Electronic Supplementary Information (ESI) for:

Novel pathway and seeded polymerizations of aggregates at the thermodynamic

state for an amido-anthraquinone compound

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1. Materials and methods

Chemicals and reagents: All conventional solvents and reagents purchased from Energy Chemical, and used without further purification, unless otherwise noted. Products purified by column chromatography with silica gel (300-400 mesh).

NMR spectroscopy: ¹H NMR and ¹³C NMR spectra were collected on Bruker Avace Neo 400MHz NMR spectrometer using tetramethylsilane as an internal standard for the calibration of chemical shifts. Multiplicities for proton signals are abbreviated as s, d, t and m for singlet, doublet, triplet and multiplet, respectively.

Mass spectra: Mass spectra were recorded on an Agilent 6530 Accurate-Mass Q-TOF LCMS spectrometer by ESI in positive mode.

UV/Vis spectra: UV/Vis absorption spectra were recorded on a Persee Tu-1950 spectrophotometer equipped with a SPV 1.0×1.0 temperature controller. The solvents for spectral studies were spectroscopic grade and used as received. Quartz cuvettes of 1.0 cm thickness were used and the molar absorptivity coefficient (ε) was calculated according to Lambert-Beer's law¹: $\varepsilon = A / (b^*[1]_T)$, where *A* is the absorbance, *b* is thickness the cuvettes, $[1]_T$ is the total concentration of 1.

Fluorescence spectroscopy: The steady state fluorescence spectra were measured under ambient conditions on an Edinburgh FLS980 spectrofluorometer.

Scanning electron microscopy: SEM measurements were performed on a JSM-7800F microscope operated at 20 kV landing energy. The aggregates sample was prepared by drop-casting of the supramolecular aggregate solution on mica.

Preparation of the aggregates and seeds: The amido-anthraquinone compound **1** was dissolved in 2propanol/CH₃OH (4:1, v/v) by sonication in 5 min at 333 K, and a clear solution was obtained. The solution was kept at 278 K for 5 h, and the aggregate solution was obtained. The aggregate seeds obtained by sonication of the aggregate solution at 278 K for 10 min.

2. Synthesis and characterization



Scheme S1. Synthesis of 1 with conditions: (i) toluene, reflux, 24 h, 82%.

Compound 1 (1-[3,4,5-tris(dodecyloxy)benzamide]-9,10-anthracenedione): 3,4,5-tri(dodecyloxy) benzoyl chloride² (0.85 g, 1.23 mmol, 1.10 equiv) in toluene (50 mL) was added drop-wisely to a solution of 1-aminoanthraquinone (0.25 g, 1.12 mmol, 1 equiv) in toluene (50 mL) which was stirring at 0 °C, then the mixture was heated to reflux for 24 h. The completion of the reaction was detected by thin layer chromatography (TLC). After completion, the solvent was removed and the residues were dissolved in CH₂Cl₂ conferring a clear solution. The solution was washed with 5% aqueous Na₂CO₃ (50 mL) and H₂O (100 mL), respectively. The organic layer was dried with anhydrous Na₂SO₄ and then concentrated under vacuum; the crude product obtained was purified by silica gel column chromatography using an eluent of petroleum ether/CH₂Cl₂ (1:4, v/v, $R_f = 0.59$) to obtain a yellow solid (0.81 g, 0.92 mmol, Yield: 82%). ¹H NMR (400 MHz, CDCl₃, ppm): $\delta = 13.28$ (s, 1H), 9.34 (d, *J* = 8.5, 1.2 Hz, 1H), 8.37-8.26 (*m*, 2H), 8.11 (*d*, *J* = 7.6, 1.2 Hz, 1H), 7.89-7.77 (*m*, 3H), 7.40 (*s*, 2H), 4.17 (*t*, *J* = 6.6 Hz, 4H), 4.07 (*t*, *J* = 6.6 Hz, 2H), 1.89 (*m*, *J* = 7.0 Hz, 4H), 1.77 (*m*, *J* = 7.1 Hz, 2H), 1.57-1.22 (*m*, 54H); 0.88 (*t*, J = 6.9, 3.3 Hz, 9H). ¹³C NMR (101 MHz, CDCl₃, ppm): $\delta = 186.04$, 181.03, 164.70, 152.04, 141.39, 140.58, 134.67, 133.10, 132.90, 132.68, 131.51, 127.75, 126.05, 125.79, 124.59, 121.16, 116.28, 104.79, 72.44, 68.05, 30.96, 30.93, 29.40, 28.80, 28.76, 28.70, 28.64, 28.51, 28.42, 28.39, 28.35, 25.18, 25.13, 21.69, 13.10, IR (KBr, cm⁻¹): $\tilde{v} = 3447$, 2918, 2849, 1675, 1643, 1580, 1506, 1468, 1337, 1272, 1123, 706. HRMS (ESI): m/z calculated for C₅₇H₈₅NO₆Na [M + Na]⁺, 902.6269; found, 902.6270. Elemental analysis: calculated for C₅₇H₈₅NO₆ (%): C 77.77, H 9.73, N 1.59; Found: C 77.76, H 9.76, N 1.56.



