and 11-bromo-1-undecene (1.7 ml, 7.66 mmol) were added in a suspension of  $K_2CO_3$  (209 mg, 1.51 mmol) in dry DMF and the reaction mixture was stirred for about 48 hours. It was then poured into water and extracted with diethylether ( $30 \times 30$  ml). The aqueous layers were neutralized using saturated  $NH_4Cl$  solution, extracted again and the combined organic layers were dried over  $Na_2SO_4$  and the solvent was subsequently evaporated to obtain a yellow oil. The crude product so obtained was purified by column chromatography using *n*-pentane/diethylether (4:1) as the eluent to obtain the desired product (165 mg, 50% yield);  $^1H$  NMR (400 MHz,  $CDCl_3$ , 25 °C):  $\delta$  = 7.22 (s, 2H, ArH), 5.81-5.71 (m, 3H,  $\gamma$ -H), 4.97-4.87 (m, 6H,  $\omega$ -H), 4.31 (q,  $J$  = 7.2 Hz, 2H,  $OCH_2CH_3$ ), 3.43 (t,  $J$  = 7.1 Hz, 6H,  $\omega$ -H), 2.00 (q,  $J$  = 7.3 Hz, 6H,  $\beta$ -H), 1.81-1.73 (m, 6H,  $3 \times CH_2$ ), 1.71-1.26 (m, 36H,  $18 \times CH_2$ ). 1.16 (t,  $J$  = 7.0 Hz, 3H,  $OCH_2CH_3$ ). MS (MALDI-TOF, matrix: DCTB) calcd for  $C_{42}H_{70}O_5$ : 654.523, found: 654.23 for  $[M]^+$ .

#### Synthesis of 3,4,5-triundec-1-ene-oxybenzylalcohol

To a stirred suspension of  $LiAlH_4$  (15.3 mg, 0.37 mmol), a solution of the 3,4,5-triundec-1-ene-yloxybenzylester (160 mg, 0.24 mmol) was added and the reaction mixture was stirred at 0 °C in an ice bath. The stirring was continued for 3 h and when the reaction was completed

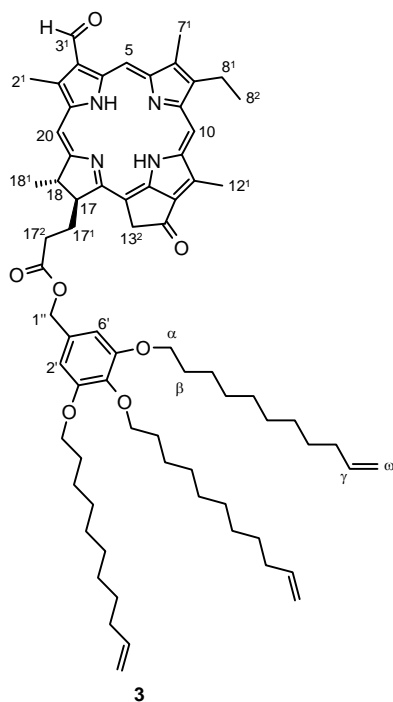
as indicated by the TLC, it was quenched with a few drops of water and extracted with diethyl ether. The aqueous layer was neutralized with dilute H<sub>2</sub>SO<sub>4</sub>, combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and solvent was evaporated to obtain the alcohol as a colorless oil (137 mg, 92% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 6.56 (s, 2H, ArH), 5.81-5.71 (m, 3H, γ-H), 5.02-4.91 (m, 6H, ω-H), 4.59 (d, *J* = 4.8 Hz, 2H, CH<sub>2</sub>OH), 3.98-3.91 (m, 6H, α-H), 2.05 (q, *J* = 7.3 Hz, 6H, β-H), 1.81-1.73 (m, 6H, 3 × CH<sub>2</sub>), 1.46 (s, 1H, OH) 1.71-1.26 (m, 36H, 18 × CH<sub>2</sub>). MS (MALDI-TOF, matrix: DCTB): calcd for C<sub>40</sub>H<sub>68</sub>O<sub>4</sub>: 612.23, found: 612.516 for [M]<sup>+</sup>.

### Synthesis of compound **3**

Chlorin 17<sup>2</sup>-carboxylic acid **2** was obtained from pheophorbide *a* by literature methods.<sup>2-4</sup> To a solution of the 17<sup>2</sup>-carboxylic acid derivative **2** (120 mg, 0.2238 mmol) in 10 ml dry dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), 3,4,5-trisundec-1-ene-oxybenzylalcohol (163.3 mg, 0.38 mmol) was added and stirred under argon atmosphere at room temperature. Subsequently the coupling reagents dicyclohexylcarbodiimide (DCC) (461.7 mg, 2.238 mmol), 4-dimethylaminopyridine (DMAP) (138.9 mg, 1.119 mmol), 4(dimethylamino)pyridinium *p*-toluenesulfonate (DPTS) (329.5 mg, 1.119 mmol) were added to the reaction mixture. After 20 min, 57 μl of diisopropylethylamine (Hünig's base) was added and stirred under room temperature for several hours and then the reaction mixture was stirred overnight. To the reaction mixture, 25 ml H<sub>2</sub>O was added and then extracted with CH<sub>2</sub>Cl<sub>2</sub> and the aqueous layers were neutralized using saturated NH<sub>4</sub>Cl and extracted again with 10 ml CH<sub>2</sub>Cl<sub>2</sub>. The combined organic extracts were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and solvent was removed under vacuum. The crude product was purified using silica gel column chromatography with diethylether/*n*-pentane (60:40) as the eluent to isolate the aldehyde compound **3** (140.8 mg, 56% yield).

Analytical HPLC: The solvent combination used was methanol/CH<sub>2</sub>Cl<sub>2</sub> (75:25), compound was eluted at 8.92 min. M.p. 130–135 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 11.52 (s,

1H, CHO), 10.34 (s, 1H, 10-H), 9.64 (s, 1H, 5-H), 8.82 (s, 1H, 20-H), 6.56 (s, 1H, ArH-6), 6.45 (s, 1H, ArH-2), 5.88-5.74 (m, 3H,  $\gamma$ -H), 5.10-4.88 (m, 10H, 13<sup>2</sup>-CH<sub>2</sub>, 13<sup>2</sup>-CH<sub>2</sub>, 1''H, 1''H,  $\omega$ -H), 4.50 (dq,  $J = 4.5$  Hz,  $J = 2$  Hz, 1H, 18-H), 4.30 (td,  $J = 8.5$  Hz,  $J = 2.68$  Hz, 1H, 17-H), 3.96-3.76 (m, 8H, 8<sup>1</sup>-H, 3  $\times$  CH<sub>2</sub>), 3.75-3.41 (m, 15H, 12<sup>1</sup>-H, 2<sup>1</sup>-H, 7<sup>1</sup>-H,  $\alpha$ -H), 2.66-2.54 and 2.56-2.26 (m, 4H, 17<sup>1</sup>-H, 17<sup>2</sup>-H), 2.03-2.00 (m, 6H,  $\beta$ -H), 1.77-1.70 (m, 6H, 18<sup>1</sup>-H, 8<sup>2</sup>-H), 1.39-1.20 (m, 36H, 18  $\times$  CH<sub>2</sub>), 0.36 (s, 1H, NH), -1.75 (s, 1H, NH); HRMS (ESI):  $m/z$  calcd for C<sub>72</sub>H<sub>98</sub>N<sub>4</sub>O<sub>7</sub>: 1131.7517, found: 1131.7513 for [M+H]<sup>+</sup>.

