Electronic Spplementary Information (ESI) for:

Hierarchically supramolecular polymerization of anthraquinone dye to chiral aggregates via 2D-monolayered nanosheets: An unanticipated role of pathway complexity

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1. Materials and methods

Chemicals and reagents: Conventional solvents and reagents were mainly purchased from Energy Chemical, and used without further purification. The products purified by column chromatography with silica gel (300-400 mesh). The solvents of 2-propanol and CH_3OH used in the FTIR experiments were commercial guaranteed reagent grade materials, and retreated by the operations of removing oxygen and water.

NMR spectroscopy: ^1H NMR, ^{13}C NMR, HMBC (^1H-^{13}C) and 2D NOSEY (^1H-^1H) NMR spectra were recorded on a Bruker Avace Neo 400 MHz NMR spectrometer using TMS as the internal standard for the calibration of chemical shifts. Multiplicities for proton signals were abbreviated as *s*, *d*, *t* and *m* for singlet, doublet, triplet, and multiplet, respectively.

Mass spectra: ESI high resolution mass spectra were recorded on an Agilent 6530 Accurate-Mass Q-TOF LCMS spectrometer as positive mode.

UV/Vis spectra: UV/Vis absorption spectra were recorded on a Persee Tu-1950 spectrophotometer with a SPV 1.0 x 1.0 temperature controller. The solvents for spectral studies were of spectroscopic grade, and quartz cuvettes of 1.00 cm thickness were used. The molar absorptivity coefficient (ε) was calculated according to Lambert-Beer's law[1]: $\varepsilon = A/(L*[1]_T)$, where A is the absorbance, L is thickness the cuvettes, $[1]_T$ is the total concentration of dye **1**.

CD measurements: The CD spectra of the soution of Agg II were recorded on J-810 CD Spectrometer which used a quartz cell (1.0 cm). Each spectrum was scaned with a scanning speed at 200 nm·min^{-1}.

Atomic Force Microscope (AFM): AFM measurements were performed on a BioScope Resolve AFM. The aggregate samples were prepared by dropping of the supramolecular aggregate solutions on mica. The height profile analysis in the work was assisted by using the NanoScope Analysis software distributed by Bruker.

Dynamic light scattering (DLS): The hydraulic diameters of dye **1** in 2-propanol/CH_3OH (4/1, v/v) at different temperatures were recorded on by a Nano ZS90 Zetasizer.

2. Synthesis and Characterization of dye 1
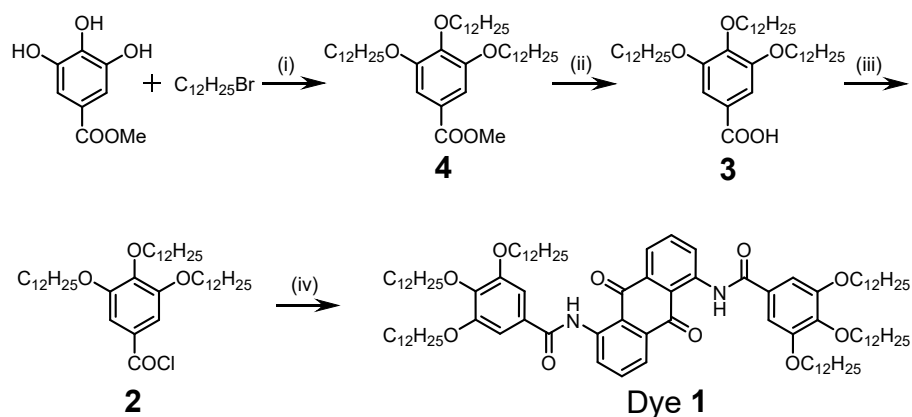
Scheme S1 Synthetic route of dye **1**. Reagents and conditions: (i) K_2CO_3, DMF, 80 °C, overnight, 95.2%; (ii) KOH, $V_{THF}/V_{CH_3OH}/V_{H_2O}$ = 10/4/1, overnight, 93%; (iii) $SOCl_2$, reflux, 5 h, 100%; (iv) 1,5-diaminoanthraquinone, toluene, NEt_3, 78%.

