Supporting Information

Solvent-dependent supramolecular assembly behavior of a coumarin-headed amphiphile

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The cooperative model for LG-Cm aggregation in toluene

Cooperative self-assembly model[1] has been described by a nucleation-growth model, which is characterized by the unfavorable formation of nuclei of a critical size, followed by a favorable elongation process. The nucleation and elongation regime are governed by the following equations S1 and S2 respectively.

$$\phi_n = K_a^{1/3}\ exp\left[(2/3\ K_a^{-1/3} - 1)\frac{h_e}{RT_e^2}(T - T_e)\right] \quad \text{S1}$$

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

Φ_n is the degree of aggregation, and Φ_n/Φ_{SAT} is a factor introduced to the equation such that does not exceed unity. h_e is the molecular enthalpy released due to noncovalent interactions during elongation, T_e is the elongation temperature, T is the absolute temperature, K_a is the dimensionless equilibrium constant of the nucleation process at T_e and R is the gas constant.

The relationship between equilibrium constant of elongation K_e and the degree of aggregation also is given by S3; Gibbs free energy of elongation ΔG can be expressed as a function of absolute temperature by making use of the Van 't Hoff equation S4:

$$\alpha = 1 - \frac{[A]}{c_T} = 1 - \frac{1}{K_e c_T} \quad \text{S3}$$

$$\ln K_e = -\frac{\Delta G}{RT} \quad \text{S4}$$

The isodesmic model for LG-Cm aggregation in DMSO

The isodesmic model[2] is approximated by Equation S5 in which T_m is the melting temperature defined as the temperature for which α =0.5, ΔH is the molar enthalpy release related to the formation of non-covalent intermolecular interactions and R is the gas constant. It is also known as the equal-K model. In an isodesmic mechanism, the degree of aggregation, α is related to temperature T by equation below:

$$\alpha(T) = \frac{1}{1 + exp\left[-0.908\Delta H\frac{T - T_m}{RT_m^2}\right]} \quad \text{S5}$$

The above equation could be utilized to fit the experimental data obtained from the CD absorption change at different temperature such that ΔH and T_m could be obtained.

From the degree of aggregation, the number-averaged degree of polymerisation, DP_N, can be calculated directly by equation S6:

$$DP_N(T) = \frac{1}{\sqrt{1-\alpha(T)}} \qquad \text{S6}$$

Furthermore, the number-averaged degree of polymerisation is also related to the total concentration of molecules, c_T, and the equilibrium constant, K_e, via equation S7:

$$DP_N(T) = \frac{1}{2} + \frac{1}{2}\sqrt{4K_e(T)c_T + 1} \qquad \text{S7}$$

The temperature dependence of the degree of aggregation can be expressed as a function of absolute temperature by making use of the Van 't Hoff equation S8:

$$\ln K_e = -\frac{\Delta G}{RT} \qquad \text{S8}$$

Supplementary Figures

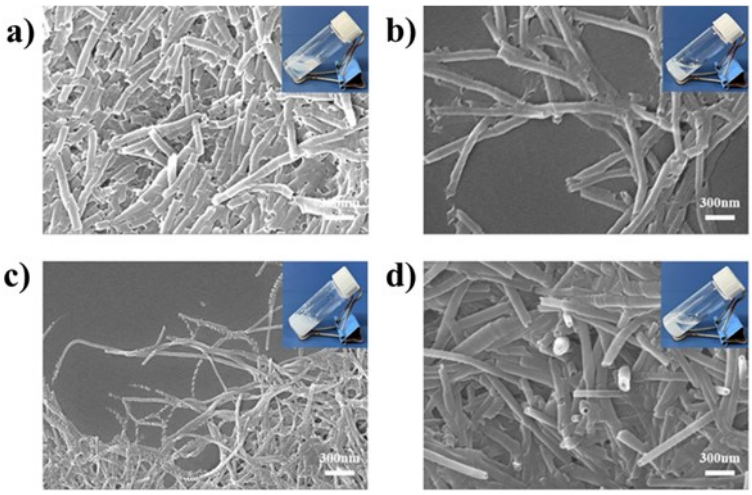

Figure S1. SEM image of **LG-Cm** in different polar solvents. a) **LG-Cm** in DCM, b) **LG-Cm** in EA, c) **LG-Cm** in ACN, d) **LG-Cm** in DMF.

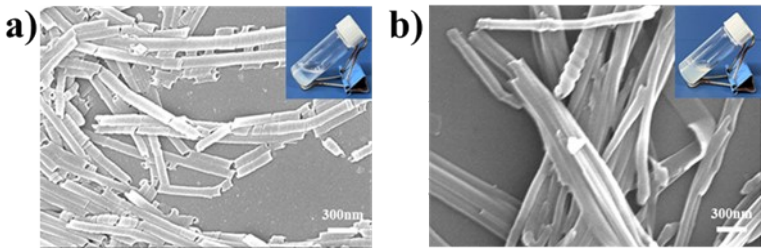

Figure S2. SEM image of **DG-Cm** in toluene and DMSO. a) **DG-Cm** in toluene, b) **DG-Cm** in DMSO.