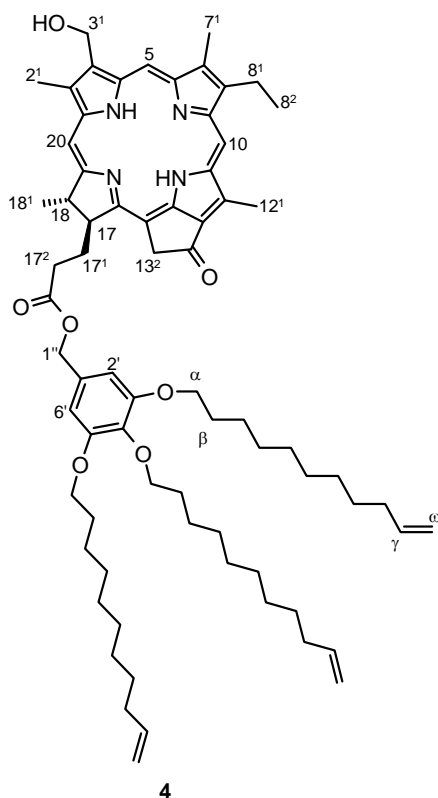


#### Synthesis of compound 4

The 3<sup>1</sup>-aldehyde compound **3** (140 mg, 0.1238 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and boronhydride (*tert*-butyl) amine reagent (107 mg, 1.2389 mmol) was added to it. The reaction mixture was then allowed to stir under argon at room temperature for two hours. Subsequently, 20 ml H<sub>2</sub>O was added to the reaction mixture and then extracted with CH<sub>2</sub>Cl<sub>2</sub> and the aqueous layers were neutralized using saturated NH<sub>4</sub>Cl and extracted again with

CH<sub>2</sub>Cl<sub>2</sub>. The combined organic extracts were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under vacuum. The crude product was purified using silica gel column chromatography using diethyl ether/*n*-pentane (70:30) as the eluent to isolate the desired alcohol compound **4** as an olive green solid (115 mg, 82% yield).

Analytical HPLC: The solvent combination used was methanol/dichloromethane (70:30), compound peak was obtained at 6.72 min. M.p. 98–105 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 9.52 (s, 1H, 10-H), 9.49 (s, 1H, 5-H), 8.56 (s, 1H, 20-H), 6.56 (s, 1H, ArH-2), 6.26 (s, 1H, ArH-6), 5.83-5.74 (m, 5H, 3<sup>1</sup>-H, γ-H), 5.07-4.88 (m, 10H, 13<sup>2</sup>-CH<sub>2</sub>, 13<sup>2</sup>-CH<sub>2</sub>, 1''-H, 1''-H, ω-H), 4.48 (dq, *J* = 4.5 Hz, *J* = 2 Hz, 1H, 18-H), 4.36-4.30 (m, 2H, 17-H, 3<sup>1</sup>-OH), 3.93-3.81 (m, 8H, 8<sup>1</sup>-H, 3 × CH<sub>2</sub>), 3.67 (s, 3H, 12<sup>1</sup>-H), 3.42-3.37 (m, 6H, α-H), 3.29 (s, 3H, 2<sup>1</sup>-H), 3.26 (s, 3H, 7<sup>1</sup>-H), 2.75-2.28 (m, 4H, 17<sup>1</sup>-H, 17<sup>2</sup>-H), 2.03-2.00 (m, 6H, β-H), 1.84-1.70 (m, 6H, 18<sup>1</sup>-H, 8<sup>2</sup>-H), 1.39-1.27 (m, 36H, 18 × CH<sub>2</sub>), 0.36 (s, 1H, NH), -1.79 (s, 1H, NH); HRMS (ESI): *m/z* calcd for C<sub>72</sub>H<sub>100</sub>N<sub>4</sub>O<sub>7</sub>: 1155.7636; found: 1155.7464 for [M+Na]<sup>+</sup>

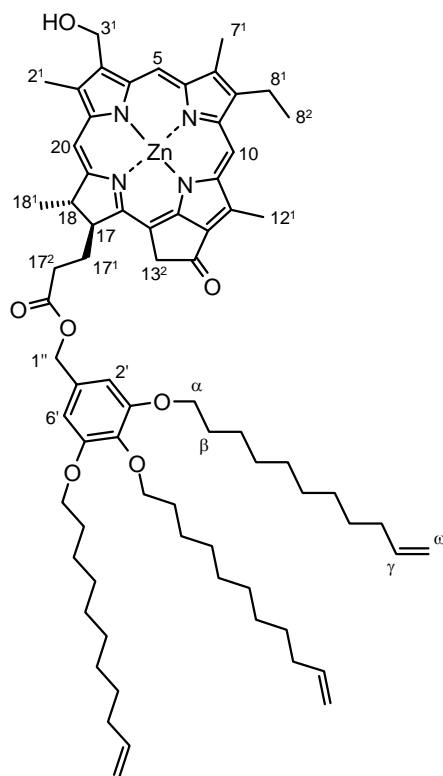


## Synthesis of ZnChl **1**

To a solution of alcohol compound **4** (70 mg, 0.0617 mmol) in THF (15 ml), a saturated solution of Zn(OAc)<sub>2</sub> in MeOH was added (10 ml) and the reaction mixture was stirred under argon at room temperature for two hours. Subsequently, 20 ml H<sub>2</sub>O was added to the reaction mixture and it was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the aqueous layer was neutralized with saturated NaHCO<sub>3</sub> solution and extracted again with CH<sub>2</sub>Cl<sub>2</sub>. The organic extracts were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under vacuum. The crude product was then rapidly purified using silica gel column chromatography with THF/MeOH (1:1) as eluent to isolate the zinc chlorin compound **1** which is a turquoise green solid, and was purified subsequently at the HPLC with a solvent combination of methanol/dichloromethane (4:1) to obtain pure compound **1** (45 mg, 61 % yield).

Analytical HPLC: The solvent combination used was methanol/dichloromethane (70:30), compound was eluted at 5.82 min. M.p. 190–196 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 9.61 (s, 1H, 10-H), 9.49 (s, 1H, 5-H), 8.48 (s, 1H, 20-H), 6.56 (s, 1H, ArH-6), 6.53 (s, 1H, ArH-2), 5.88-5.72 (m, 5H, 3<sup>1</sup>-H, γ-H), 5.07-4.87 (m, 10H, 13<sup>2</sup>-CH<sub>2</sub>, 13<sup>2</sup>-CH<sub>2</sub>, 1<sup>1</sup>H, 1<sup>1</sup>'H, ω-H), 4.52 (dq, *J* = 4.5 Hz, *J* = 2.0 Hz, 1H, 18-H), 4.44-4.29 (m, 2H, 17-H, 3<sup>1</sup>-OH), 3.98-3.81 (m, 8H, 8<sup>1</sup>-H, 3 × CH<sub>2</sub>), 3.67 (s, 3H, 12<sup>1</sup>-H), 3.42-3.37 (m, 6H, 3 × CH<sub>2</sub>), 3.29 (s, 3H, 2<sup>1</sup>-H), 3.26 (s, 3H, 7<sup>1</sup>-H), 2.75-2.58 and 2.33-2.24 (m, 4H, 17<sup>1</sup>-H, 17<sup>2</sup>-H), 2.05-2.00 (m, 6H, β-H), 1.77-1.69 (m, 6H, 18<sup>1</sup>-H, 8<sup>2</sup>-H), 1.39-1.27 (m, 36H, 18 × CH<sub>2</sub>); HRMS (ESI): *m/z* calcd for C<sub>72</sub>H<sub>98</sub>N<sub>4</sub>O<sub>7</sub>Zn: 1195.6724; found: 1195.6799 for [M]<sup>+</sup>.