Dye 1: 3,4,5-tri(dodecyloxy)benzoyl chloride (**2**) was prepared from the methyl gallate and $C_{12}H_{25}Br$ in our laboratory according to the reported procedure.[2] Compound **2** (1.73 g, 2.50 mmol, 2.50 equiv) in toluene (50 mL) was added drop-wisely to a solution of 1,5-diaminoanthraquinone (238 mg, 1.00 mmol, 1.0 equiv) in toluene (50 mL containing 2 mL NEt_3) which was under the stirring at 0 °C, after the completion of adding, the mixture was heated to reflux overnight. The solvent was removed and the residues were dissolved in CH_2Cl_2 conferring a clear solution. The solution was washed with 5% aqueous Na_2CO_3 (50 mL) and then with H_2O (100 mL). The organic layer was dried over anhydrous Na_2SO_4 and then concentrated under vacuum; the crude product obtained was purified by silica gel column chromatography using an eluent of petroleum ether/CH_2Cl_2 (1:2, v/v, R_f = 0.48). The pure and yellow solid was obtained (1.21 g, 0.78 mmol, Yield: 78%). ^1H NMR (400 MHz, $CDCl_3$, 293 K, ppm, assignments based on $^1H,^{13}C$-HMBC NMR spectra): δ = 13.20 (s, 2H), 9.33 (d, J = 8.5 Hz, 2H), 8.08 (d, J = 7.7 Hz, 2H), 7.82 (t, J = 8.1 Hz, 2H), 7.38 (s, 4H), 4.16 (t, J = 6.5 Hz, 8H), 4.07 (t, J = 6.5 Hz, 4H), 1.90 (p, J = 6.8 Hz, 8H), 1.78 (q, J = 7.1 Hz, 4H), 1.53 (q, J = 7.3 Hz, 12H), 1.28 (dd, J = 13.5, 6.1 Hz, 96H), 0.92-0.84 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 186.65, 166.08, 153.20, 142.51, 141.86, 135.92, 134.52, 128.80, 126.01, 122.47, 117.02, 106.01, 73.56, 69.21, 31.99, 31.97, 30.42, 29.82, 29.79, 29.76, 29.73, 29.66, 29.53, 29.45, 29.43, 29.37, 26.20, 26.15, 22.73, 14.14. IR (KBr, cm^{-1}): $\tilde{v}$ = 3441, 2955, 2922, 2851, 1682, 1637, 1581, 1504, 1335, 1264, 1180, 1120, 709. HR-MS (ESI): m/z calculated for $C_{100}H_{162}N_2O_{10}Na$ [M + Na]$^+$, 1574.2122; found, 1574.2112.
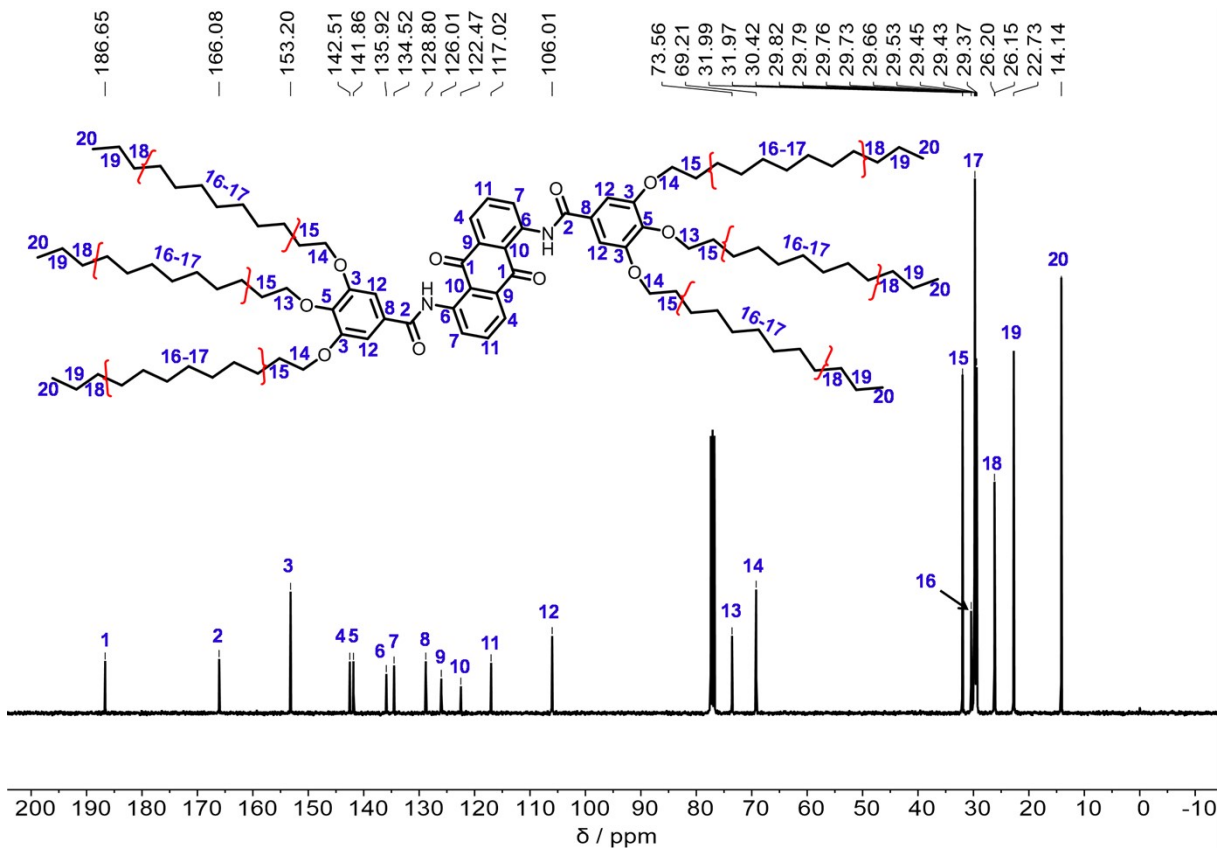
Fig. S1 ^{1}H-NMR spectrum of dye **1** in CDCl$_3$ recorded at 400 MHz and 293 K with its chemical structure and corresponding signal assignments.
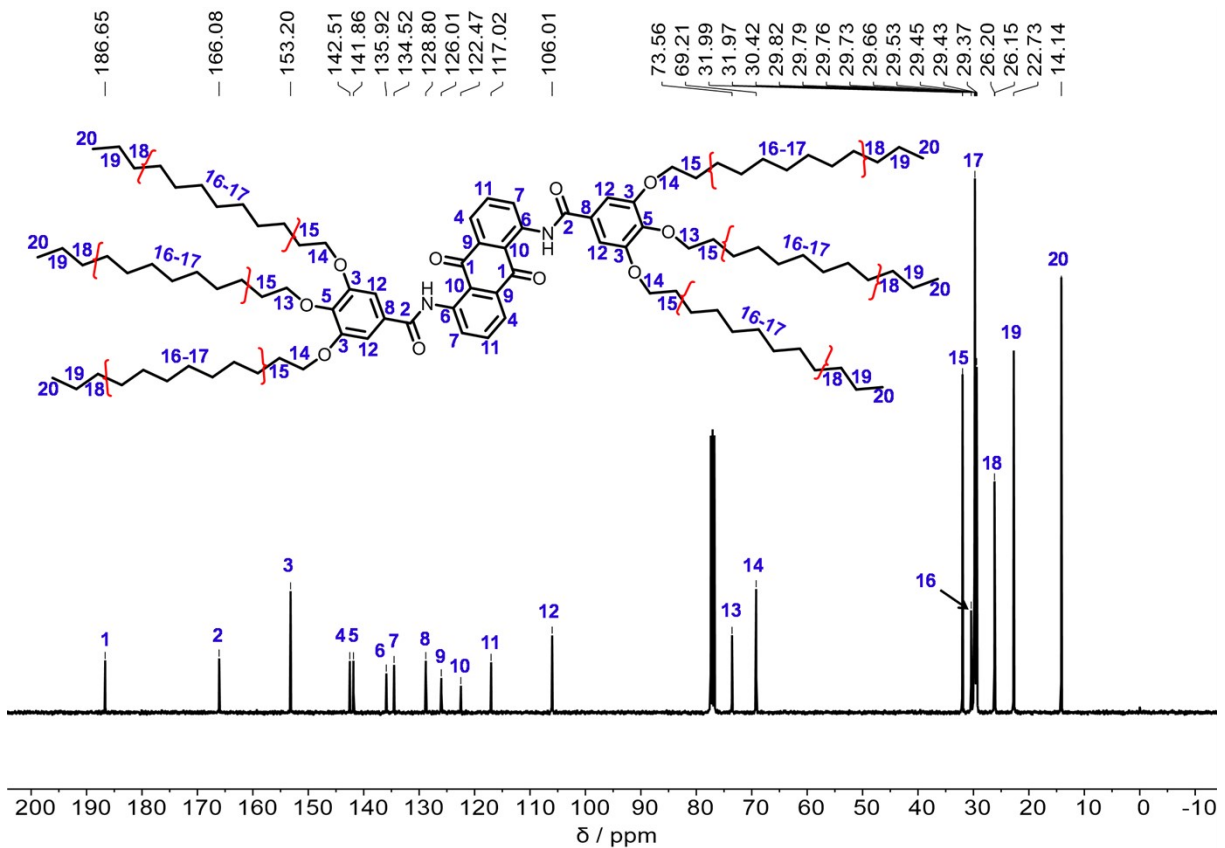