Figure S1. ¹H NMR spectrum of 1 in CDCl₃ recorded by a 400 MHz spectrometer at 293 K. The structure of 1 and the main signal assignments are given in the figure.



Figure S2. ¹³C NMR spectrum 1 in CDCl₃ recorded at 101 MHz and 293 K.



Figure S3. ¹H-¹³C HSQC spectrum of 1 in CDCl₃ recorded at 293 K.



Figure S4. FT-IR of 1 recorded as KBr pellets at room temperature.



Figure S5. UV/Vis absorption and fluorescence spectra ($\lambda_{ex} = 370 \text{ nm}$) of 1 in CHCl₃ at the concentration of 2.0×10⁻⁵ M and 1.0×10⁻⁶ M, respectively.

3. Thermodynamic and kinetic aspect of the supramolecular aggregation

Figure S6. Temperature-dependent fluorescence emission spectra of 1 in 2-propanol/CH₃OH (4:1, v/v, $[1]_T = 5.0 \times 10^{-5}$ M) upon cooling from 333 K to 278 K with a cooling rate of 0.1 K min⁻¹.

Figure S7. Temperature-dependent UV/Vis absorption spectra of **1** in 2-propanol/CH₃OH (4:1, v/v, $[\mathbf{1}]_T = 5.0 \times 10^{-5}$ M) upon cooling from 333 K to 278 K with a cooling rate of 10 K min⁻¹.

Figure S8. Temperature-dependent UV/Vis absorption at 481 nm of the aggregates 1 in 2-Propanol/CH₃OH (4:1, v/v, $[1]_T = 5.0 \times 10^{-5}$ M).

Nucleation-elongation model:

Plots of the molar fraction in the supramolecular polymerization as a function of temperature were fitted by the nucleation–elongation model descripted by Meijer and co-workers³ (Eq. S1 and

Eq. S2).
$$\alpha_{\text{agg}} = \alpha_{\text{SAT}} \left\{ 1 - exp \left[\frac{-\Delta H_e}{RT_e^2} (T - T_e) \right] \right\}$$
 (S1)

$$\alpha_{\text{agg}} = K_{\text{a}}^{1/3} \exp[(2/3K_{\text{a}}^{-1/3} - 1)\frac{\Delta H_{\text{e}}}{RT_{\text{e}}^{2}}(T - T_{\text{e}})]$$
(S2)

where ΔH is elongation enthalpy change in the polymerization, T_e stands for the critical elongation temperature, and R is the gas constant.