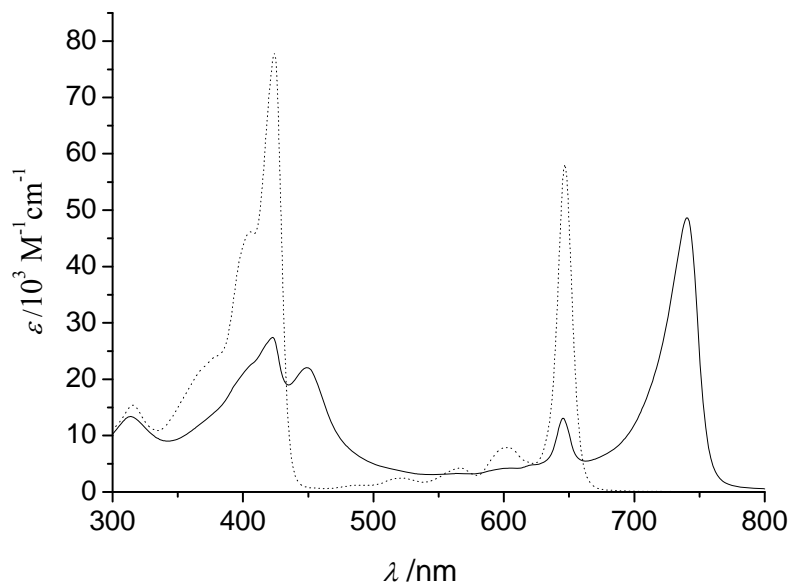
ZnChl 1

### Procedure for Grubbs metathesis reaction:

A monomer stock solution of ZnChl 1 was prepared by adding THF (50  $\mu\text{l}$ ,  $c = 1.1 \times 10^{-4}$  M) to the weighed amount of compound (0.007 mg, 0.0058  $\mu\text{mol}$ ) and diluted to 5 ml with *n*-hexane to prepare the aggregate solution ( $c = 1.1 \times 10^{-6}$  M). The formation of aggregates was then confirmed by UV/Vis spectroscopy. Subsequently,  $\sim 0.01$  mg of Grubbs catalyst, benzylidenebis(tricyclohexyl-phosphine)dichlororuthenium complex, was added to the aggregate solution at room temperature. The reaction mixture was stirred in dark for 3-4 hours and subsequently quenched with few drops of ethyl vinyl ether. The reaction mixture was then filtered to remove the residual catalyst and the filtrate was subjected to spectroscopic and microscopic investigations without further purification.

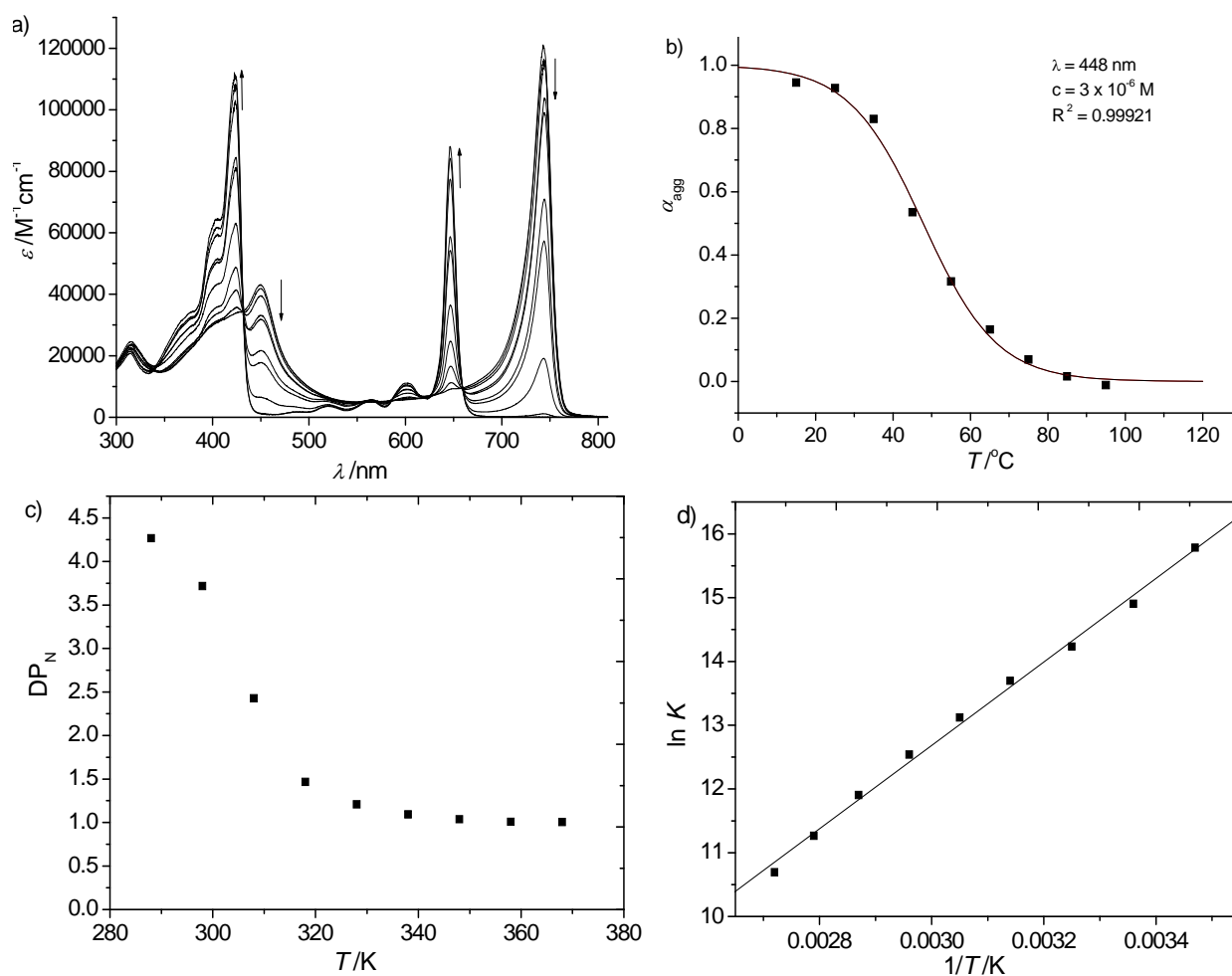
### Self-assembly of ZnChl 1

**UV/Vis Spectroscopy:** The UV/Vis absorption of monomers of ZnChl **1** in THF and its aggregates in *n*-hexane/THF (100:1) are shown in Fig. S1.