Fig. S2 ^{13}C NMR spectrum of dye **1** in CDCl$_3$ recorded at 101 MHz and 293 K.
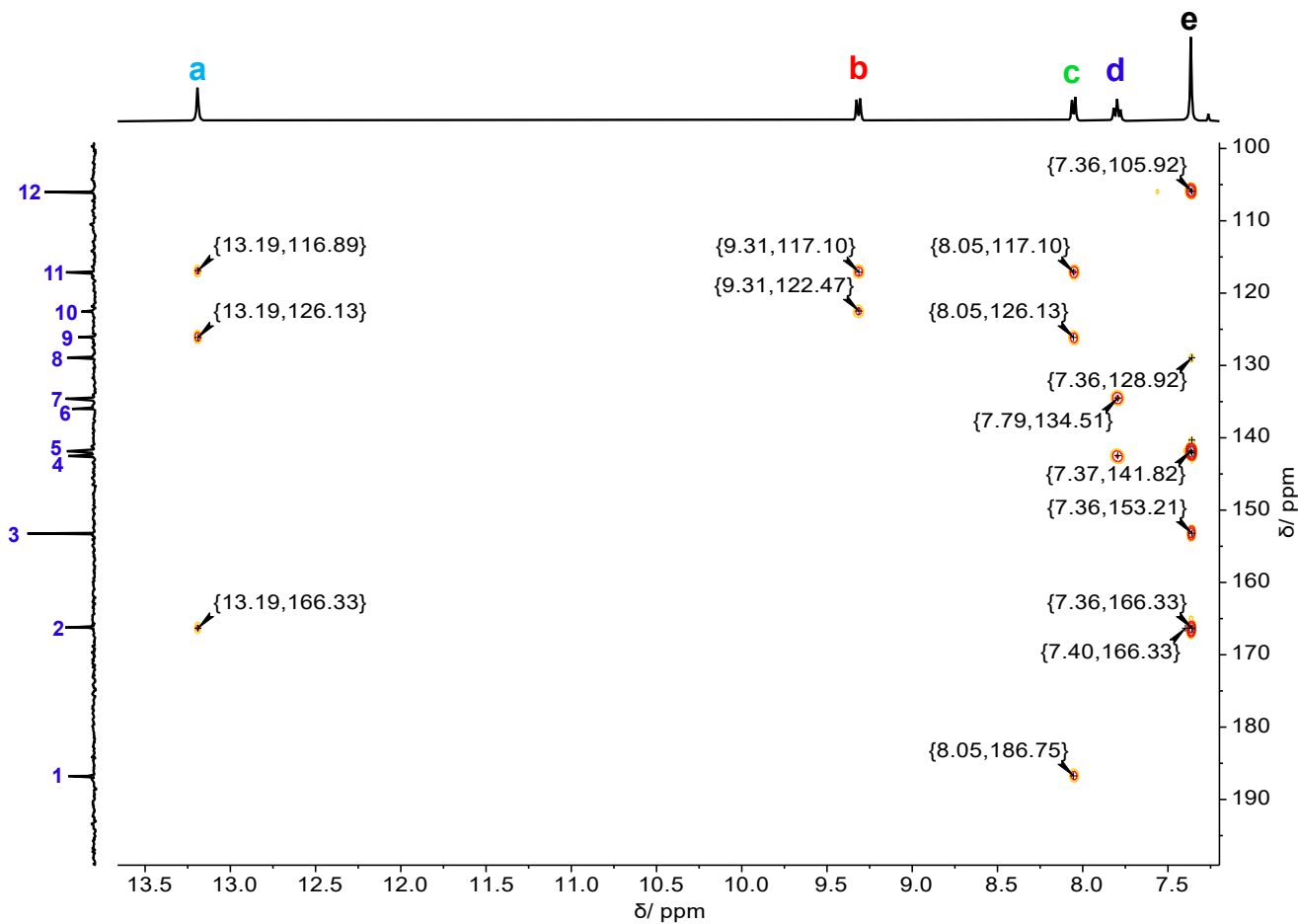
Fig. S3 ^{1}H, ^{13}C-Heteronuclear multiple bond correlation (HMBC) NMR spectrum of dye **1** (5.0 × 10^{-3} M) in CDCl$_3$ recorded at 400 MHz and 293 K.
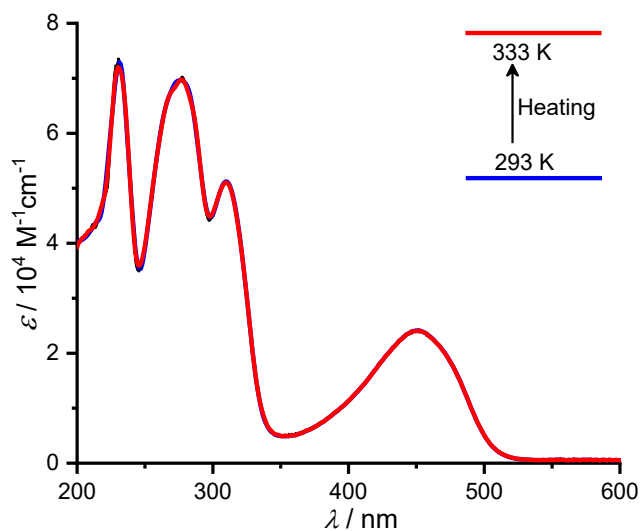
3. Spectral and morphological studies of dye 1

