

Supporting Information

Cooperative supramolecular helical assembly of a pyridinium-tailored methyl glycyrrhetate

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1. Materials and methods

The synthesis of C4-MGP has been described in our previous work,¹ and solvents used for all the experiments are deionized water. UV-Vis absorption spectra were attained on a Agilent Cary Series UV-Vis spectrophotometer; Transmission electron microscopy (TEM) images were obtained on Hitachi H-7650B electron microscope operating at the accelerating voltage of 80 kV; High resolution transmission electron microscopy (HRTEM) was performed on JEM-2010 with the accelerating voltage of 120 kV; The samples were prepared by drop-casting the sol on the carbon coated copper grid, and then dried in air; Scanning electron microscopy (SEM) images were taken on a SU-8010 instrument with an accelerating voltage of 10 kV. Before the measurement, samples were placed on a silicon wafer, dried in air, and then coated with gold to increase the contrast. Circular dichroism (CD) spectra were recorded on a Pistar π -180 instrument (Applied Photophysics Ltd) with a 150 w xenon lamp as the light source; X-ray diffraction (XRD) analysis was achieved using a Rigaku D/max 2500v X-ray diffractometer with CuK α radiation ($\lambda = 1.5406$ Å), operating at 45 kV and 100 mA.

2. Supramolecular polymerization model

The temperature-dependent CD data obtained for C4-MGP at 254 nm, exhibited clearly non-sigmoidal cooling curves, which is an indication of cooperative self-assembly. To analyse the polymerization mechanism deeply, we have applied the nucleation-elongation (cooperative) model developed by Ten Eikelder, Markvoort, Meijer and co-workers.² This model describes the equilibrium between the monomer pool and supramolecular polymers, and the cooperative growth of the latter. It extends nucleation-elongation based equilibrium models for growth of supramolecular homopolymers to the case of two monomer and aggregate types, and can be applied to symmetric supramolecular copolymerizations, as well as to the more general case of non-symmetric supramolecular copolymerizations.

Due to the fact that supramolecular polymerization occurs *via* a cooperative mechanism,² the process can be divided into a nucleation and an elongation state in which the formation of a thermodynamically unfavourable species composed of a limited number of monomeric units

(nucleation) is followed by a more favourable elongation step. The values T_e , ΔH°_{nucl} , ΔH° and ΔS° can be found by a non-linear least-square analysis of the experimental melting curves. The equilibrium constants associated to the nucleation and elongation phases can be calculated using equations 1 and 2.

$$\text{Nucleation step: } K_n = e^{\left[\frac{-(\Delta H^0 - \Delta H_{Nuc1}^0) - T\Delta S^0}{RT} \right]} \quad (1)$$

$$\text{Elongation step: } K_e = e^{\left[\frac{-(\Delta H^0 - T\Delta S^0)}{RT} \right]} \quad (2)$$

$$\text{The cooperative factor } (\sigma) \text{ is given by: } \sigma = \frac{K_n}{K_e} = e^{\left(\frac{\Delta H_{Nuc1}^0}{RT} \right)} \quad (3)$$

In the elongation regime,³ the fraction of aggregated species (α_{agg}) can be defined by the following equation:

$$\alpha_{agg} = \alpha_{SAT} \left(1 - \exp \left[\frac{-\Delta H_e}{RT_e^2} (T - T_e) \right] \right) \quad (4)$$

Where ΔH_e is the molecular enthalpy release due to the noncovalent interactions during the elongation process, T is the absolute temperature, T_e is the elongation temperature, and R is the gas constant. α_{SAT} is introduced as a parameter to ensure that $\alpha_{agg}/\alpha_{SAT}$ does not exceed unity.

At temperatures above the elongation temperature ($T > T_e$, the nucleation regime) the fraction of aggregated species (α_{agg}) can be described by the following equation:

$$\alpha_{agg} = K_a^{1/3} \exp \left[\left(2/3 K_a^{-1/3} - 1 \right) \frac{\Delta H_e}{RT_e^2} (T - T_e) \right] \quad (5)$$

Where K_a is the dimensionless equilibrium constant of the activation step at T_e , which reflects the cooperativity of the system.