**Fig. S1** UV/Vis absorption spectra of monomers of ZnChl **1** in THF (dotted line) and aggregates in *n*-hexane/THF (100:1, v/v) (solid line) at a concentration of  $3 \times 10^{-6}$  M.

For the characterization of the self-assembly of ZnChl **1**, the aggregation process was investigated by temperature-dependent UV/Vis spectroscopy in the temperature range between 288 K and 368 K at 10 K steps in a solvent mixture di-*n*-butyl ether/*n*-heptane (1:4) ( $c = 3 \times 10^{-6}$  M). For this purpose, ZnChl **1** was dissolved in di-*n*-butyl ether, followed by the addition of non-polar solvent *n*-heptane (*n*-heptane/di-*n*-butyl ether 80:20, v/v) to initiate the self-assembly process. Temperature dependent spectra showed that with increasing temperature, the  $Q_y$  band of the aggregates at 741 nm decreases and the monomer band at 647 nm increases (Figure S2a). Upon cooling to initial temperature of 288 K, the  $Q_y$  band was completely recovered, which is indicative of the reversibility of the aggregation of ZnChl **1**. Another remarkable feature of ZnChl **1** is that no precipitation was observed upon heating and cooling processes, proving the thermodynamic stability of these aggregates in the given solvent system.



**Fig. S2** a) Temperature-dependent UV/Vis spectra of ZnChl **1** in *n*-heptane/*di-n*-butyl ether (80:20) at a concentration of  $3.1 \times 10^{-6} \text{ M}$ . The initial temperature of 288 K was increased successively in intervals of 10 degrees up to 368 K and at each temperature the solution was allowed to equilibrate for 1 h prior to measurement; arrows indicate changes upon increasing temperature. b) Plot of degree of aggregation,  $\alpha$ , calculated from the UV/Vis absorption at 448 nm vs temperature ( $T$ ) fitted to isodesmic model (black line). c) Number-averaged degree of polymerisation,  $DP_N$ , as a function of temperature. d) van't Hoff plot ( $\ln K$  vs  $1/T$ ) for ZnChl **1**.

From the temperature-dependent ( $T$ -dependent) measurements, the transition from the monomeric (at high  $T$ ) to the polymeric state (at low  $T$ ) can be probed and the relevant thermodynamic parameters for the aggregation process can be deduced. The  $T$ -dependent

absorption data were normalized to obtain the degree of aggregation,  $\alpha$ , and fitted to the isodesmic model,<sup>5</sup> in which  $\alpha$  is approximated by equation (S1), with  $\alpha_{\text{agg}}(T)$  being the mole fraction of aggregated species at each temperature, and  $\varepsilon(T)$ ,  $\varepsilon_{\text{agg}}$ , and  $\varepsilon_{\text{mon}}$  are the apparent absorption coefficients of the aggregate at temperature  $T$ , and the absorption coefficients of the aggregate, and monomer, respectively. The UV/Vis absorption coefficients of aggregate bands at 448 nm and 741 nm are plotted as a function of temperature and the fitted curve shows a clear sigmoidal shape (Fig. S2b), which is indicative of an isodesmic self-assembly mechanism.<sup>5</sup> The absorption coefficients of pure monomer  $\varepsilon_{\text{mon}}$  and aggregate  $\varepsilon_{\text{agg}}$  were determined by extrapolation of the measured apparent absorption coefficients to their asymptotic values at high and low temperatures.

$$\alpha(T) = \frac{\varepsilon(T) - \varepsilon_{\text{max}}}{\varepsilon_{\text{agg}} - \varepsilon_{\text{max}}} \quad (\text{S1})$$

By applying the degree of aggregation  $\alpha$  in equation (S2), the degree of polymerization,  $DP_{\text{N}}$  (Figure S2c) as well as the equilibrium constant,  $K(T)$ , at temperature  $T$  were obtained.

$$DP_{\text{N}} = \frac{1}{\sqrt{1 - \alpha(T)}} = \frac{1}{2} + \frac{1}{2} \sqrt{4K(T)c_{\text{T}} + 1} \quad (\text{S2})$$

The average  $K$  value at 288 K at two different wavelengths of the aggregate bands (741 nm, 448 nm) is determined to be  $4.5 \times 10^6 \text{ M}^{-1}$  from  $T$ -dependent UV/Vis absorption data. Also, by plotting the logarithm of  $K$  versus the reciprocal temperature (van't Hoff plot, Fig. S2d), a  $\Delta H^\circ$  value of  $-54.4 \text{ kJ mol}^{-1}$  and  $\Delta S^\circ$  value of  $-57.8 \text{ J mol}^{-1} \text{ K}^{-1}$  obtained from a linear relationship. Gibbs free energy  $\Delta G^\circ$  was calculated to be  $-37.7 \text{ kJ mol}^{-1}$  at 288 K using the  $\Delta H^\circ$  and  $\Delta S^\circ$  values obtained from the van't Hoff plot and the van't Hoff equation (S3).

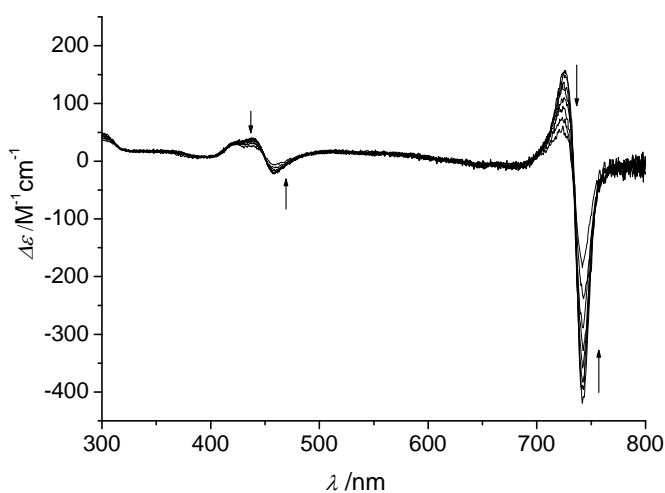
$$\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (\text{S3})$$

Comparison of the enthalpy and entropy contributions to the Gibbs free energy changes for aggregation leads to the conclusion that the self-assembly process of ZnChl **1** is enthalpically driven, whereas it is entropically disfavored. The values at 741 nm and 448 nm are very similar thus only the latter ones were used for further analysis of temperature-dependence. The temperature dependence of equilibrium constant  $K$  at 448 nm is shown in Table S1.

**Tab. S1** Thermodynamic parameters  $K$  ( $M^{-1}$ ),  $DP_N$  obtained from monitoring the aggregate band at 448 nm from temperature-dependent self-assembly of ZnChl **1** ( $c = 3.1 \times 10^{-6}$  M in *n*-heptane/*di-n*-butyl ether = 80:20 vol%) based on the isodesmic model.