Fig. S4 Temperature-dependent UV/Vis absorption spectra of dye **1** in CDCl$_3$ ([**1**]$_T$ = 5.0 × 10^{-4} M) heating from 293 K to 333 K.
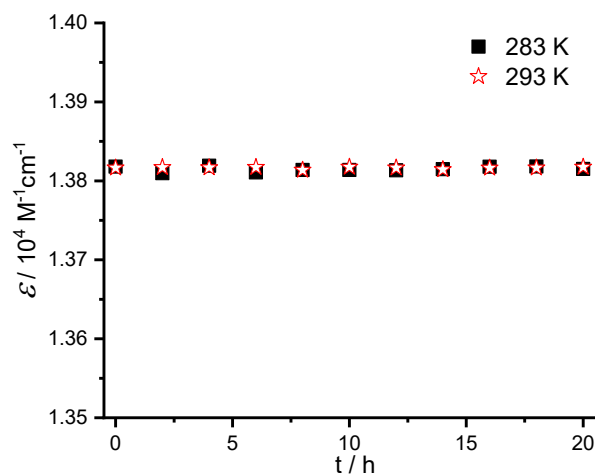
Fig. S5 Time-dependent absorption change at 505 nm for the Agg II in 2-propanol/CH$_3$OH (4/1, v/v, [**1**]$_T$ = 1.0 × 10^{-5} M) monitored at 293 K and 283 K, respectively.
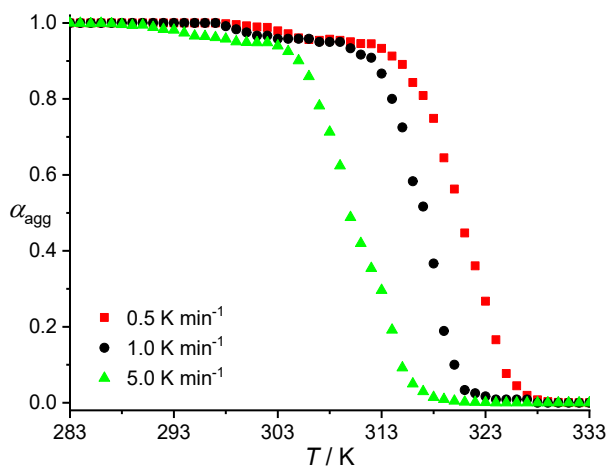