The fraction of aggregated molecules (α_{agg}) can be estimated according to Eq. (3) based on the assumption that the build blocks fully aggregated ($\alpha_{agg} = 1$) at lowest temperature (T = 278 K) and existed all in the monomers ($\alpha_{agg} = 0$) at highest temperature (T = 333 K).

$$\alpha_{\text{agg}}(T) = 1 - \frac{\varepsilon(T) - \varepsilon_{\text{agg}}}{\varepsilon_{\text{mon}} - \varepsilon_{\text{agg}}}$$
(S3)

where ε_{mon} and ε_{agg} stands for absorption coefficients of the monomer and fully aggregated state, respectively.

c / \times 10 ⁻⁵ M	$\alpha_{ m SAT}$	$T_{\rm e}$ / K	$\Delta H_{ m e}$ / kJ mol ⁻¹
0.5	1.022	312	99.2
1	1.014	315	98.5
2	1.022	318	97.6
5	1.035	321	99.4
10	1.021	325	98.8

Table S1. The critical temperatures (T_e) and elongation enthalpies (ΔH_e) of **1** in 2-propanol/CH₃OH (4:1, v/v) upon heating processes from 278 K to 333 K at different concentrations.

Figure S9. The van't Hoff plot of natural logarithm of the reciprocal concentrations of **1** as a function of the reciprocal T_e showing the linear relationship (correlation coefficient 0.997).

Table S2 The kinetic parameters in the transformations of monomeric 1 with different concentrations in 2-Propanol/CH₃OH (4:1, v/v) at 278 K.

C / $ imes$ 10 ⁻⁵ M	t ₅₀ / s	τ/s	R ²	t _D / s
2	1308	106	0.999	1096
5	868	120	0.998	628
10	316	149	0.976	18

4. Studies on intramolecular H-bonding interactions

Figure S10. Temperature-dependent UV/Vis absorption spectra of **1** in CHCl₃ ($[\mathbf{1}]_T = 5.0 \times 10^{-4} \text{ M}$) upon cooling from 333 K to 293 K.

Figure S11. Temperature-dependent ¹H NMR spectra of **1** in CDCl₃ ([**1**]_T = 5.0×10^{-4} M) upon cooling from 333 K to 293 K.

5. Calculations based on molecular exciton theory

According to the molecular exciton theory⁴, the excitonic energy splitting ΔE can be calculated theoretically. For the two rotationally packing dimeric chromophores with a torsion angle (α) between the transition dipoles, the excitonic energy splitting (ΔE_{dimer}) of two transition dipole moments can be calculated by the absorbance spectrum. The energy can be expressed as the Equation (S4):

$$\Delta E_{dimer} = \frac{|M|^2}{2\pi\varepsilon_0\varepsilon_r r^3} \left(-\sin\theta_1\sin\theta_2\cos\alpha + 2\cos\theta_1\cos\theta_2\right)$$
(S4)

where the *M* is the transition dipole moment of the molecule; *r* is the centre-to-centre distance between the chromophores; ε_0 and ε_r are the permittivity of the vacuum and the relative permittivity of the solvent, respectively; θ_1 and θ_2 are the angles between the two transition dipoles and the line connecting the centres of the two molecules. To simplify the calculation, $\theta_1 = \theta_2$, $\alpha = 0^\circ$ were estimated in this work. The experimental value of ΔE_{dimer} for the aggregates was obtained by the bathochromically shifted band in UV/Vis spectra, and $\Delta E_{\text{dimer}} = 3312 \text{ cm}^{-1}$.

The transition dipole moment of **1** was calculated from the UV/Vis spectra of the monomer according to Equation (S5):

$$|M|^{2} = \frac{3h\varepsilon\varepsilon_{0}\ln 10}{2\pi^{2}N_{A}} \int_{\widetilde{v_{1}}}^{\widetilde{v_{2}}} \frac{\varepsilon(\tilde{v})}{\tilde{v}} d\tilde{v}$$
(S5)

where ε is the molar absorptivity coefficient at the corresponding wavenumber \tilde{v} , c is the speed of light, h is the Planck's constant, N_A is the Avogadro's number, and ε_0 is the permittivity of vacuum. The transition dipole moment of monomeric **1** in CHCl₃ was calculated to be: 1.41×10^{-29} C m.

6. References

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