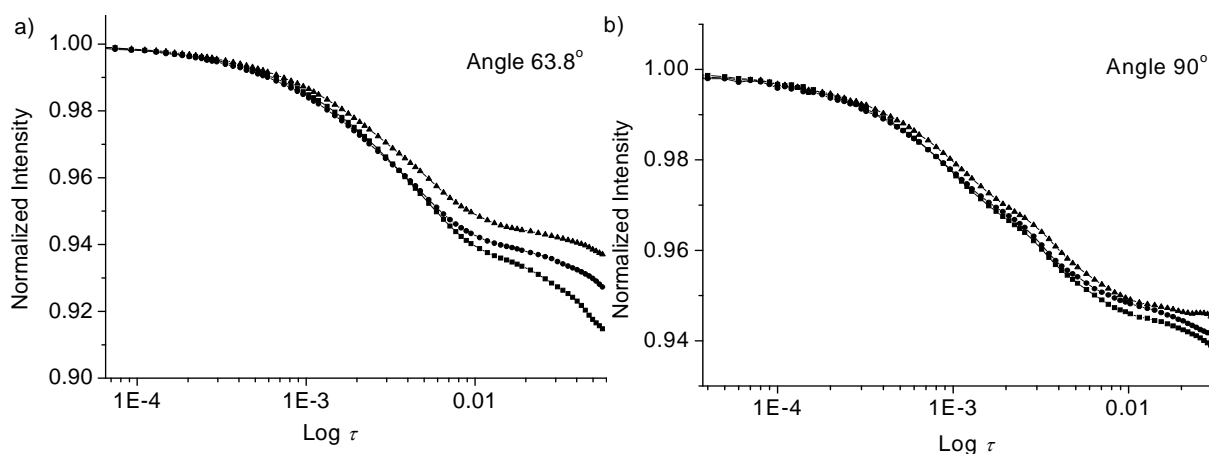
$T$ (K)	$1/T$ (1/K)	$K$ ( $M^{-1}$ )	$\ln K$	$DP_N$
288	0.00347	$4.5 \times 10^6$	15.3	4.3
298	0.00336	$3.3 \times 10^6$	15.0	3.7
308	0.00325	$1.1 \times 10^6$	13.9	2.4
318	0.00314	$2.2 \times 10^5$	12.3	1.5
328	0.00305	$8.2 \times 10^4$	11.3	1.2
338	0.00296	$3.3 \times 10^4$	10.4	1.1
348	0.00287	$1.2 \times 10^4$	9.4	1.0
358	0.00279	$2.6 \times 10^3$	7.8	1.0
368	0.00272	$2.0 \times 10^3$	7.6	1.0

**CD Spectroscopy:** Further insight into the aggregation process for ZnChl **1** was obtained by temperature-dependent CD spectroscopy in *n*-heptane/*di-n*-butyl ether (80:20, vol%) in the temperature range between 15 °C and 95 °C at 10 °C. The shape of the CD spectrum and the position of the Q<sub>y</sub> absorption band show the distinct features of zinc chlorin rod aggregates,<sup>3</sup> an induced CD effect which occurs on chiral excitonic coupling of transition dipole moments and consist of two bands with opposite signs (+/-) in the region of Q<sub>y</sub> aggregate band. This excitonic coupling reversibly arises and disappears on temperature change and does not undergo any time-dependent changes at a particular temperature.

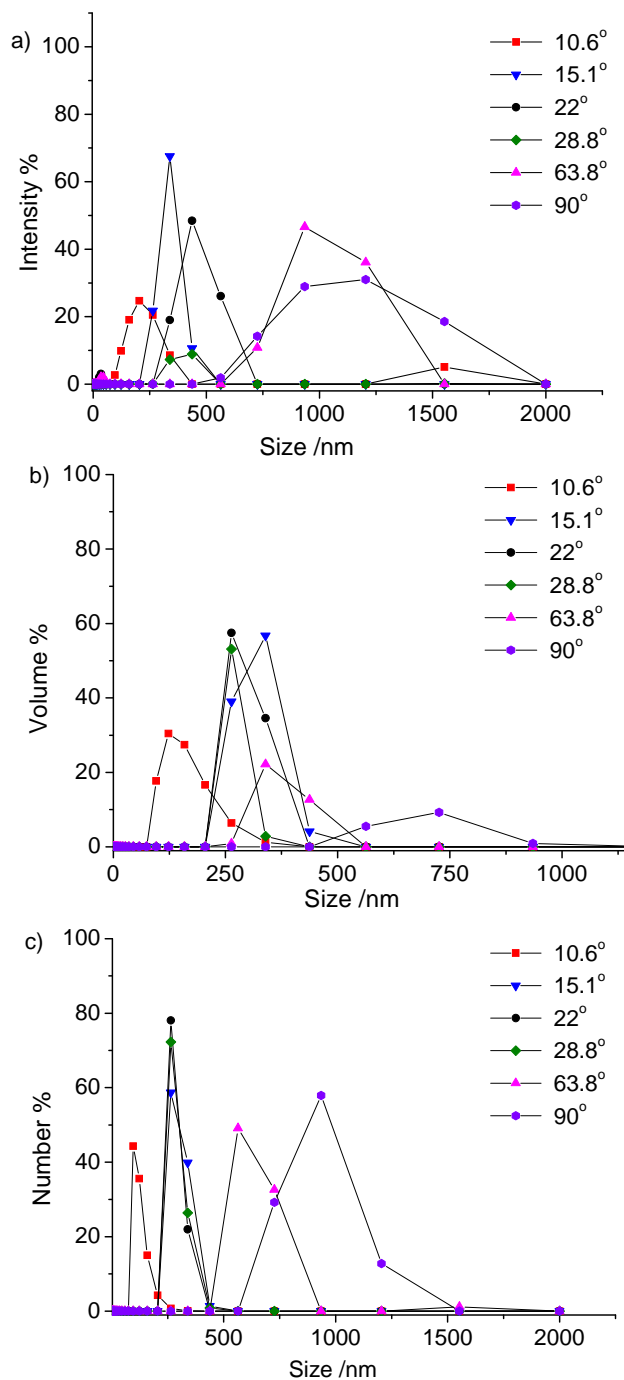


**Fig. S3** Temperature-dependent CD spectra of aggregates of ZnChl **1** in *n*-heptane/*di-n*-butyl ether (80:20) at a concentration of  $3.1 \times 10^{-6}$  M. The initial temperature of 15 °C was increased successively in 15 °C steps up to 95 °C and at each temperature the solution was allowed to equilibrate for 1 h prior to measurement; arrows indicate spectral changes upon increasing temperature.

**Dynamic Light Scattering (DLS):** Dynamic light scattering measurements provide quantitative information regarding the size distribution of aggregates in solution. DLS measurements were performed for  $1.2 \times 10^{-4}$  M solution of aggregates of ZnChl **1** in *n*-hexane/THF (100:1, v/v). The dynamic light scattering data were collected for at least two different samples and at six scattering angles twice to check for reproducibility, and the results were consistent within the experimental error. The autocorrelation functions at scattering angles of 63.8 and 90° were obtained from three sets of measurements and a sigmoidal behavior is observed in all the cases (Fig. S4). Angle dependent DLS results show different size distributions at different angles (Fig. S5), thereby providing evidence for the anisotropy of the aggregates of ZnChl **1** and their one dimensional (rod-like) shape.