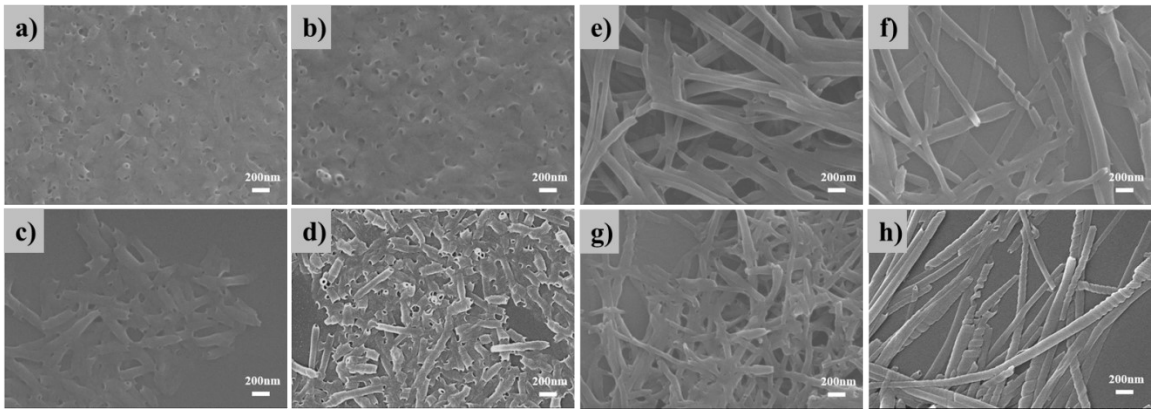

Figure S3. The SEM images of **LG-Cm** in toluene at different concentrations with a) 1×10^{-4} M, b) 5×10^{-4} M, c) 1×10^{-3} M, d) 5×10^{-3} M, and in DMSO with e) 1×10^{-4} M, f) 5×10^{-4} M, g) 1×10^{-3} M, h) 5×10^{-3} M.

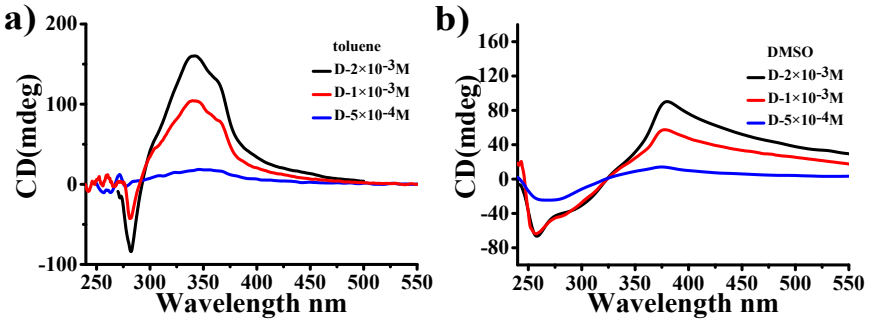

Figure S4. The relevant CD data of different concentrations (c=5×10^{-4} M, 1×10^{-3} M, 2×10^{-3} M) of **DG-Cm** in toluene and DMSO.

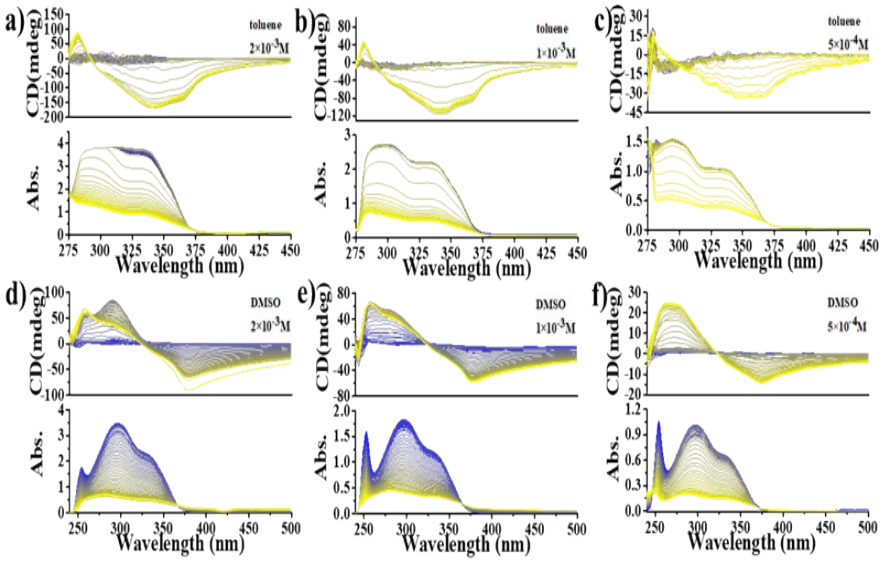

Figure S5. Temperature dependent CD for **LG-Cm** (c=2×10^{-3} M, 1×10^{-3} M, 5×10^{-4} M) in (a-c) toluene and (d-f) DMSO with cooling rate of 1K min^{-1}.