In the elongation regime, the number-averaged degree of polymerization, averaged over all active species, $\langle N_n \rangle$ is given by the following expression:

$$\langle N_n \rangle = \frac{1}{\sqrt[3]{K_a} \alpha_{SAT} - \alpha_{agg}} \alpha_{agg} \quad (6)$$

By introducing the value of K_a obtained in the nucleation and the parameters α_{SAT} and α_{agg} from the elongation regimes, respectively, the number-averaged degree of polymerization $\langle N_n \rangle$ can be calculated and plotted at different temperatures, according to equation 6.

The average length of the stack $\langle N_n \rangle$ averaged over the nucleated species at the T_e is given by:

$$\langle N_n(T_e) \rangle = \frac{1}{\sqrt[3]{K_a}} \quad (7)$$

Thus, the substitution of K_a in equation (7) gives the number of aggregated molecules at the elongation temperature.

Calculation of the α_{agg} :

As the values for the monomeric (ϵ_M) and aggregate (ϵ_A) species can be extracted from the temperature-dependent CD or UV-Vis experiments, the fraction of aggregated species (α_{agg}) can be calculated by substituting the respective values at each temperature (ϵ_T) in the following equation:

$$\alpha_{agg} = \frac{\epsilon(T) - \epsilon_M}{\epsilon_A - \epsilon_M}$$

This parameter varies between 0 and 1 depending on whether all monomeric units are in a molecular dissolved ($\alpha_{agg} = 0$) or an aggregated state ($\alpha_{agg} = 1$), respectively. The plot of α_{agg} against temperature will subsequently define a curve, whose shape will determine the self-assembly mechanism.

3. Additional figures

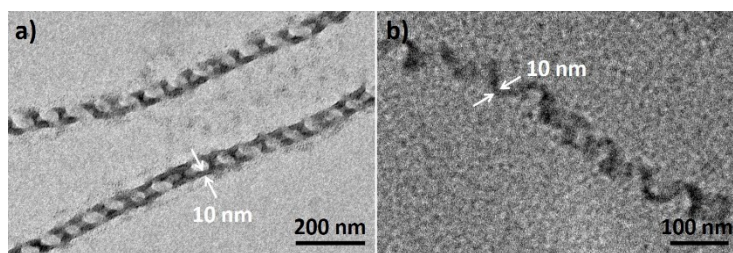


Fig. S1 (a) TEM and (b) HRTEM images of C4-MGP assemblies under the concentration of 7.0×10^{-4} M. Arrows indicate the thickness of the helical nanoribbons.

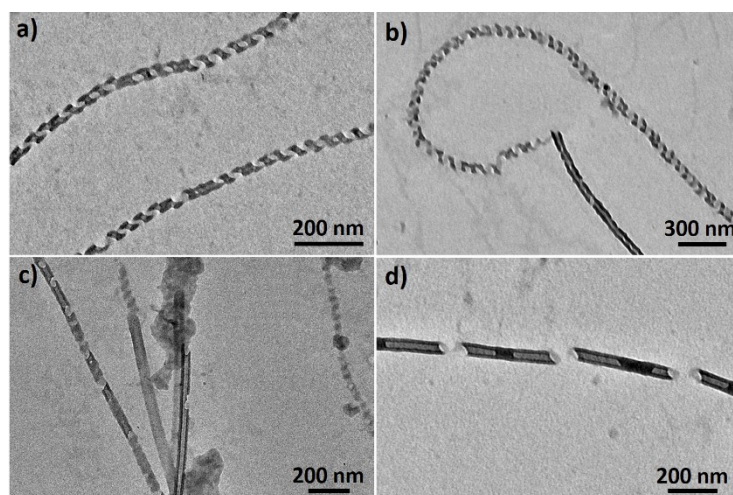


Fig. S2 Time-evolution TEM images of C4-MGP assemblies under the concentration of 7.0×10^{-4} M: (a) 24 h, (b) 72 h, (c) 1 week, and (d) 2 weeks.