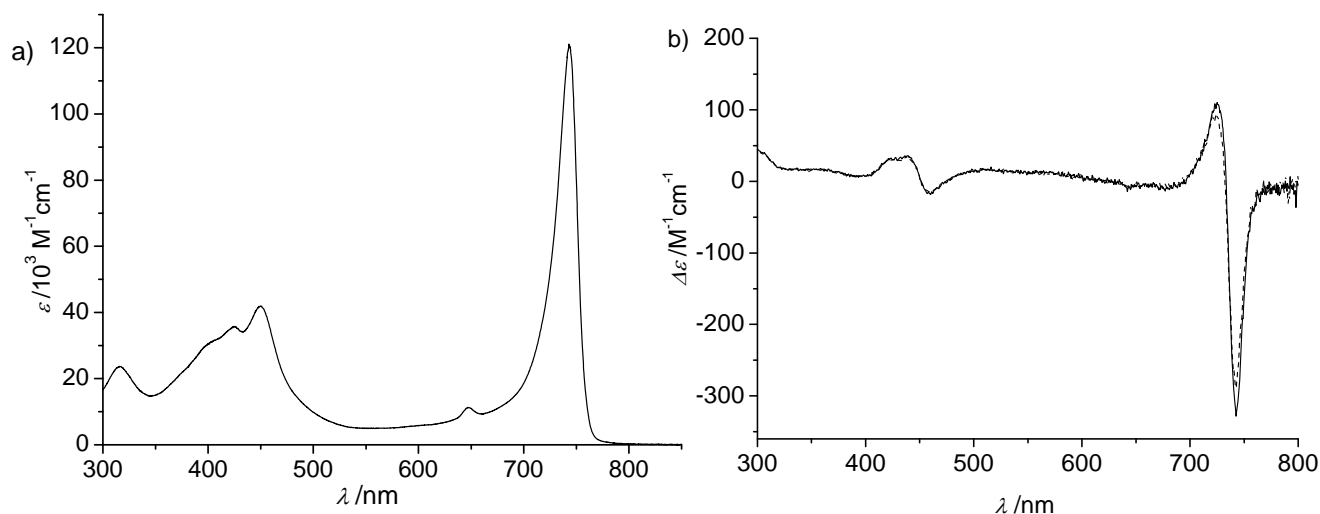
**Fig. S4** Logarithmic autocorrelation functions with normalized intensities at scattering angles of a) 63.8° and b) 90° for the aggregates of ZnChl **1** in *n*-hexane/THF (100:1, v/v) ( $c = 1.24 \times 10^{-5}$  M) obtained by DLS measurements.



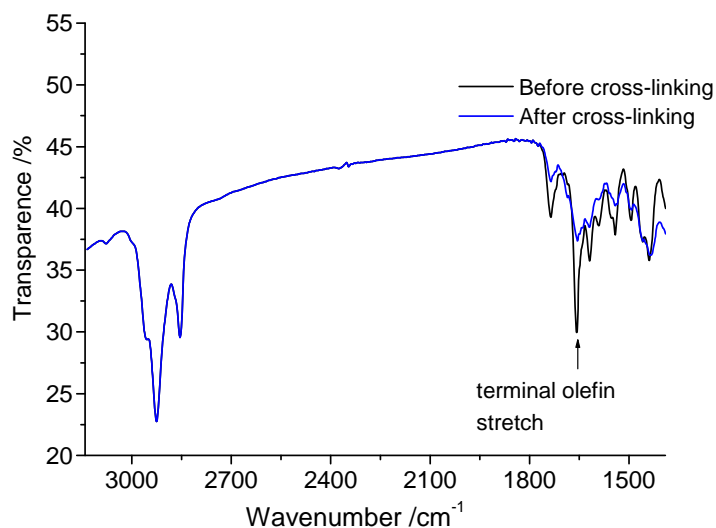
**Fig. S5** a) Intensity distribution of aggregates of ZnChl **1** in *n*-hexane/THF (100:1, v/v) ( $c = 1.24 \times 10^{-5}$  M) obtained at scattering angles of  $10.6^\circ$ ,  $15.1^\circ$ ,  $22^\circ$ ,  $28.8^\circ$ ,  $63.8^\circ$  and  $90^\circ$  from DLS measurements. b) Volume distribution of aggregates of ZnChl **1** in *n*-hexane/THF (100:1) ( $c = 1.24 \times 10^{-5}$  M) obtained from DLS measurements. c) Number distribution of aggregates of ZnChl **1** in *n*-hexane/THF (100:1, v/v) obtained from DLS measurements.