Fig. S6 The aggregated fractions of dye **1** in 2-propanol/CH$_3$OH (4/1, v/v, [**1**]$_T$ = 1.0 × 10^{-5} M) in the cooling process from 333 K to 283 K measured at 505 nm at different cooling rates.
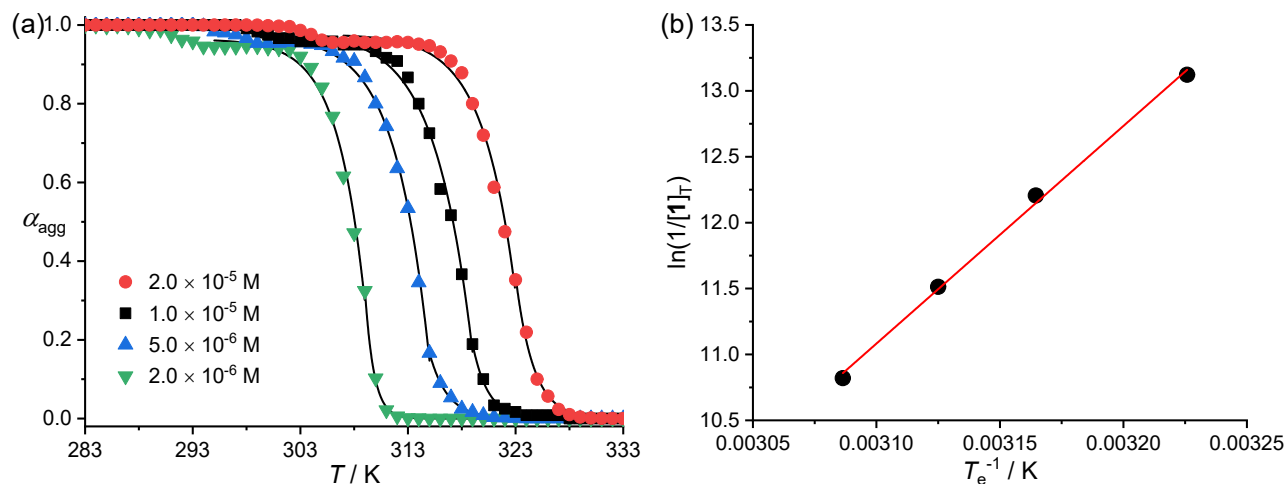