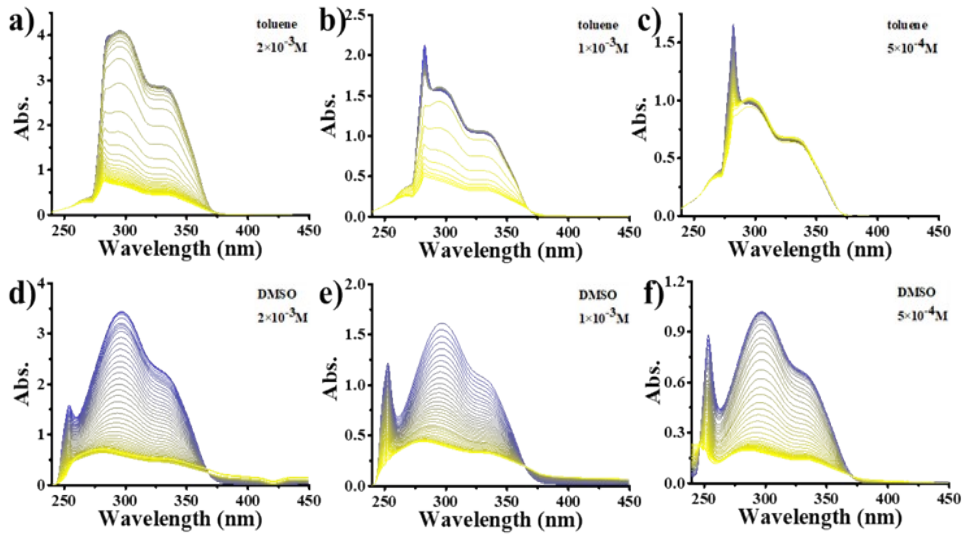

Figure S6. Temperature dependent UV-vis spectra for **LG-Cm** (c=2×10^{-3} M, 1×10^{-3} M, 5×10^{-4} M) in (a-c) toluene and (d-f) DMSO with cooling rate of 1K/min.

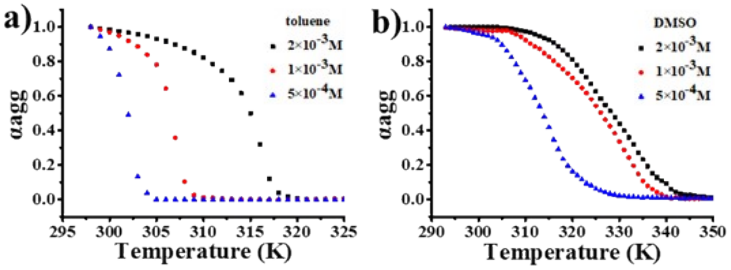

Figure S7. The temperature-dependent degree of aggregation (α_{agg}) of **LG-Cm** assemblies in (a) toluene and (b) DMSO of **LG-Cm** (c=2×10^{-3}M black, 1×10^{-3}M red, 5×10^{-4}M blue) determined by temperature dependent UV-vis spectra upon cooling from 325/350 K to 298 K (1 K/min).

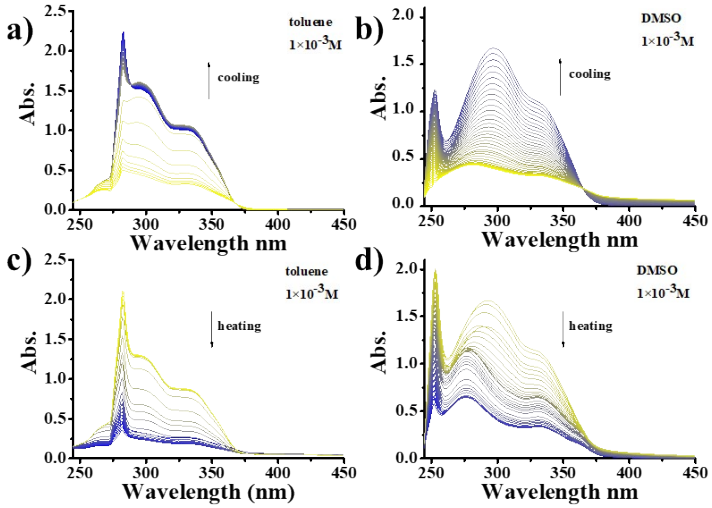

Figure S8. Temperature dependent UV-vis spectra for **LG-Cm (**c =1×10^{-3}M**)** in (a) toluene and (b) DMSO upon cooling from 325/350 K to 298 K, and in (c) toluene and (d) DMSO upon heating from 298 K to 325/350 K (1 K min^{-1}).

References

1 P. Jonkheijm, P. van der Schoot, A. P. H. J. Schenning and E. W. Meijer. *Science*, 2006, **313**,80-83.

2 M. M. J. Smulders, M. M. L. Nieuwenhuizen, T. F. A. de Greef, P. van der Schoot, A. P. H. J. Schenning and E. W. Meijer. *Chem. Eur. J.,* 2010, **16**, 362-367.