### Cross-linking of nanorods of ZnChl 1:

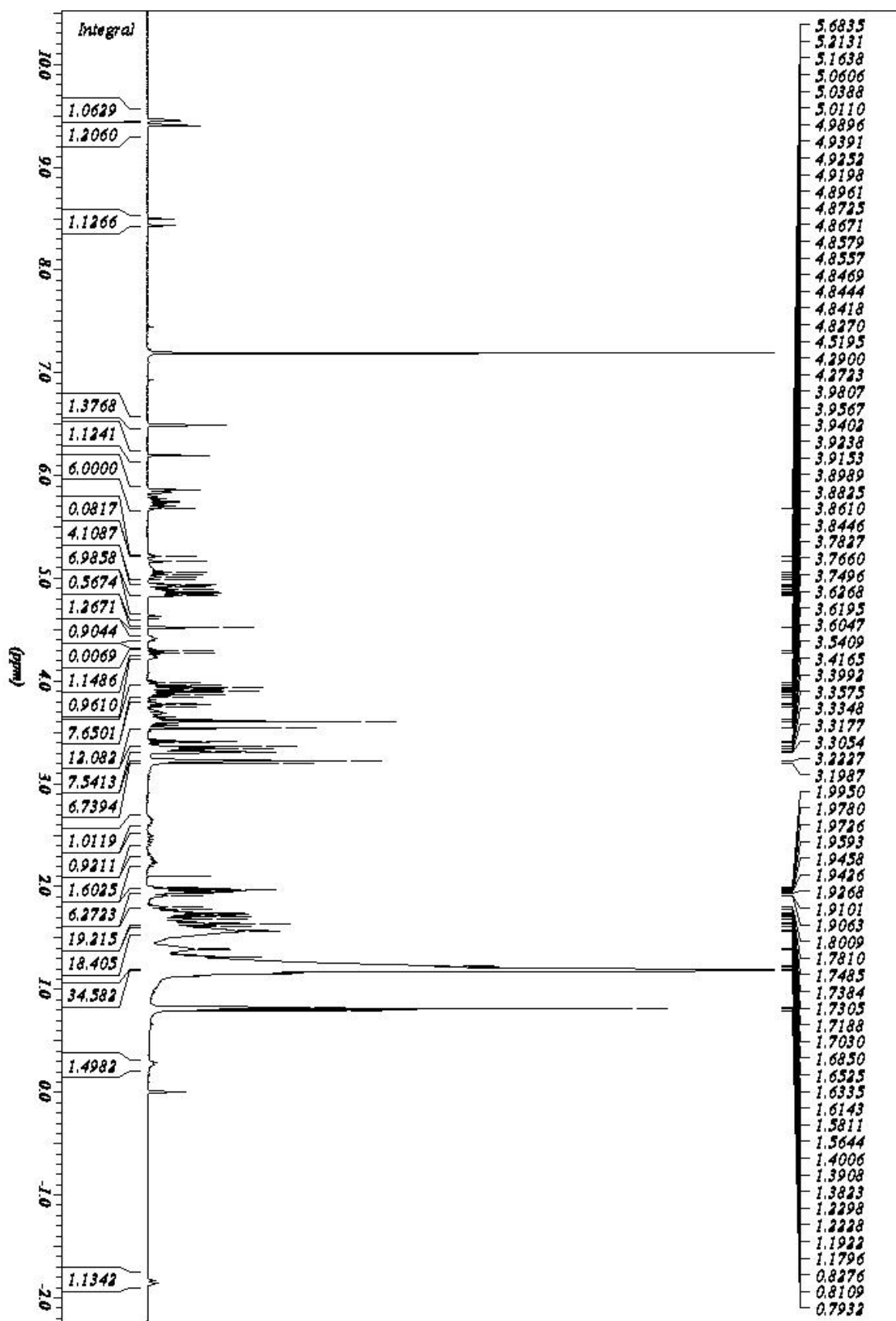


**Fig. S6** UV/Vis (a) and CD spectra (b) of cross-linked aggregates of ZnChl **1** at 50 °C. Comparing with the spectra at room temperature, no changes for UV/Vis spectrum was observed, while only slight decrease in the intensity of CD spectrum was observed at 50 °C (dotted line in b). For comparison, see Figures S2a and S3 (temperature-dependent UV/Vis and CD spectra).

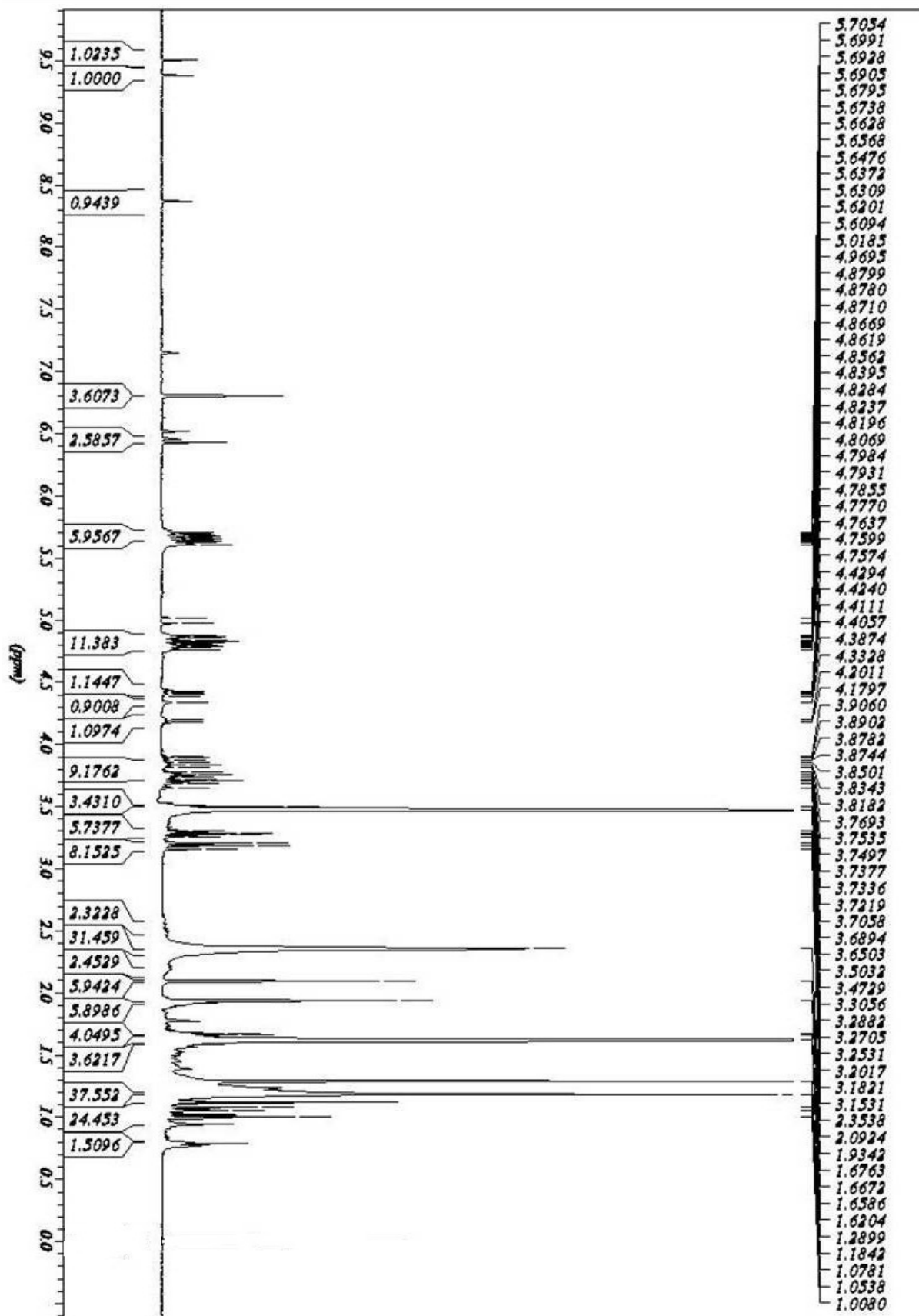


**Fig. S7** FTIR spectra (KBr) of self-assembled ZnChl **1** (black line) and cross-linked product isolated from the aggregate solution after in-situ metathesis reaction (blue line). Spectra are normalized at 2920 cm<sup>-1</sup>.