Fig. S7 (a) The aggregated fractions of dye **1** in 2-propanol/CH$_3$OH (4/1, v/v) at different concentrations in the cooling process from 333 K to 283 K at 1 K min^{-1}, calculated by the absorption values measured at 505 nm. The black lines were well-simulated by the nucleation-elongation model. (b) The van't Hoff plot for the cooling processes of monomeric dye **1** (R^2 = 0.9978).

Table S1. Thermodynamic parameters of dye **1** in 2-propanol/CH$_3$OH (4/1, v/v) at different concentrations in the cooling process obtained by the simulation with nucleation-elongation model.

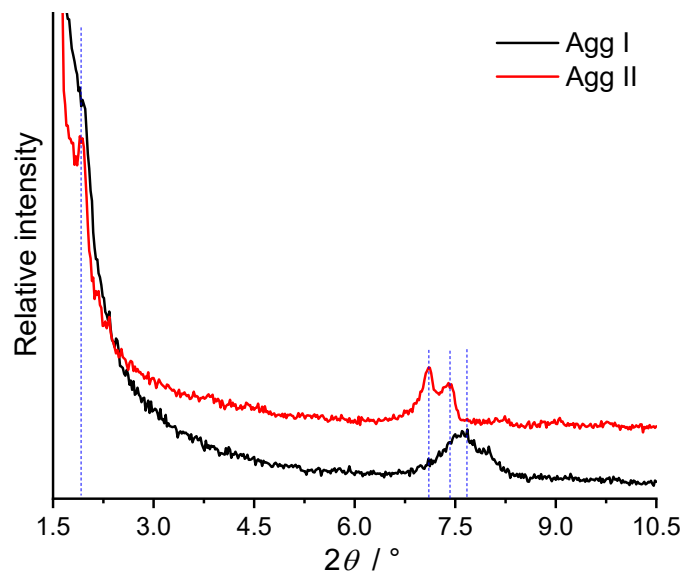| $10^5 C_T$/M	T_e/K	ΔH_e/kJ mol^{-1}	R^2
2.0	324	-104	0.9985
1.0	320	-101	0.9973
0.5	316	-107	0.9991
0.2	310	-102	0.9987

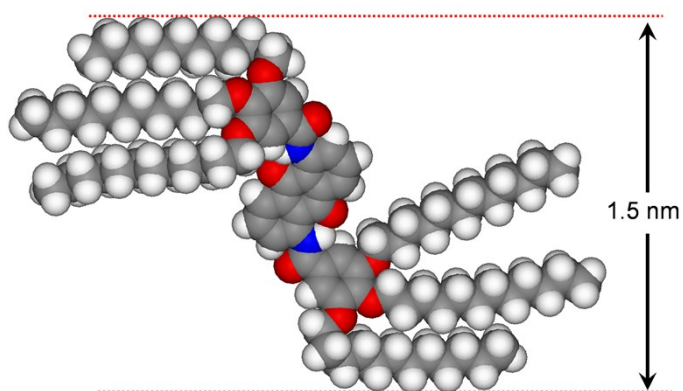**Fig. S8** Powder XRD patterns of Agg I and Agg II of dye **1**.

Fig. S9 Computer-generated molecular size of dye **1** with a width of the anthraquinone core was 1.5 nm. The atoms represented by each color in the model: blue, nitrogen; red, oxygen; dark gray, carbon; and light gray, hydrogen.
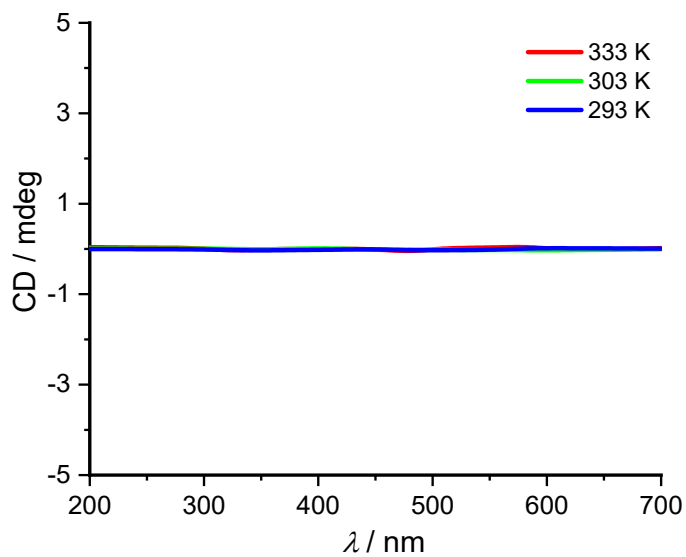

Fig. S10 CD spectra of monomer (at 333 K), Agg I (at 303 K) and Agg II (at 293 K) in 2-propanol/CH_3OH (4/1, v/v, $[\mathbf{1}]_T = 1.0 \times 10^{-5}$ M).