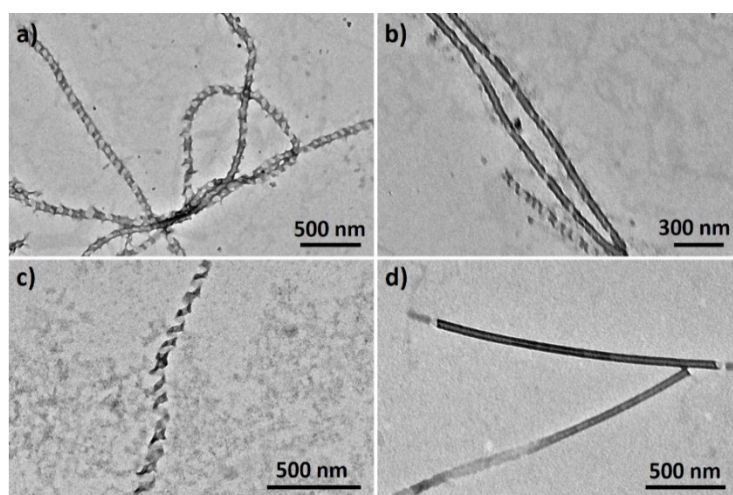


Fig. S3 TEM images of C4-MGP assemblies under different concentrations: (a) (b) 5.5×10^{-4} M, (c) (d) 8.5×10^{-4} M.

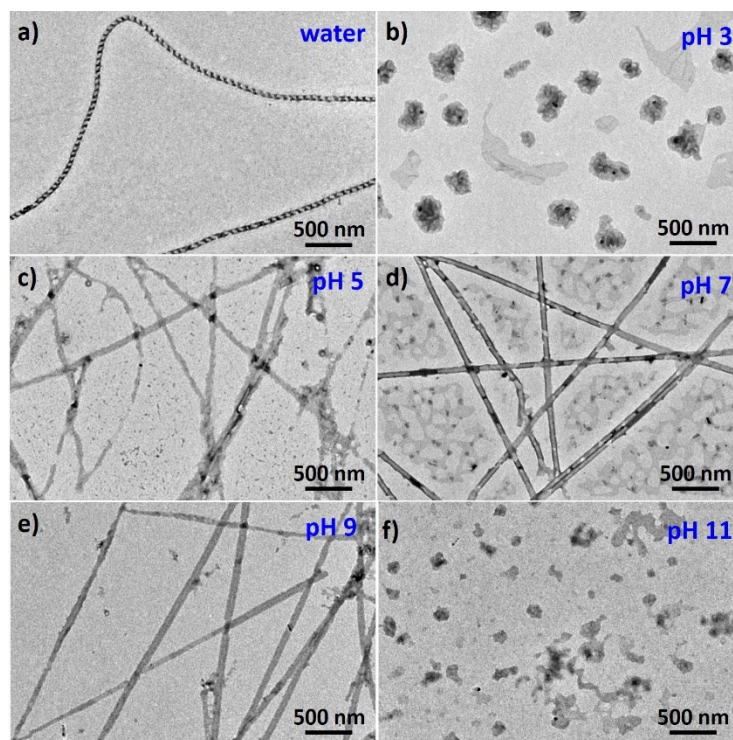


Fig. S4 TEM images of C4-MGP assemblies in different solvents: (a) deionized water, (b)-(f) sodium chloride saline solution with different pH values.