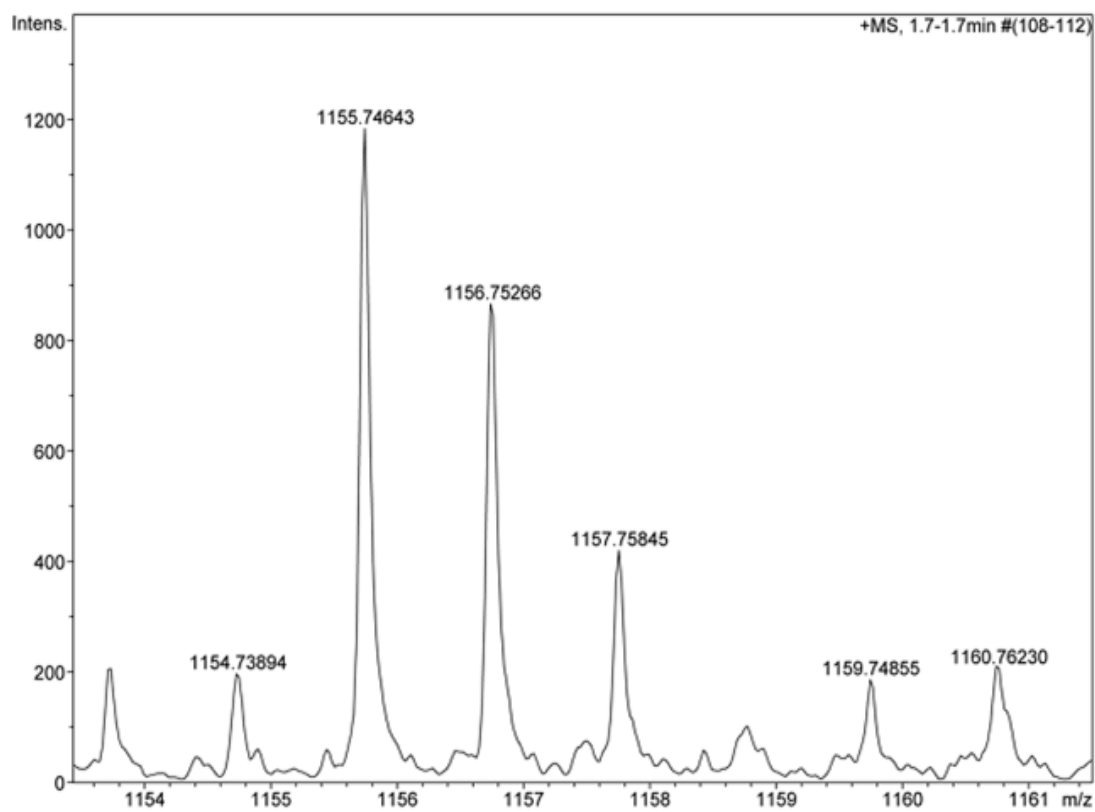
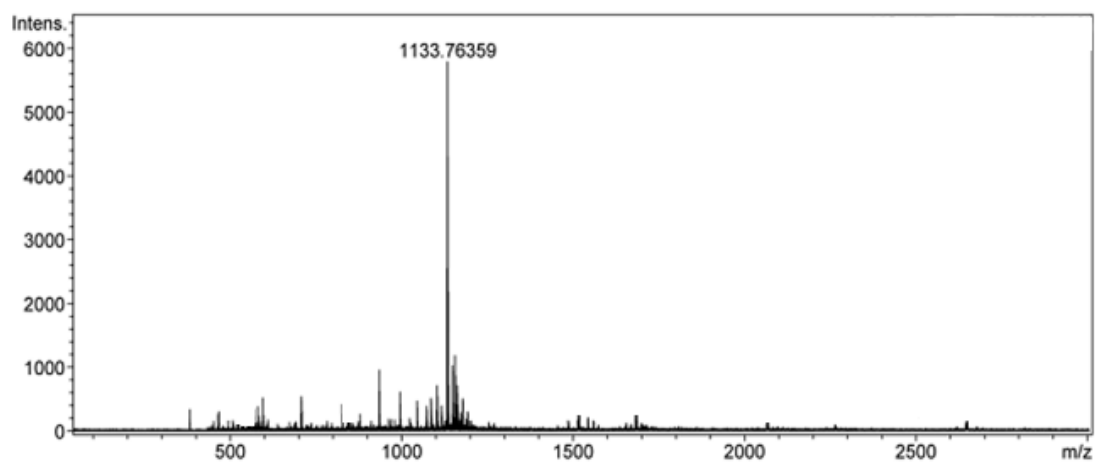
<sup>1</sup>H NMR (400 MHz) spectrum of compound 4



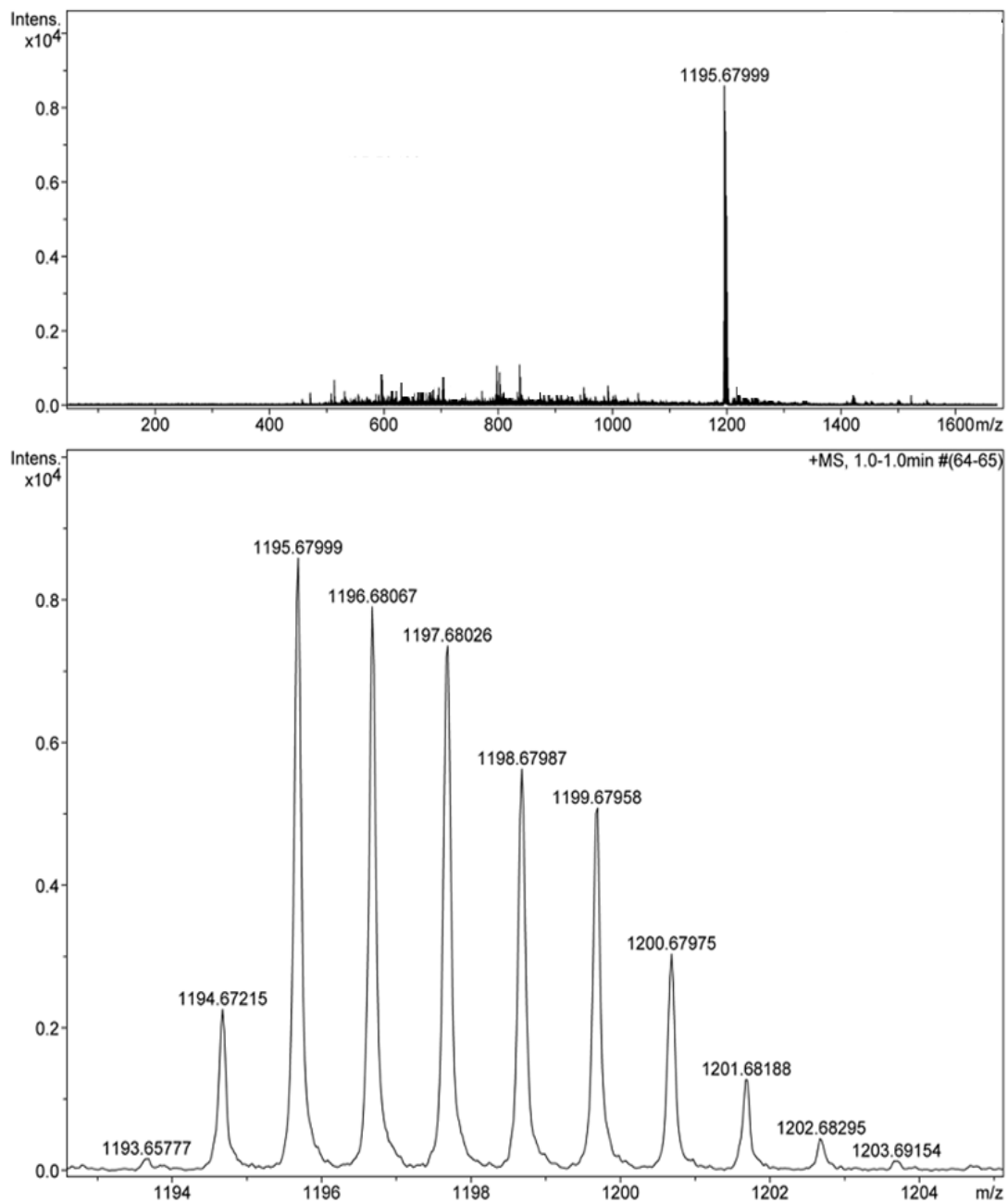
$^1\text{H}$  NMR (400 MHz) spectrum of ZnChl 1



### High resolution ESI mass spectrum of compound 4



### High resolution ESI mass spectrum of ZnChl 1



## References:

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