4. Temperature-dependent measurements of Agg II in the heating process
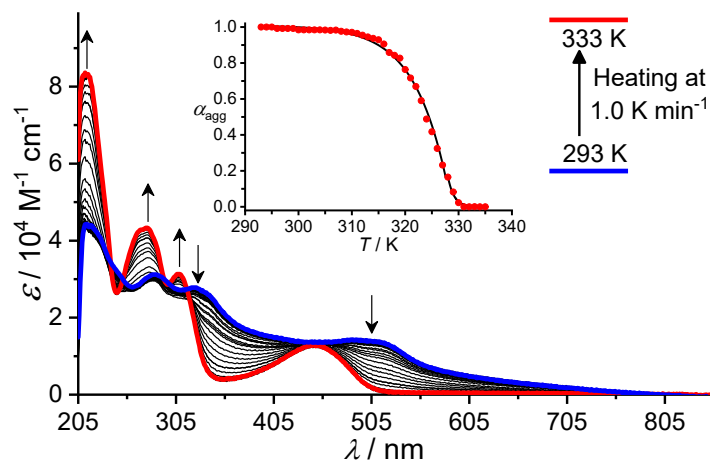

Fig. S11 Temperature-dependent UV/Vis absorption spectra of dye **1** in 2-propanol/CH₃OH (4/1, v/v, $[1]_T = 1.0 \times 10^{-5}$ M) upon heating from 293 K to 333 K with a heating rate of 1.0 K min⁻¹. Inset: the fractions of aggregated dye **1** in heating process calculated from the absorption values at 505 nm, and the black curve was obtained by the simulation of the fraction data by the nucleation-elongation model.
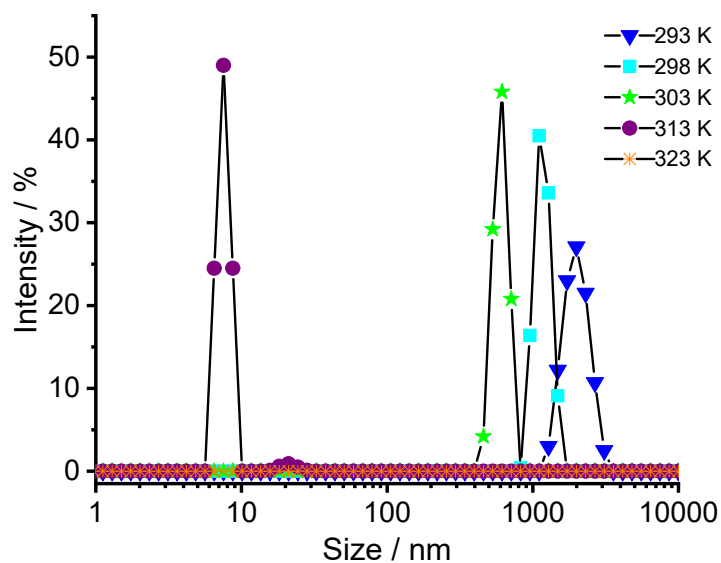

Fig. S12 Temperature-dependent DLS measurements of dye **1** in 2-propanol/CH₃OH (4/1, v/v, $[1]_T = 1.0 \times 10^{-5}$ M) upon heating from 293 K to 323 K.

5. References

[1]   I. Botev, *Fresenius' Zeitschrift für analytische Chemie*, 1979, **297**, 419-419.

[2]   A. R. A. Palmans, J. A. J. M. Vekemans, H. Fischer, R. A. Hikmet, E. W. Meijer, *Chem. Eur. J.*, 1997, **3**, 300-307.