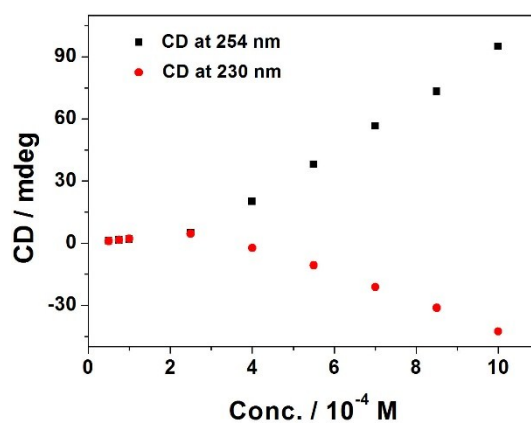


Fig. S5 Plot of CD intensity at 254 nm (black cube) and 230 nm (red dot) versus concentration of C4-MGP.

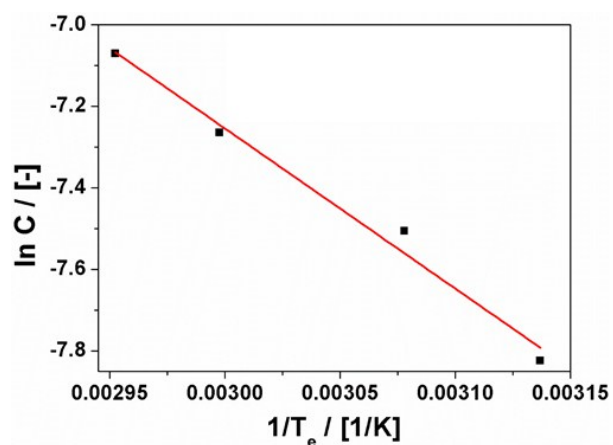


Fig. S6 Van't Hoff Plot (the natural logarithm of concentration versus reciprocal temperature) of C4-MGP in water. The red line represents the linear fit of the data points, whose slope (-3928.84) is proportional to the enthalpy (ΔH).

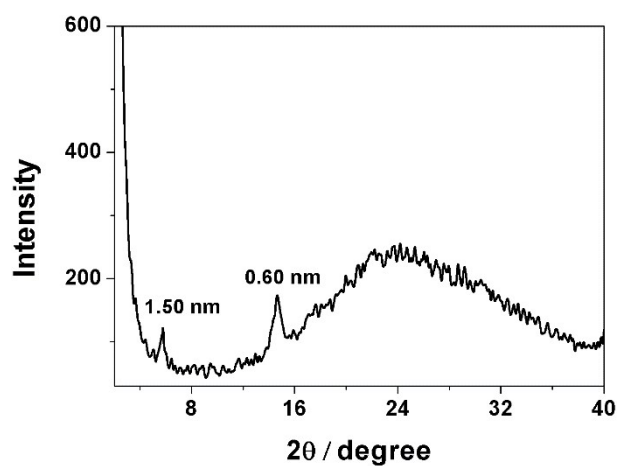


Fig. S7 XRD pattern of helices assembled from C4-MGP in water (7.0×10^{-4} M).

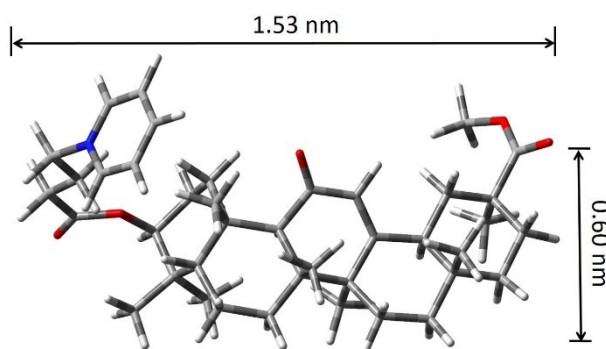


Fig. S8 Theoretical optimized structure of C4-MGP using ChemBio 3D Ultra software.

4. References

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2. (a) H. M. M. ten Eikelder, A. J. Markvoort, T. F. A. de Greef and P. A. J. Hilbers, *J. Phys. Chem. B*, 2012, **116**, 5291; (b) A. J. Maarkvort, H. M. M. tenEikelder, P. A. J. Hilbers, T. F. A. de Greef and E. W. Meijer, *Nature Commun.*, 2011, **2**, 509.
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